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TITLE: A Review of the Literature of Material Flammability, Combustion and Toxicity Related to Transportation

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ABSTRACT: Certain materials used in transportation vehicles are combustible. 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.

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 related to: fire initiation; fire spread; products of combustion; and practical fire prevention in vehicles and other modes of transportation. The goal of this review is to provide a technical overview of the literature of transportation fire safety.

KEYWORDS: Transportation; vehicles; flame; fire; safety; flammability; combustion; toxicity; flame spread; crashes.

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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 related to: fire initiation; fire spread; products of combustion; and practical fire prevention in vehicles and other modes of transportation. The goal of this review is to provide a technical overview of the literature of transportation fire safety.

I. 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.

With time, larger numbers of potentially-combustible materials have been used in transportation vehicles. The precise reasons are many, although two design considerations have been (1) mass reduction, resulting in increased fuel efficiency, and (2) reduced manufacturing costs. The complications arising from the burning of materials may include: 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, flammable, decomposition gases; and flame spread to nearby combustible materials.

This review was prepared pursuant to an agreement between General Motors and the U.S. Department of Transportation. The document outlining this research agreement is described in [1]. Part of the research program established by this agreement included a literature search of articles related to transportation fire and materials flammability. Of the more than 1,000 articles culled from research journals, approximately 150 were abstracted. To avoid copyright infringement, copyrighted abstracts were not included in the Transportation Fire Safety (TFS) Bibliography developed by GM [2]. Original abstracts for the approximately 150 selected articles were written by the author of this review and included in the GM TFS Bibliography. The present article is in part a topically organized and condensed version of these abstracted articles.

The intent of this review is to provide a systematic examination of features of materials associated with transportation fires. It is assumed that the reader has sufficient scientific or engineering background to understand the technical content of this review. The background discussion in each subsection is meant to outline relevant fundamental concepts and methods in each research field.

I.1 Fire Safety:

There are three means for addressing the problem of fire safety in vehicles and other modes of transportation. 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 [3].

In *fire minimization*, one might employ fire resistant materials in locations where fire is 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-flammable, 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 condition of the system and its exposure to environmental changes, all of which can alter its effectiveness. Fire suppression is important in forms of transportation where large volumes of highly volatile fuel are stored near flammable, lightweight materials.

The scientific and technical questions raised in fire prevention, fire minimization and fire suppression are distilled into three research categories. These are fire initiation, fire growth, and fire chemistry. All aspects of fire prevention, minimization or suppression can be discussed in terms of initiation, growth and chemistry of fire. 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. We outline the basic features of fire initiation, fire growth and fire chemistry in turn.

I.1.1 Fire Initiation:

Fire initiation occurs when ignition produces 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, temperature, temperature of ignition source, 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. There are exceptions, such as combustion in solids (e.g., propellants) and smolder fronts, but these subjects are not extensively considered in this review. Pure gas-phase initiation occurs when a flammable gaseous mixture of fuel and oxidizer has been formed. In this case the gaseous deflagration is usually referred to not as a fire but as a flame.

The model apparatus employed for fire initiation testing is the Cone Calorimeter. It is the most widely used device for static material flammability tests though other methods survive, like the French “épiradiateur.”

I.1.2 Fire Growth:

The incipient flame kernel may propagate (in the gas) or spread (over a liquid or solid). The expansion of the flame is referred to as fire growth, although there are some qualifications. A small $O(1-10\text{ cm})$ 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.* Thus, the words flame and fire are associated with scale. The former is an element of the latter, never vice-versa. We refer to “fire growth” because fire safety requires that we deal at a minimum with human-scale conflagrations, not small or laboratory-scale flames.

Fire growth is therefore a multidimensional 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 in the LIFT (Lateral Ignition and Flame Spread Test) apparatus, devised by J. Quintiere. 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 be *static*.

* A very small flame is called a “flamlet” in turbulent combustion. A large fire may consist of many flamelets.

I.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. This can produce differences from laboratory experimental studies in which fire toxins and other products of combustion are examined in a homogeneous chemical calorimeter 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 [4]: "...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." And, we add, the processes that transport the by-products of combustion.

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

I.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, there is no need to discuss growth and chemistry: initiation is the most important. If initiation cannot be absolutely prevented, growth and chemistry must be examined. If initiation and growth are possible, the chemical production and transport of species (chiefly products of combustion) is important. All articles abstracted for this review deal with one or another of these stages of fire.

I.2 Discussion:

This review is based on the abstracts written for the TFS Bibliography. The TFS Bibliography included over 1000 citations. It was not within the scope of the project to review and abstract 1000 scientific articles. As described previously, approximately 150 articles were abstracted for the TFS Bibliography. The selection of these articles was biased towards motor vehicle fire safety. Therefore, this review is focused primarily on materials and fluids used in automotive applications.

This review is organized as follows. In Section II we examine fire initiation, subdivided into flammability and ignition studies and testing based on the Rate of Heat Release (RHR), Cone Calorimetry, and diagnostic methods for material degradation and combustion. In Section III 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 IV we consider fire chemistry. Principal focus is on products of combustion, with greatest emphasis on toxins. The subcategories are products of combustion, toxicity, smoke, retardants, and inhibition. In Section V we address some practical studies related to transportation fires and commonly used combustible materials like polyurethane (PU). A brief conclusion terminates this review. References are listed separately for each section in the order called. Introductory parts of sections containing background discussion and general information have been added by the author of this review and are not contained in the TFS Bibliography. As a result, several references include books and articles which have discussed the subjects of this review either more fundamentally or more broadly. An attempt is made to note the articles belonging to the TFS Bibliography, although these should also be clear to the discerning reader from their context in the review. Nevertheless, an asterisk is added to the reference citation to indicate that it did not belong to the TFS Bibliography.

II. 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.

Combustion 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 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. Any or all of these mechanisms are possible in fire, singly and in combination. 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.

II.1 Natural Phenomena:

We describe the natural phenomena occurring in the ignition of gases, liquids, and solids.

II.1.1 Gases:

Ignition will occur when a volume of gas is heated, uniformly, to a sufficiently high temperature for exothermic chemical reaction to occur. 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 [1,2]. As combustion proceeds, the burning gas volume will extinguish when the reactant in shortest supply (the “limiting” reactant [2]) is finally consumed. A typical graph of the ignition event, including eventual extinction, is shown in Fig. II.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) is followed by a temperature plateau of steady combustion. A simple equation illustrating this balance is

$$\rho cV \frac{dT}{dt} = \dot{Q}_{gen} - \dot{Q}_{loss}. \quad (II.1)$$

If the heat generated in the volume V is greater than the heat lost, the temperature will rise, and vice versa. The chemical heat generation term is of the form $\dot{Q}_{gen} = |\Delta H_c| V B C_R^n \exp(-E/RT)$, 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, $|\Delta H_c| = Q$ is the heat release per mole of mixture, 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 $\dot{Q}_{loss} = hS(T - T_o)$, where S is the surface area of the volume of gas and h is a “heat-loss coefficient” [3,4,5]. Such models with lumped parameters are useful for characterizing the complex phenomena of ignition.

The analysis of Eq. (II.1) is straightforward. Consider a plot of the two heating terms as functions of temperature, see Fig. II.2. 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.* Case (1) is always explosive, case (3) is explosive only if $T > T_2$. 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

$$Se = \frac{1}{e} = \frac{\text{(chemical rate of heat release)}}{\text{(rate of heat loss to surroundings)}} = \frac{Q(kC_R^n \nu)}{h(RT_o^2 / E)S}, \quad k = Be^{-E/RT_o} \quad (\text{II.2})$$

When $Se < 1/e$, the mixture is in regime (1), explosive, when $Se > 1/e$, the mixture is in regime (3), potentially non-explosive. Se is the ratio of heat generation rate to heat loss rate, so the physical interpretation of the criterion $Se \geq e^{-1}$ is straightforward. Se is increased by increasing S/U : of all common geometric shapes the sphere has the largest S/U value. It is increased by increasing the heat loss coefficient h , and by decreasing the chemical reaction rate (either by decreasing B or increasing E , or both).

It is also straightforward 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, and the continual thermal energy feedback produces a sharp rise in the heating rate, or rate of temperature rise. 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

$$t_{ig} = \frac{\rho C_v \nu (RT_o^2 / E)}{q \nu k C_R^n}, \quad k = Be^{-E/RT_o}. \quad (\text{II.3})$$

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

Consequently the ignition of a combustible gas mixture can be understood on the basis of 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 (characteristic linear dimension approximately comparable to flame thickness [6]), the ignition temperature must be sufficiently high (greater than or equal to T_2 in Fig. II.2), and reactant depletion cannot be an

* The real case in which reactant depletion finally diminishes the generation term is not examined here, but the extension can be found in the literature [5].

important limitation in the early stage of ignition. These concepts are useful for understanding ignition of flame over liquid and solid fuels, for ignition occurs in the gas.

There are several limitations to this idealized picture of ignition. One of these is that the heated gas volume \mathcal{V} must be approximately at least as wide as the characteristic flame thickness during combustion. If the heated volume is smaller, the heat losses to the surroundings are large enough to self-quench the incipient reaction, regardless of temperature [6,7]. 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 [8] and whose uses in ASTM testing are listed in [9]. Another means of ignition keeps pressure, not volume, constant. Here the gas volume changes during heating. It is difficult to conduct systematic ignition experiments because the buoyancy-induced flow caused by the rising heated gases adds fluid-dynamic complexity to ignition. Thermal expansion and associated buoyant flow introduce flows that are difficult to physically 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 for fire initiation, however, because the latter generally occurs at constant pressure, not constant volume. Other complications include crossflows, concentration gradients, multi-stage ignition [10], oscillatory ignition 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 [11].

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 of condensed phase pyrolysis or gasification must, in general, be sufficient to produce the *lower flammable limit* of the fuel/oxidizer mixture. This mixture can be ignited by an external (pilot) source. Numerous complications exist, however. Among these are: spatially-inhomogeneous temperatures and reactant concentrations, heat losses from gas to condensed phase, flows in both phases, influences of buoyancy. Self-ignition is generally not relevant to many applications in fire. Piloted ignition tests are more common [12,13]. 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.

II.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, there are two limits of flammability or ignitability. 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 produce a flame whose heat release rate is large enough to overcome heat losses to the liquid, the ambient gas and any nearby walls. Two common measures of liquid fuel flammability exist. These are

the closed-cup flash point and the 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 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 actual surroundings.

The 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 top layer. Consequently, inhomogeneity and transient evolution may alter ignitability in the flash point test [12,13].

II.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. 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. 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 existing flames, 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 about ten times smaller than the characteristic sample heat-up time, as measured by the quotient of the square of the sample thickness and its thermal diffusivity, $t_{heat-up} \approx L^2/\alpha$, $\alpha = \lambda/\rho c$. Because a knowledge of the influences of the heat flux is crucial, the conditions at the rear of the heated sample (see

Figure II.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 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 in the opposite case, when the thermal response of the front and rear faces occurs simultaneously.

Experimental data are always interpreted through a theoretical explanation. Consider Refs. 14 and 15, 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 in [14] 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

$$t_{ig} = \rho_s c_s \ell (T_{ig} - T_\infty) / \dot{q}'' \quad (\text{II.4})$$

for piloted ignition of the thin sample of thickness ℓ and

$$t_{ig} = \frac{\pi}{4} \rho_s c_s \lambda_s (T_{ig} - T_\infty)^2 / \dot{q}''^2 \quad (\text{II.5})$$

for piloted ignition of the thick sample. Here t_{ig} is the time to ignition of the material, which is subjected over this time period to the heat flux \dot{q}'' . The solid properties 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 Figures II.4a,b. The extrapolation to $t_{ig} = \infty$ is not permitted by this simple model. A more detailed examination of this limit is found in [15] 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. (II.4,5) break down.

We notice from Eqs. (II.4) and (II.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 flammable; and (3) the mass gasification rate is sufficiently high, then a self-sustaining flame may be produced over the heated combustible surface. Transition from ignition to flaming will then occur, resulting in fire initiation.

II.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 Sec. II.2.1. Then we describe the TFS Bibliography references on flammability and ignition in Section II.2.2.

II.2.1 Fundamentals of Flammability and Ignition (a Practical 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 [16]. 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 (see Eqs. (II.4), (II.5), Ref. 17); critical fuel mass flux \dot{m}''_{ig} [18]; critical mean solid temperature [19]; and, for cellulosic or charring materials, critical char depth [20]. According to [16], "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 [16], these four ignition criteria are indirect measures, which are presumed to be closely related to ignition. The actual ignition process requires first that the heated solid fuel chemically decompose, resulting in the injection of fuel gases into 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 with a heat release rate large enough to overcome heat losses to the surface and the ambient surroundings.

A full computational description of piloted ignition requires a transient, multidimensional model for the simultaneous processes of solid-phase thermochemical decomposition and gas-phase mixing and combustion [16]. Limited progress toward such computational models has been made [21,22]. The "absence of such comprehensive models has necessitated the various attempts to develop the (empirical) ignition criteria" [16] that were outlined at the beginning of Sec. II.1.3. The merits of detailed computational models can be debated, and strong opinions exist for either side [23,24]. Many fields of scientific, technical and engineering research develop – and employ – such models ranging from astrophysics to the aerospace industry to combustion in engine cylinders (e.g., KIVA) to weather prediction to the spread of large smoke plumes [25]. It is not the purpose of this review to choose sides in the debate. However, a few points can be made: (1) Detailed computational models differ in degree, not in kind, from simpler, solvable, even lumped parameter models. (2) As detail is added and model complexity rises, ease of predictability and conceptual understanding diminish proportionally. (3) All computational models must be "validated" by comparison with the experimental data they purport to simulate, i.e., all computational models contain empirical parameters that can be "adjusted". (4) The most primitive, fundamental and reliable or robust means for understanding any complex subject is still through observation, experimental measurement and theoretical (conceptual) reasoning [26], which includes dimensional analysis [27]. (5) If detailed computational models can be

constructed and validated, they may facilitate design alterations and improvements. Many large industrial corporations, national laboratories and universities devote significant effort to the development of computational models, and numerous companies exist for the sole purpose of developing and marketing computational programs for technical engineering processes and problems [28]. (6) The trend for computational models is one of rapid increase. This is true also in fire research [29].

In order to establish ideas, we presently examine the history, from inception of heating to ignition*, of heated red oak as shown in Fig. II.5 [16]. 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 ($\dot{q}'' \sim O(0.1 \text{ kW/m}^2)$), there is a sufficient elapse of time 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. Nevertheless, because of the counterweighing heat losses from the surface, sustained ignition is not achieved during the flashes. From Figure II.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 in [16]: "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 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)." Reference 16 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 [16] incorporates all four ignition criteria described at the beginning of Sec. II.1.3.

II.2.2 TFS Bibliography References on Flammability and Ignition:

The first group of articles reviewed from the TFS Bibliography examine flammability and ignition of solid and liquid combustibles. References 30-35 employ the critical temperature as the ignition criterion. References 36 and 37 employ the critical mass flux. Reference 38 employs the Limited Oxygen Index (LOI: ASTM D-2863) test. None of these references 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 a book on fire safety [39]. In [30], a discussion is provided of pre-1972 methods for obtaining the autoignition temperature (i.e., no pilot flame) via

* Reference [16] 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 700K and deviations are usually not more than 10-20%. See the data in Appendix F of Ref. I.3.

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 sample into a heated flash in the presence of air, 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.

The authors of [30] found the largest discrepancies in T_{ig} data between combustion engine studies and fire safety studies. The authors suggested the adoption and use of normalized T_{ig} values in order to eliminate the biases between different test apparatuses. These same authors continued their work in [31], where they compiled T_{ig} values for over three hundred liquefied organic chemicals. Their list provides the lowest reported T_{ig} value using the glass flask apparatus discussed in [30]. Fire-protection groups also commonly report lowest values. 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.

In contrast to [30,31], the work of [32] 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, and the sample and plate touched for two seconds, then the plate was lowered and its temperature raised by 25°C until ignition occurred upon subsequent two-second contact. The maximum temperatures for non-ignition lay between 650°C (nylon, viscose) and 750°C (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 allow direct contact between test sample and heat source because of the many complexities associated with the direct contact test configuration. 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 these ignition temperatures are nearly 300K higher than those measured using non-contact techniques [see previous footnote].

Subsequent work has emphasized radiant heating, which mirrors more accurately the situation in real fires. In [33] the ignition of solid polymers was studied using a radiant heater and a pilot in the form of a periodically discharged Tesla coil. Samples, whose sizes ranged from 5×5×4mm to 20×20×17mm (last dimension is depth), included plexiglas (PMMA), polyethylene (PE), polycarbonate (PC), and red oak. Some of these materials melt under heating. Some, such as oak, PC, PE, form char. PMMA was the only material which 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. It was not clear from [33] why small (25mm²) samples were harder to ignite than large (400mm²) samples. In [34], 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 10-40 kW/m². PS had the highest T_{ig} of 370°C (643K) at a heat flux of 19kW/m². The time to ignition at this heat flux was little over a minute, $t_{ig}=67s$. 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. (II.5)) of POM. Changes in the spectral radiant distribution of the source produced large changes in T_{ig} . The changes in T_{ig} followed no discernable pattern. Below 20mm^2 surface area, however, T_{ig} became a function of the irradiated area. The sample surface temperature was monitored using thermocouples.

A similar experiment was carried out in [35], 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 15K 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 12kW/m^2 (ranging from 10 to 15kW/m^2) to 50kW/m^2 . The t_{ig} values averaged approximately 1400s at the former and 44s 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 thirty. The authors of [35] determined that the critical surface temperature for piloted ignition was a suitable engineering quantity because qualitative and quantitative agreement was obtained from the ISO tests and tests using another apparatus (the EU test [35]).

One of the measures of material flammability is critical mass flux at ignition \dot{m}''_{ig} , see Sec. II.1.3. An advantage of this measure is high accuracy using precise weight-measurement techniques such as TGA [16]. As discussed in Sec. II.1.3, Ref. 3 of [16] and Refs. 30-35, however, the surface temperature and the heat flux are also important. The study of [37], though focused primarily on critical mass fluxes at flash point [39] for radiant fluxes between $13\text{-}33\text{kW/m}^2$, demonstrated that convective heat transfer at the surface must be included in a complete ignition analysis. Recall from [15] 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, the authors of [37] examined flame-retarded PP and PS, finding the following: (1) Flame retarded PP and PS could only be ignited for heat fluxes between $25\text{-}33\text{kW/m}^2$ (unlike the non-retarded PP and PS, which could be ignited between $3\text{-}25\text{kW/m}^2$). (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 [37] suggest 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 in [40,41]. 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 [40,41]. 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 [42,43] and electrical cables [44,45]. In [42] a general theory is developed for the prediction of "closed-cup" flash points of mixtures of flammable and non-flammable liquids. See Sec. II.1.2 for a definition of the closed-cup flash point. Experimental values of flash points of pure liquids are available.

For example [43] contains data for twenty-two 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 Sec. II.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 [43]. The fire point, at which sustained combustion occurred, was approximately 210°C [43]. In [42], the flammability of two types of mixtures was studied. In the first, all components were separately flammable. In the second, some components are non-flammable. These non-flammable additives suppress flammability through vapor-phase inhibition. Thus, consistent with results for solid flammability [37,40,41], combustible fluid flammability can be altered by additives.

The flammability of materials used for the insulation and sheathing of electrical cables was studied [44,45]. In [44], various fire retardant (FR) and low smoke and fume (LSF) materials were examined. The fire parameters considered in [44] 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 [45] 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.

II.3 Heat Release Rate (HRR): 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. Principal focus is placed on the Cone Calorimeter. Then the TFS Bibliography references are discussed in Sec. II.3.2.

II.3.1 Background and Principles of the Cone Calorimeter:

As the need for quantifying the flammability of materials increased, methods were devised that could measure important flammability parameters. These tests include the Oxygen Index (OI) test, pyrolysis and thermal analysis, and gas analysis, as described in [46]. 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 [46], 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 notes that “...this test should not be used for the description or appraisal of the fire hazard of materials, products or systems under actual fire conditions” [46]. Pyrolysis and thermal analysis involves the heating of small, presumably homogeneous, material samples rapidly to a specified “pyrolysis” temperature, then using 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 [47]. According to [46], the pyrolysis of polymers has been "often" studied by thermoanalytical methods, the most common of which is Thermogravimetry (TG), which is "... (routinely) used for determination of the (polymer) degradation temperatures and the formations of char." Numerous methods exist for analyzing the gaseous by-products of combustion and pyrolysis. According to [46] the report ISO/TR 9122-3 [48] 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 [46] including numerous references to their particular uses.

Experimental diagnostics in ignition and flammability testing have increasingly placed principal emphasis on heat release rate (HRR). The following quotation from [49] 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" [39]. The function \dot{Q} is also commonly referred to as HRR.

The importance of HRR in fire is discussed in References 49 and 50. The authors of [49] explain in detail why HRR can characterize the flammability and fire hazard of combustible materials. According to [50], although fire deaths are primarily caused by toxic gases, HRR is the best predictor of subsequent fire hazard. The logical ordering of fire hazard is a local ignition, with a HRR sufficient to sustain fire, which, in turn, produces toxic gases. In [50], a definition of the heat of combustion is provided. The complete (or theoretical) heat of combustion is an inaccurate measure of Δh_c because complete combustion is generally not attained in real fires. The author of [50] discusses means for defining realistic estimates of heats of combustion. Reference 39 provides a very concise, precise means for determining HRR. The oxygen consumption calorimeter "works on the principle that the heat of combustion per unit mass of oxygen consumed is nearly a constant (13kJ/g) for a wide range of ordinary (hydrocarbon) fuel compounds." A simple example of the calculation of HRR by the principle of oxygen consumption 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 value of HRR. Shown in Table II.1 are values of the heats of combustion per unit mass of oxygen consumed for numerous pure hydrocarbon fuels. HRR 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, numerous authors have attempted to relate ignition and fire HRR to the flame spread rate [51].

Such considerations led in the late 1970s and early 1980s to the rapid development of devices for measuring material flammability in the context of fire hazard. Among them was the furniture calorimeter [52,53]. In [52], the influences of fabric type, padding type (cotton, PU foam, etc.) and frame types are assessed. The advantages of furniture calorimeter testing over conventional room-fire testing are discussed. These are primarily a greater ability to specify fire growth in a vague, undefined region (a "room") as compared with a well-defined, single object (a piece of furniture, whose flammability properties can be measured). In [53], the analysis of a large number of tests demonstrated that for most specimens a good approximation to the graph of HRR as function of time is a suitably drawn triangle. Methods for generating triangular HRR vs. time curves, which are used for fire protection engineering hazard determinations, were developed in [53].

The furniture calorimeter suffered from the same vagueness with respect to individual furniture as did the room fire with respect to individual items of furniture. This ambiguity resulted in the subsequent development of the individual material calorimeter, which measured the flammability of a single, 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), only the latter has become a universally accepted testing device.

The Cone Calorimeter consists of a cone-shaped array of electrically-heated radiant coils which impose a known heat flux 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 Figure II.6. The Cone Calorimeter can measure [54] peak rate of heat release, total heat released after a specified time interval, time to ignition, smoke factor, chemical composition of product gases, mass loss rate during burning, as well as time to ignition, heat flux at ignition and all other parameters related to fire initiation discussed in Sec. II.1.3. There are certain conditions that 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 oxygen concentration, variable material thickness and composition. Under some of these conditions the materials may gasify vigorously, but ignition cannot be sustained (as described previously in [16]). Flammability is also altered where the absence of buoyant flow produces conditions favorable to ignition [55].

II.3.2 Use of the Cone Calorimeter and other Fire Diagnostic Devices (TFS Bibliography):

In its development stages, many questions were raised concerning the effectiveness of the Cone Calorimeter. Answering these concerns has required devising comparisons with other bench-scale test methods, and with some large-scale tests. In [56], low-flammability wall lining materials representative of aircraft cabin walls were studied. 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. In [56], techniques for predicting full-scale performance from bench-scale tests were also discussed. In [57], the issues of sample preparation and mounting are addressed. It is believed that edge flow and heat transfer produced

by sample edge frames may alter the flammability measurements. Reference [57] showed that insulated edge frames produce measurements that are more consistent and "slightly closer to expected true values." For routine fire testing, [57] does 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, reflecting near-constant conditions away from the frame. In other words, one must realize that 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 [58-63], polymeric materials including PVCs, PE, PP, acrylonitrile-butadiene-styrene and polyphenylene oxide/PS [54], polyethimide, polyethersulfone, polycarbonate, polyether ethylketone, polyphenyleneoxide, high impact PS, polybutylene terephthalate, and PVC [64], 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 [65]. In [58,59] 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 [58], with an average reduction of 37kW/m^2 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 HRR reduction, but was opposite in smoke yield. Much of the information in [58] is presented in convenient graphical form. Results were obtained in [59] for three commercial PU foams and cotton, polyester and polypropylene. The three foams tested in [59] 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 $10\times 10\times 2.5\text{cm}^3$, the exposure heat flux was 25kW/m^2 . In [60] the relative contributions of fabric and foam to fire-hazard parameters were measured. The EHOC of the individual foams and fabrics was determined with a flux of 25kW/m^2 . The high-resilience (HR) PU foam had the highest EHOC. PP had the highest EHOC of the fabrics tested. As shown in [61], measurements of large heat release were associated with large sample densities. The work of [62] continues that of [59-61] while adding 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. These investigators concluded that post-ignition performance of the materials was determined mostly by the fabric, whereas ignition characteristics are determined by foam and fabric.

The work of [63] compares the combustion behavior of some polymeric materials in the Cone Calorimeter with behaviors in some "traditional" tests which 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. The authors of [63] 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 [65] showed that the combination of two combustible components in a single 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. Additional bench-scale Cone Calorimeter tests on composites were conducted in [66].

The work of [67] attempted to "more completely characterize foamed plastic flammability" by subjecting ten 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 [68]. The results showed a dependence 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 HRR. As discussed in [39], the width of the HRR curves, or more accurately, the area under the HR curves, is a measure of the quantity of fuel burned. The authors of [68] also described various smoke tests. The development of quantitative means for making smoke production measurements and species evolution measurements using the Cone Calorimeter is discussed in [69]. Smoke production measurements are needed for toxicity determinations to compare fire-retarded and non-retarded materials, as in [59-62].

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 in [70]. 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.

III. 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?" In Secs. III.1,2 we describe the principles of fire spread over liquid and solid fuels, respectively. In Sec. III.3 we outline the articles reviewed in the TFS Bibliography on this subject.

III.1 Principles of 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, 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 [1-3]. This surface-tension driven mechanism of flame spread with accompanying liquid phase motion, which does not exist 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 a much greater percentage of the flame heat release. For the latter, some solid materials must both liquefy and then vaporize, requiring the application 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 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. III.1. Such flows can be visualized in ordinary candle flames by observing the circular motion of ash and contaminant particulates. 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”, see Ref. 4. 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. 5,6,7 as the controlling mechanisms of pulsation, but there is work which suggests that the liquid phase alone is responsible for the pulsation [8]. The issue of sub-flash-point pulsating flame spread over liquid fuels remains an open research topic.

Although flame spread over liquids is conceptually easy to explain, it is dynamically more complicated than flame spread over solid fuels because of the liquid motion. Much research has been carried out in this field, as summarized in an exhaustive review [5]. Basic research sponsored by NASA has demonstrated that fuel pool size (especially width) strongly influences flame spread across the surface, see Fig. III.2. 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.

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 [5]. To quote [5]: “...the subject of most recent research, convective motion couples both gas and liquid phase in unique ways and greatly 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 material [9], in which case spread partly resembles that over solid fuels.

III.2 Principles of Fire Spread Over Liquid and Solid Fuels:

We describe some of the basic features of ignition and flame spread for liquid fuels. An important quantity is the “flash” temperature, defined [5] 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 in [5] the quantity T_{flash} is “not a unique property of a liquid fuel...(but is instead an artifact) of the experimental apparatus...” There is much empirical support for this assertion. The interested reader is referred to [5]. 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 highly transient. Clearly, of these four spread regimes (1) and (2) contain the most liquid-phase physics. Regime (2) is difficult to describe without including significant detail, so its treatment is foregone in this introductory review. We shall instead focus on some model features of regime (1).

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 [5]. 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 . We focus herein 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. We write $d\sigma/dx = \gamma dT/dx$ and ignore the gas-phase shear in comparison with liquid-phase shear to find $\gamma dT/dx \approx \mu_l(\partial u_l/\partial y)_s$. We scale coordinate x with the distance over which the surface temperature changes 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,

$$V_i \sim \frac{h}{\mu L} \gamma \Delta T. \quad (\text{III.1})$$

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 (III.1) gives, after rearrangement,

$$V_i \sim \left[\frac{\gamma^2 \Delta T^2}{\mu^2} \frac{\nu}{L} \right]^{1/3} = \left[\frac{\gamma^2 \Delta T^2}{\rho \mu L} \right]^{1/3}, \quad (\text{III.2})$$

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.

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. 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. III.3.a. 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 is vertically upward flame spread, see Fig. III.3.b. 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 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 Sec. II can be carried over directly to fire spread. In order to demonstrate this, consider the so-called fundamental equation of flame spread [10], $\rho_s V A \Delta h = \dot{Q}$, where ρ_s is the fuel density, V is the flame spread rate, $A = w \cdot \ell$ 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 Figure III.4. The heating rate can be rewritten, in terms of the flame heat flux (\dot{q}''), and the characteristic flame tip extent (δ), and its lateral width (w), as $\dot{Q} = \dot{q}'' \delta w$, whereupon $V = \dot{q}'' \delta / \rho_s c_{ps} \ell (T_v - T_\infty)$. The quantity $\rho_s c_{ps} \ell (T_v - T_\infty) / \dot{q}''$ can be interpreted with the support of Eq. (II.4) as the ignition time. Thus, in its general form the fundamental equation of flame spread is

$$V = \delta / t_{ig}, \quad (III.3)$$

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 , Eqs. (II.4) and (III.3) give

$$V = \frac{\dot{q}'' \cdot \delta}{\rho_s c_{ps} \ell (T_v - T_\infty)}.$$

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 $\lambda_g(T_f - T_v)/\ell_q$, 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 “DeRis/Delichatsios equation” for flame spread over a thin fuel,

$$V = \frac{\lambda_s}{\rho_s c_{ps} \ell} \left(\frac{T_f - T_v}{T_v - T_\infty} \right), \quad (\text{III.4})$$

where $\ell_q \approx \delta$ 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. (II.5) we obtain by substitution into Eq. (III.3) the result $V = \delta (\dot{q}'')^2 / [\rho_s c_{ps} (T_v - T_\infty)^2]$. When we write $\dot{q}'' \approx \lambda_g (T_f - T_v) / \ell_q$, where the flame quenching distance ℓ_q is approximately equal to the characteristic extent of the flame tip, δ , we obtain

$$V = V_g \frac{\rho_g c_{pg} \lambda_g}{\rho_s c_{ps} \lambda_s} \left(\frac{T_f - T_v}{T_v - T_\infty} \right)^2. \quad (\text{III.5})$$

Here we used $\delta \approx \ell_q \approx \lambda_g / \rho_g c_{pg} V_g$ 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. Equation (III.5) is the “DeRis equation” for wind-opposed flame spread over a thermally thick solid fuel. See Figures III.5.a,b for diagrams of the thermally thick and thin configurations.

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 described in [11] demonstrates the essence of wind-aided flame spread. If the overhanging flame of Figure III.3.b 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,

$$\frac{dx_p}{dt} = \frac{x_f - x_p}{t_{ig}}. \quad (\text{III.6})$$

For thin fuels we use Eq. (II.1) for t_{ig} . For thick fuels Eq. (II.2) is used for t_{ig} . Equation (III.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 carried out [11-19].

It is necessary for the reader to understand that the preceding models describe two-dimensional flame spread across flat combustible surfaces. Real flame spread is almost never two dimensional nor are combustible materials necessarily flat. Multi-dimensional flame spread occurs over objects in complicated geometric arrangements, such as cables in confined spaces. The preceding formulas offer guidance and provide generally accurate proportionalities to material properties and characteristic temperature differences but caution must be used when simplified correlations are adapted to complicated real-life problems.

III.3 Fire and Flame Spread Over Materials:

A review of wind-opposed flame spread containing a discussion of flame spread from a historical viewpoint may be found in [20]. The earliest researchers in flame spread quickly understood that certain polymeric materials possessed nearly ideal burning behaviors which rendered them suitable for repeatable scientific testing. PMMA (polymethylmethacrylate), for example, has been described 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 1968 PhD thesis of J.N. DeRis [21], 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 [20], subsequent works on flame spread have focused their efforts on one or more of the features originally described in [21].

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 there is no single, unique gasification temperature. However, many polymeric materials have nearly invariant gasification temperature, as demonstrated in [22] for polycarbonate, for which $T_v \cong 580^\circ\text{C}$.

Another feature of DeRis' theory was the distinction between thermally thick and thin flame spread. As shown in [20], this distinction was not clearly made before DeRis published his PhD thesis.

Subsequently, numerous experimental investigators examined flame spread over varying fuel-bed thicknesses. In [23], for example, an experimental study was conducted 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 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 (see Eq. (III.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. An increase of mass burning rate with increased ℓ was believed to be partly caused by forward heat transfer from the flame to the unburned material through 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.

Another study [24] examined thick and thin sheets of PMMA. For $\ell < 0.2$ cm, they found $V \propto \ell^{-1}$ as predicted by Eq. (III.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 ($\ell > 2$ cm) fuels.

Another component of the DeRis model focused on the role of the external heat flux, which is always present in real fires. The influence of the external radiant flux appears in Eqs. (III.4,5) as the increase of the effective flame temperature, T_f . The result is a linear increase of V for the thin case and a quadratic increase for the thick case. Experimental work over many years has confirmed the accelerative influence of the "background" radiant flux on both wind-opposed and wind-aided flame spread. Flame will not spread over wood unless there is a sufficient background radiant flux. This fact is confirmed by common experience, for samples of wood never burn in isolation.

A simplified model of flame spread developed by J. Quintiere [25] incorporated the radiation term and led to the subsequent development at NBS (now NIST) of the LIFT apparatus discussed in Sec. II.3.2. This test couples the ignitability criteria described for the Cone Calorimeter (and similar devices) in Sec. II.3.2 with the subsequent evaluation of radiantly-assisted creeping flame spread. Parameters defined in an analytical correlation [25] 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 former rate slower than the latter. 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. Ref. 26 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 in [27]. One composite was a honeycomb panel, the other a composite armor. The ignition behavior of all materials was correlated by a simple predictive model.

The final 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 in [28]. Other sophisticated diagnostic methods have since been used to measure features of the spreading flame, see [29].

The structure of the spreading flame leading edge dictates the subsequent spread and surface gasification behavior. The flame leading edge structure is a challenging fundamental problem of

combustion science. The flame leading edge generates the heat flux received by the combustible fuel beneath the flame. This quantity has been very difficult to determine both theoretically and experimentally. Numerical solutions are easier to generate but their complexity diminishes insight, reducing them to detailed descriptions of isolated special cases. Current solvable mathematical models of flame spread [20,21] produce infinite heat fluxes near the flame leading edge. The unreality of these predictions can only be eliminated at the expense of much greater complexity of the equations and solution methods. Theoretical progress has recently been made in this subject [30-32]. Heat flux measurements were made in [33] and later in [34]. These results enabled the determination in [35] that, for most cases of flame spread, the gas-to-solid Peclet number ratio P was much larger than unity. The ratio P is in the Nomenclature, and essentially represents a ratio of convection-to-conduction in the gas to that in the solid. A detailed table of flame heat fluxes for an idealized model was provided in [36], showing which types of heat flux (conductive, convective) passed across which planes in the gas and solid, see Figure III.6. When $P \gg 1$, as is usual, the balance is between gas-phase conduction across the vertical plane from the origin at the flame tip to the upstream surface, thence to the solid, along with downstream convection across the vertical (solid-phase) plane in the solid. This latter contribution is especially important in $P \gg 1$ flame spread, and becomes negligible only when $P \ll 1$, an unlikely case. The energy balance of [36] was used in [37] in the derivation of a modified version of Eq. (III.5), which included a multiplicative factor on the right-hand side accounting for finite-rate chemistry through a suitably defined Damköhler number.

Flame heat fluxes to nearby surfaces have been described in simpler terms than above. In particular, [38] produces 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 [39] to determine how much is known about the heat fluxes from flame to surface in opposed-flow spread. There were few reported studies, and even 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 exists. The LIFT theory, however, employs an empirical formula for the "driving force" for flame spread and does not explicitly quantify the heat flux. Thus, there is a need to experimentally measure flame heat fluxes in LIFT and in other geometries.

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 can potentially lead to fire. The study of [40] 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.

A more detailed and also more fundamental study of similar questions was made for U.S. Navy shipboard structures and installations [41]. In addition to making 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 U.S. Navy's fire evaluation of composite materials.

Another fundamental question concerns quantifying the influences of fire retardant chemicals on flame spread. An ambitious study dealing with influences of fire retardants on total fire hazard was undertaken in [42]. The tests employed were Cone Calorimeter, NBS furniture calorimeter and NBS toxicity. In all categories except overall smoke production, the chemically treated samples performed better than the non-treated samples. In particular, reduced burning rates were not obtained at the expense of 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.

Another area of great practical concern involves flame spread associated 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 existing literature on fire tests for wire and cable has been published [43]. Comparisons are made to British and other international standards for such materials. Approximately three hundred references are compiled in [43]. The scientific study of flame spread in cylindrical geometries is 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 [44]. 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 and ambient gas temperature; oxygen concentration in the ambient gas; regression of pyrolyzing surface; and char formation at the pyrolyzing surface. As shown in Eqs. (III.4,5) the ambient temperature T_∞ can strongly influence V . As $T_\infty \rightarrow T_v$, the flame speed approaches infinity, which is flashover. A study that included variations of sample temperature for various polymers was conducted in [45], 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 [46], 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. (III.4,5) through the enthalpy ratio, this time through T_f , the flame temperature. As the oxidizer mass fraction Y_O is increased, T_f dramatically increases, [47,48,35,20].

Numerous simplified versions of Eqs. (III.4,5) 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 [20,29] was founded on such correlations, which are used to ascertain the influences of finite-rate chemistry [20,49]. 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 [50]. 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 work of Altenkirch and colleagues [51,52]. Experimental work and limited comparisons are available, especially in the microgravity limit [53]. A plausible theoretical explanation based on a revised Damköhler number correlation including radiant heat losses has been advanced in [20]. Theoretical work [37] states that 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 do produce a char or carbonized surface layer, see [54]. 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.

IV. FIRE CHEMISTRY

The objective of fire chemistry studies is to describe the details of chemical reactions responsible for propagating the reaction, releasing thermal energy, and forming combustion products. In studies of fire, much of the research has focused on combustion by-products because these may contain toxic compounds. Our review of the TFS Bibliography focuses on this literature of combustion by-products.

Fire and flame chemistry with principal emphasis on transient, intermediate reaction propagation and energy release and reaction mechanisms also has a large and burgeoning research literature, with many reviews and articles of technical interest [1-5]. 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. We shall not review this literature because our principal and immediate 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, nature and influence of the actual combustion by-products. Nevertheless, in more detailed investigations the influence of chemical formation rates on the ultimate concentrations of combustion by-products must be examined.

After a brief description of basic principles of fire chemistry (IV.1), this section describes four principal areas of fire chemistry: (II.2) products of combustion, (II.3) toxicity, (II.4) smoke and retardants, and (II.5) inhibition. There is overlap in these categories (e.g., the analysis of combustion products of fire-inhibited combustibles).

IV.1 Principles of Fire Chemistry for Toxicity Studies:

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. Because toxicology is the study of the harmful effects of chemicals on living organisms, it is interested in the amount of chemical that reaches its site of harmful action in the organism as well as the ability of the chemical to initiate an effect at that site. This is known as its intrinsic toxicity. It is believed 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. Another important factor in quantitative studies of chemical toxicity is the fate of the chemical inside the organism prior to reaching its internal site of toxic action [we will not address these aspects of toxicological combustion by-product research here]. 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, toxicological research focuses mostly on quantifying the response of the organism to received chemical insult [6].

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 hot and light and buoyancy can rapidly carry them far from their location of origin, thus rendering concentration fields of the chemical by-products of combustion both transient and inhomogeneous. 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.

IV.2 Products of Thermal Decomposition and Combustion:

In order for a possibly lethal event to occur in a fire, active flaming is not necessary [7] because low-temperature smoldering and moderate-temperature thermal decomposition of most HC combustibles releases gaseous volatiles and toxicants [8]. For example, at approximately 300°C cellulosic materials such as wood and paper actively decompose [9].

Because toxic products of material thermal degradation 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 easier to provide a homogeneous test environment for laboratory animals that inhale the gases, which later appear in

their bloodstream and 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. Nevertheless, transport of the by-products of combustion in non-homogeneous environments is an important part of their 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 another approach, the host is considered to have been exposed to the toxicant, but the actual passage of the chemical from its entry into the nasal passage to the lung surface is examined and modeled. In an influential paper, Nikula et al. [10] 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 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. In [11] the authors 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 in [12] and references cited therein. The authors state in [12] 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.

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 $\text{CH}_4 + 2(\text{O}_2 + 3.76\text{N}_2) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2$ describing the stoichiometric methane oxidation in air. In actuality, the reactants CH_4 and O_2 , which decompose very 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. The intermediate in this example is principally CO , which is oxidized to CO_2 slowly. Thus, the oxidation of a HC fuel generally proceeds in several stages. These can be represented as a *rapid* production of CO from the parent fuel followed by a *slow* oxidation of the CO to the final product CO_2 . CO oxidation chemistry, which is very sensitive to trace amounts of impurities, moisture and other influences, is described in detail in Refs. 4 and 13. For our purposes it suffices to observe that CO is a potentially highly toxic gas whereas CO_2 is relatively non-toxic by comparison. Consequently toxicity measures depend upon: spatial location, because of the convective moment of combustion products; time, because toxin production rates

vary in time, even if the system is homogeneous; and time, because of duration of exposure of the subject to the toxicant.

Heavier 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 [14]. In Ref. 14, the samples were exposed for 20 minutes 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. In [15] the authors 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°C 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.

The work of [16] examines the oxidative pyrolysis of PP, finding that the pyrolyzed polymer liberates oxygenated compounds that undergo subsequent oxidation by the flame in the gas. TGA was used to show that polymer degradation begins at T=200°C and ends at T=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 oxidation of carbonyl compounds was completed and the yield of CO₂ increased. The oxidative pyrolysis of PP showed first-order kinetics. Reference 17 examines the thermal decomposition of Polycaprolactum (PA-6), Polyoenantholactam (PA-7), Polycaprylolactam (PA-8) and Rislin (PA-11) in 510, 610 and 770°C atmospheres for heating rates of 15°C/min. As in [16], weight loss began at T=200°C. The polyamides began to decompose at T=400°C: major decomposition was complete 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.

The work of [18] on PE, PP, PS and PA studied flaming and non-flaming combustion, using two different combustion chambers. One, the "CAB 4.5" simulated the combustion of large samples in a small space while the other, "CAB 650" modeled the stage of fire in which a flow of air over the burning material is employed. As expected, 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.

In [19] the University of Pittsburgh Toxicity Test Apparatus was used 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 of the material and thus higher rates of decomposition. CO and CO₂ measurements were also performed in Refs. 20 and 21. For PP, mixed polyester (PMPS), and polystyrene, the former 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 10L/min air crossflow. Enhanced radiant fluxes produced accelerated rates of decomposition. The latter study [21] demonstrated 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 combustion products of polymeric materials. A measure of the sensitivity of the CO measurements in [21] is the experimental reproducibility, which varied with respect to the chemical diagnostic technique used.

PU foams, which are commonly used in many forms of transportation, have been studied for toxicity. In [22] a flash-fire cell test method was developed 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 in [22] for various PU foams and other polymers of potential interest to the aircraft industry. In Refs. 23 and 24 the authors examined the thermal degradation of "model" rigid PU foams to determine the influence of chemical structure, fire-retardant structure and fire-retardant chemistry [23]. The LOI was determined for foams with different retardant levels. As the temperature of pyrolysis was increased, the quantity of light volatile gases also increased. The major product at 500°C and 1000°C was CO₂, whose concentration depended more on pyrolysis temperature than retardant concentration. The retardant did not influence the breakage of the urethane bond. 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. Also, 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 [24] the same authors investigated model urethane foams for combustion products and polymeric structural changes using thermoanalysis, direct-probe analysis, and residue/volatile analysis. Pyrolysis consisted of igniting foams in He at 500°C, 750°C 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. A kinetic model with rate parameters was derived.

Reference 25 examined small 100-200 mg samples heated at 5°C/min. in a 30ml/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).

An examination of large-scale fires of PU foam (and wood) was conducted in [26] to study full-scale conditions in mine fires. The tunnel was 200m long, 2.12m wide and 1.14m high. The tunnel was ventilated by a fan, with airspeed 4.9 m/s. Measured quantities included gas concentrations, fume temperature and flame speed. Prior to ignition a vapor cloud of decomposition products formed in the upper level of the tunnel. When the gas ignited, the fire rapidly propagated downwind and completely filled the tunnel with intense flames. Fire also spread upwind at approximately 0.02 m/s, but much slower than the approximately 2 m/s downwind speed. The toxicity, temperature and oxygen deficiency of the fire fumes each reached near-fatal levels. Foam fires are of short duration because of the high foam burn rate, but wood burned much longer.

PVC is an important polymeric material in common use. References 27, 28 and 29 studied the decomposition products of primarily PVC under external heating. In [27], DTA and TGA were used 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 300-600°C; (2) weight loss rate varied with temperature and was most rapid below 280°C 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 Ref. 28 examined 11 PVC samples of varying compositions (and also 7 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. In [29], direct-inlet mass spectrometry (DIMS) was used to study and identify PVC degradation and imization products. At low temperatures of 160 and 180°C the volatiles 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. The duration of the degradation experiments was 30 min.

The decay of HCl generated as a combustion by-product is itself a question of fire science. In Ref. 30 the authors 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 consume HCl, for which evidence is provided by progressively decreased consumption rates in repeat experiments with the same material. This study demonstrates the importance of mass transport on toxic product gas behavior.

Finally, Ref. 31 conducted a "fingerprint" sampling and analysis to study the chemical nature of fires of wood, PP, PMMA, and PS foam, using a 24m³ compartment-corridor fire-test rig. Gas samples of 250ml were extracted during various stages of the fire and analyzed using gas

chromatography and mass spectrometry. It was found that the types of combustion products were similar for all fuels used, but their concentrations varied widely. CO concentrations were usually higher than the total concentrations for all other compounds at the same point in the fire. After CO, the most toxic substance measured was acrolein. The acrolein concentrations were low, with CO still the dominant toxic product when the acrolein concentration exceeded the lethal limit of 10 ppm.

IV.3 Toxicity:

Because this subject is vast and the number of articles reviewed is large, we subdivide this section as follows: After an initial discussion of the basic scope and nature of toxicity analysis, we begin in Sec. IV.3.1 with a discussion of PVC and fire gas toxicity. This discussion is a natural extension of the previous section IV.1. In Sec. IV.3.2 we discuss polymer decomposition and toxicity, including polymers considered generally, as well as specific polymers such as ABS and other polymers which contain Nitrogen. In Sec. IV.3.3 we consider the broad class of PU foam toxicity. Finally, Sec. IV.3.4 summarizes several reviewed articles describing toxicity of fire-retarded materials, practical material and foams, and the influences of physical variables, such as heating rate, on toxicity.

Toxicological studies are conducted to determine the adverse influences of chemicals on living organisms. Due to ethical concerns associated with human experimentation, surrogate test species (e.g., rats, mice) are often used to help characterize the potential health hazard associated with exposure to combustion by-products.

Toxicological measurements often include such quantities as times to incapacitation, staggering, convulsions, collapse and death. Respiratory rates may in some cases be recorded and other measures may also be constructed to determine the pre-death influences of chemical toxins. Pathological examinations of the tested animals can yield additional information about the nature of the response mechanism. Tissue damage and toxic concentrations can be systematically examined. The study of Ref. 32 assessed toxicity from material combustion using various "toxicological endpoints." Two of the "endpoints" were incapacitation and death. 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. The authors of [32] state that the exposure period alone is insufficient for determining which toxins were present, and that post-exposure observation (i.e., pathological 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, material comparison was based on the following measures: (1) potency of combustion product atmospheres, (2) animal observation, (3) blood analysis, (4) gross pathology, (5) atmospheric analysis. For (1), the EC₅₀ (concentration causing incapacitation in 50% of the exposed rats) and LC₅₀ (concentration 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 a higher EC_{50} and LC_{50} than UF, vice versa under flaming conditions. 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 Figure 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 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.” The authors of [32] conclude that “a multi-component test is required to detect the toxicity of an acknowledged multi-component insult.”

The work of [33] on Wilson rats used cessation of respiration to measure time of death from exposure to products of decomposition of 35 materials including wood, synthetic polymers, and textiles at three different combustion temperatures. Pathological 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. The research of [33] 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.”

In Ref. 34, toxicity indexes were developed 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 weights early mortality more heavily than late mortality, thereby suggesting a toxicity ranking scale based on fire combustion by-product toxicity.

Reference 35 showed that for numerous polymeric combustibles the influences of pyrolysis gases on toxic response could be quantified. A useful means of acute toxicity evaluation was shown to be CO concentration in test mice at death.

IV.3.1 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. and observed over at least 14 days [36]. 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.

Three articles studied specifically the toxicity of PVC degradation products [37, 38, 39]. Reference 37 tested live Swiss-Webster mice exposed for 3-5 min. in the head-only configuration to the degradation products of PVC. 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. In [38] the degradation products of PVC combustion and pyrolysis (kiln temperatures ranging from 10-1000°C in an air or N₂ flow of 100ml/min.) were measured 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, 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. Reference 26 compiles PVC thermal degradation literature over 1969-1984 (in English only). The pyrolysis of PVC homopolymer reveals poor thermal stability even at 100°C, with HCl production rapidly increasing with increased temperature. Dehydrochlorination in air and nitrogen had activation energies of 151 and 174kJ/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 to 700°C range.

Five articles on the subject of fire-gas toxicity were reviewed [40-44]. We shall discuss these articles in chronological order. In [40] the authors discuss a "new approach" to fire toxicity evaluations of fire hazard, emphasizing 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-based criteria to constrained, head-only toxicity tests on mice and rats relying on chemically-based measures of toxicity. The work of [41] summarizes the previous methods of measuring toxic potency while emphasizing four 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." Ref. 42 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 [43] the NIST group determined that the proper subject of smoke 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" [42].

Much of this work is summarized in [44] in the form of a model which amounts to a fire hazard analysis using existing 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 or other flow) is comparable to their rate of production. Thus, Refs. 40-44 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.

IV.3.2 Polymer Decomposition and Toxicity:

In Refs. 45-52 we first discuss chronologically the types of toxic compounds produced by polymer decomposition. Then Ref. 53 discusses ABS decomposition, and Ref. 54 discusses nitrogen-containing polymer degradation and toxicity.

The 1972 study of Ref. 45 presages some of the later work described in [40-44]. The author 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 for a long-term program to study the synergistic effects of various toxins was mentioned, anticipating [40-44]. Reference 46 examines PVC and flexible PU foams along with other materials, including cellulose. The PVC results are consistent with the work of Refs. 38-39. 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.

Reference 47 examined PE and isotactic PP, which are used in automobile parts, insulations, piping, and industrial production. Small 50mg 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%). Smoke studies indicate that for temperatures up to 800°C, an increase of atmospheric O₂ increases smoke production. The authors concluded that combustion and pyrolysis of PE and PP did not

result in the production of toxic compounds, although small amounts of toxic gases did arise, e.g., acrylic acid for PE, crotonaldehyde for PP.

In [47], the products of PE pyrolysis are 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 is 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.

The study of Ref. 48 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, as pointed out by later researchers seeking to quantify toxicity more systematically [40-44]. Nevertheless, [48] showed that fixed-temperature testing yielded the "more rapid incapacitation and death." According to [48], 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 existing publications in English through 1984 on PE products of decomposition, and their toxicity, appeared in Ref. 49. 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 (which could not be measured in [47]) 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 of [49] state that "polyethylenes are more toxic in the non-flaming mode than in the flaming (mode)." Consistent with the discussion in the first paragraph of Sec. IV.1 (dealing with toxic hazard assessment in real-fire conditions, which include spatially and temporally variable concentration fields, convection, buoyancy, large temperature variations) the authors of [49] 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 [47], PE was considered relatively ordinary with respect to toxicant production under fire conditions. To quote [47] "The products (of PE, excluding CO) do not contain a markedly toxic component." From [49]: "...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. 50. 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, PU, produce CO and CO₂, whereas ABSs, PUs, nylons and PVCs with nitrogen additives produce nitrogen 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.

In Ref. 51 the author examines the toxicity of numerous polymeric compounds, including 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. Also, of the three fire hazard threats, toxicity, oxygen deficiency and heat, the most important threat was stated to be toxicity. The author demonstrated that small-scale tests were useful in assessing this general hazard, consistent with later work [42-44].

Finally, Ref. 52 examined the toxic effect of eleven 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 to [47, 48]]. In the animals which 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." This result suggests the need for a more comprehensive measure of toxic hazard, as pointed out in [40-44].

One study on ABS degradation and toxicity was reviewed. In [53] ABS decomposition was 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. The overall ABS toxicity was comparable to that of materials such as Douglas fir.

One study devoted exclusively to nitrogen-containing polymers was reviewed [54]. 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 one described above for Ref. 50 (only defined for 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.

IV.3.3 PU Foam Toxicity:

Nine articles primarily addressing PU foam toxicity were reviewed [55-63]. The earliest studies [55,56,57] were concerned primarily with determining whether or not toxins of sufficient

quantity were generated by PU thermal decomposition. References 55 and 56 showed that the decomposition products were indeed toxic, but that "unusual" toxic gases were not produced in real-fire conditions [55]. Ref. 57 used the Ohio State University Heat Release Apparatus to measure the levels of CO, HCN and unburned hydrocarbons released. They showed also that different ventilation rates altered the toxin generation rates. Subsequent studies [58-63] distinguished between rigid and flexible PU foams, and quantified the earlier work. When animals were used [58, 59, 63] the LC50 test protocol was employed, with the exception of [62], which examined irritants. The principal toxicants released were CO and HCN [59-63]. Reference 63 concludes that death in the test rats occurred from CO inhalation, while HCN had no significant effect. This contrasted with [58] in which it was asserted that deaths could not be attributed to either CO or HCN alone. The work of Ref. 59 suggests an additive effect for CO and HCN. This work was followed up in [60] in an attempt to simulate "real PU fires" in which the combustion stage is preceded by a longer interval of smoldering. Reference 61, 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. Reference 62 adds that in the case of both flaming and non-flaming combustion for rigid and flexible PU, the smoke toxicity levels are "average", whereas for the flaming combustion of rigid PU the smoke toxicity is "slightly higher than average." Thus, in flaming combustion, rigid PU smoke appears to be more toxic than flexible PU smoke. Finally, Ref. 63 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.

IV.3.4 Toxicity of Fire-Retarded Materials; Toxicity of Foams and Fabrics; Influences of Heating Rates on Toxicity:

Two articles on the toxicity of fire-retarded and unretarded materials were reviewed [64, 65]. Reference 64 examined samples of 35 materials including woods, synthetics and textiles, burned for 30 min. at 500, 600 and 700°C, with effluents analyzed for CO, CO₂ and O₂ and COHb determinations 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 but enhanced toxicity when treated with fire retardants.

The research reported in [65] 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 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 in Refs. 66-69. The study of [66] 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. Reference 67 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 [68] the same authors examine polyesters, finding that temperature and atmosphere are 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 in [69] 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.

References 70, 71 also examined the influences of heating rate on the release rates of potentially toxic combustion by-products. Reference 70 showed that some materials (PE and PC polycarbonate) released more toxic gases at "intermediate" (600°C) than "high" (800°C) temperatures. Some materials such as ABS appeared insensitive to different heating schemes. Reference 71 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.

IV.4 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 TFS review of the fire retardancy literature considered test materials composed of fire-retarded synthetic polymers. Most of this review addresses the measured influences of various 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, chloroparaffins.

We begin our review with three studies addressing PVC "smoke performance" [72-74]. In [72] additives were examined for their effect on smoke production. The authors 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). Reference 73 is a general description of PVC smoke production in comparison with smoke production from other common materials. A smoke parameter evaluation demonstrates that PVC occupied the low end of the smoke spectrum, only

above PC. This was attributed to the low HRR of PVC. Reference 74 examines 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 toxic volatile production. One such group of 5 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." In [75], Brauman et al. use the following additives to the polymers PE, PP, PS, Impact PS (ImpPS), PVC and other compound mixtures. They examine: 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 the following 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." The authors 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."

The work of [76] 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, EHO, 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 materials also form external carbon layers (i.e., "char") at the surface to inhibit subsequent surface decomposition [77]. Reference 77 demonstrated, however, that an intumescent PC was not self-extinguishing. The review of intumescent materials provided in [78] 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 char formation 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 intumescence-promoting additives was "inadequate" to justify their general use. Reference 79 examines 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) [80-83]. Reference 80 demonstrated that CP inhibited oxygen use during combustion. In addition, pyrolyzed PP (polypropylene)-CP became more flame retardant because the volatile HCs generated by thermal insult were not as flammable as they were before. A companion study, however [81], suggested that under some conditions the PP-CP compounds produced greater quantities of volatiles, some of which were highly reactive at room temperature. The authors of [81] concluded that 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) is "shifted in the presence of the CP," forming 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 [82, 83], though in [82] the authors also examine CP-PP and CP-PS combinations. The CP-PP "poisoned" the flame through higher HCl production [82]. The CP-PP blend was the only combination that produced a flame-retardant response. However, a condensed-phase influence of CP was observed. This suggested that chlorinated additives might possibly produce a condensed phase method of fire suppression that is more effective than gas-flame poisoning. In [83] the thermal degradation modifications of CP-PE mixtures were examined. For the CP-PE mixture, 90% of the total weight loss was by CP volatilization, which rendered the PE insoluble. Because 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 influences of phosphorus (P) additives on various synthetic polymers is described in [84], 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 pyrolytic stability, heat evolution, fuel production, and also increase charring.

Flame retardance was also examined for various standard commercially-common materials. We describe articles reviewed for PU foams [85-88] and polyolefins [89, 90]. Reference 85 begins by reviewing 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. The authors of [85] 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 (see also [84]), (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 [87-88]. In [86] various PUs were treated 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 in [87] 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, [88] 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.

Two articles on polyolefin flame retardance [89,90] were reviewed. In [89] the retarded PP behavior depended upon the retardant's reactivity with Sb_2O_3 at high temperature, coupled with the interaction between Br release and thermal degradation. Also, the formation of HBr produced lower burning rates at higher temperatures. Reference 90 shows that for flame retarded polyolefins, ignition delay and the ignition temperature decreased relative to unretarded samples. The theoretical model supported this conclusion.

IV.5 Inhibition and Suppression:

It is difficult to distinguish between inhibition and flame retardancy. Some clarification occurs when inhibition is defined with reference solely to gas-phase reduction of flaming [91]. This suggests the possibility of injection of flame inhibitors or suppressants from sources distinct from the decomposing fuel source. A reliable distinction is the following: in fire retardancy the flame above a specific material that feeds it must be weakened by the evolution of chemical additives in the material itself, whereas flame inhibition or suppression may utilize 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 [92]. These 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.

V. VEHICLE FIRES

This section is divided into separate discussions of TFS Bibliography references for four types of vehicles. These are buses, railway and subway cars, aircraft cabins, and automobiles, light trucks and heavy trucks.

V.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-1970's, it was determined from three full-scale tests and small-scale laboratory tests that a variety of ignition mechanisms are possible [1]. 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 [2] 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 2.44m wide \times 2.13m high \times 8.23m 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 [3]. This report describes congressional mandates and NHTSA's actions to improve school bus safety, including human behavior and motor vehicle safety performance.

V.2 Railway and Subway Cars:

Eight articles on this general subject were reviewed [4-11]. In [4] a Metrorail subway car mock-up interior was ignited and smoke density, heat flux, temperature and gaseous products were examined. The interior materials were primarily plasticized PVC, acrylic PVC, and PU. Ignition was achieved (see [1]) 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.

A less technically sophisticated assessment of the San Francisco Bay Area Rapid Transit (BART) subway cars was performed in [5]. 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.

The subsequent work of [6] 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 our 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. Reference 7 is a study of 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.

Because rail transport in Europe is more extensive than in North America, Ref. 8 surveys fire research and fire practical experience for European railways, including a summary of causes of fire, fire characteristics and existing European fire protection strategies. Test methods for various railcar materials are described, techniques for smoke emission measurement are outlined, and ignitability and surface flame spread are described. The British full-scale "Phoenix" test facility is described. Detailed drawings of the facilities and test apparatuses are provided in the report. A discussion of transit undercar fire detection and suppression is found in [9]. 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. The report of the FRA's update of its guidelines on performance of materials (flammability, smoke emission, etc.) in new or rebuilt rail passenger cars is found in [10]. These guidelines are similar to the Urban Mass Transportation Administration (UMTA) recommendations to the rapid transit industry.

Reference [11] presents 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. The authors 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 HRR.

V.3 Aircraft Cabins:

The research into the subject of aircraft cabin fires has been promoted chiefly 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. Reference 12 examines 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. Efforts were directed toward promotion of "pilot plant polymers" by the various chemical companies. Preliminary toxicity data were gathered by the AMES Research Center. In [13] the thermochemical modeling of aircraft cabin fire safety is described. 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. The following "novel concepts developed at JPL" were highlighted in the report: (1) condensed phase degradation of the polymeric material is the rate-limiting step of the overall process (this was known long before from basic fire research (see Secs. II.2, III.2)); and (2) diffusion and mixing of the pyrolysis products with air is the rate-limiting step of vapor phase combustion (also known long before from basic fire research (see Sec. III.2)). The work correctly determines that certain materials like carpet cannot burn on their own but require augmentation by an external radiation source or another burning surface. Unlike the preceding "novel concepts", this latter observation was made from experiments. Global zone models for aircraft cabin fires occurring in flight or crash are developed in [14]. Simple expressions are derived for wall burning, flame heights and flame spread rates. Material properties controlling flammability are identified. Radiation and charring are discussed, as are gas flows along aircraft ceilings.

Recent work on aircraft fire safety has focused on practical means of addressing specific, often perception-driven issues related to fire safety.* References 15, 16 examine the CWSS (cabin water spray system) proposed to increase passenger evacuation and survival time following an accident. Disadvantages of CWSS are described in [15] 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. Reference 16 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. Reference 17

* 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..."

summarizes various fire suppressants, their properties, and their applicability in aircraft. Certain classes of agents are recommended for use in test protocol development. A similar study is reported in [18] for Halon replacement.

V.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 U.S. there are annually approximately 1250 crash fatalities where fire is involved (not necessarily the cause of fatality). The number of annual crashes involving fire (fatalities or not) is presently unknown to this reviewer. Three of the articles reviewed are concerned with the Federal Motor Vehicle Fire Safety Standard 301 Fuel System Integrity test (FMVSS301) [19-21]. 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 [20], only five states in [21] with primary emphasis on Michigan). The FMVSS301 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 30mph frontal barrier crashes" [20].

In Ref. 20 police accident data were examined 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. Reference 21 states 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" per year, and (3) the Standard has increased the annual consumer vehicle cost by \$850 annually.

A more detailed statistical study of fire occurrence in fatal and less serious crashes is found in [22]. Particularly helpful to this study was the fact that the Michigan policy accident report (PAR) collects data on fuel leaks, which are used to estimate the statistical relationship between fires and fuel leaks. The work of [23] 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. Reference 24 concludes that motor vehicles have remained in operation longer and have been driven further than previous estimates had indicated. This may influence their fire performance.

VI. 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.

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NOMENCLATURE

B	Pre-exponential factor $((\text{moles}/L^3)^{-(n-1)}t^{-1})$
c_{pg}	Specific heat per unit mass (of gas) $(e/m-T)$
c_{ps}	Specific heat per unit mass (of solid) $(e/m-T)$
C_i	Concentration of species i (moles/L^3)
E	Activation energy (e/mole)
h	Heat loss coefficient (e/L^3-t-T)
k	Rate constant, $k=R\exp(-E/RT)$ $((\text{moles}/L^3)^{-(n-1)}t^{-1})$
ℓ	Material thickness (L)
ℓ_q	Distance from flame tip to fuel surface (L)
\dot{m}''	Mass flux of fuel from surface of decomposing fuel (m/L^2-t)
\dot{m}''_{ig}	Mass flux at ignition (m/L^2-t)
P	Gas-to-solid Peclet number ratio, $P=(V_g L_g/\alpha_g)/(V_f L_s/\alpha_s)$ (—)
\dot{q}''	Heat flux (e/L^2-t)
\dot{Q}	Heating rate (e/t)
R	Universal gas constant $(e/\text{mole}\cdot k)$
S	Surface area (L^2)
t_{ig}	Ignition time (t)
T_f	Flame temperature (T)
T_{ig}	Ignition temperature (T)
T_N	Surface gasification or “vaporization” temperature (T)
T_∞	Ambient temperature (T)
V	Velocity (L/t)
\mathcal{V}	Volume (L^3)
w	Width of material (L)
x_f	Flame tip position (in wind-aided flame spread) (L)
x_p	Pryolysis front position (wind-aided flame spread) (L)
Y_o	Oxidizer mass fraction (—)

GREEK SYMBOLS

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)
ΔH_c	Enthalpy of combustion per mole (e/mole)
λ_g	Gas phase thermal conductivity $(e/L-t-T)$
λ_s	Solid phase thermal conductivity $(e/L-t-T)$
ρ	Density (m/L^3)

ACRONYMS

APB	Amonium Pentaborate
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ATF	Automatic Transmission Fluid
ASTM	American Society for Testing and Materials
BART	Bay Area Rapid Transit System
B-S	Broido-Shafizadeh Scheme for Cellulose Pyrolysis
CB	Cement block
CFD	Computational Fluid Dynamics
CN	Cyanide
CP	Chloroparaffins
CWSS	Cabin Water Spray System
DIMS	Direct Inlet Mass Spectrometry
DMMP	Dimethyl Phosphate
DOT	Department of Transportation
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EHOC	Effective Heat of Combustion
EP	Epoxy
EU	European Union
EVA	Ethylene-Vinyl-Acetate
FAA	Federal Aviation Administration
FHA	Fire Hardening Assessment
FINN	Finnacryl
FMRC	Factory Mutual Research Corporation
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
HRR	Heat Release Rate
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	Limited Oxygen Index
LSF	Low Smoke and Fume
MAR	Marinite
N	Nylon

NBS	National Bureau of Standards
NHTSA	National Highway and Transportation Safety Administration
NIST	National Institute for Standards and Technology
NT	Nort Test
NYCTA	New York City Transit Administration
OSU	Ohio State University
PA	Polyamide
PA-6	Polycapolactum
PA-7	Polyoenantholactum
PA-8	Polycapylolactum
PA-11	Rislin
PAR	Policy Accident Report
PC	Polycarbonate
PE	Polyethylene
PH	Phenolic Resin
PMMA	Polymethylmethacrylate ("plexiglass")
POM	Polyacetyl
PP	Polypropylene
PRHR	Peak Rate of Heat Release
PS	Polystyrene
PU	Polyurethane
PVC	Poly Vinyl Chloride
PX	Perspex
RHR	Rate of Heat Release
RHS	Right Hand Side
RUF	Rigid Urethane Foam
TC	Thermocouple
TFS	Transportation Fire Safety (Bibliography compiled at GM)
TGA	Thermogravimetric Analysis
THR	Total Heat Release
TPRHR	Time to Peak RHR
TTI	Time to Ignition
UFF	Urea Formaldehyde Foam
UMTA	Urban Mass Transit Authority
VE	Vinylester
W	Wood

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CHAPTER III

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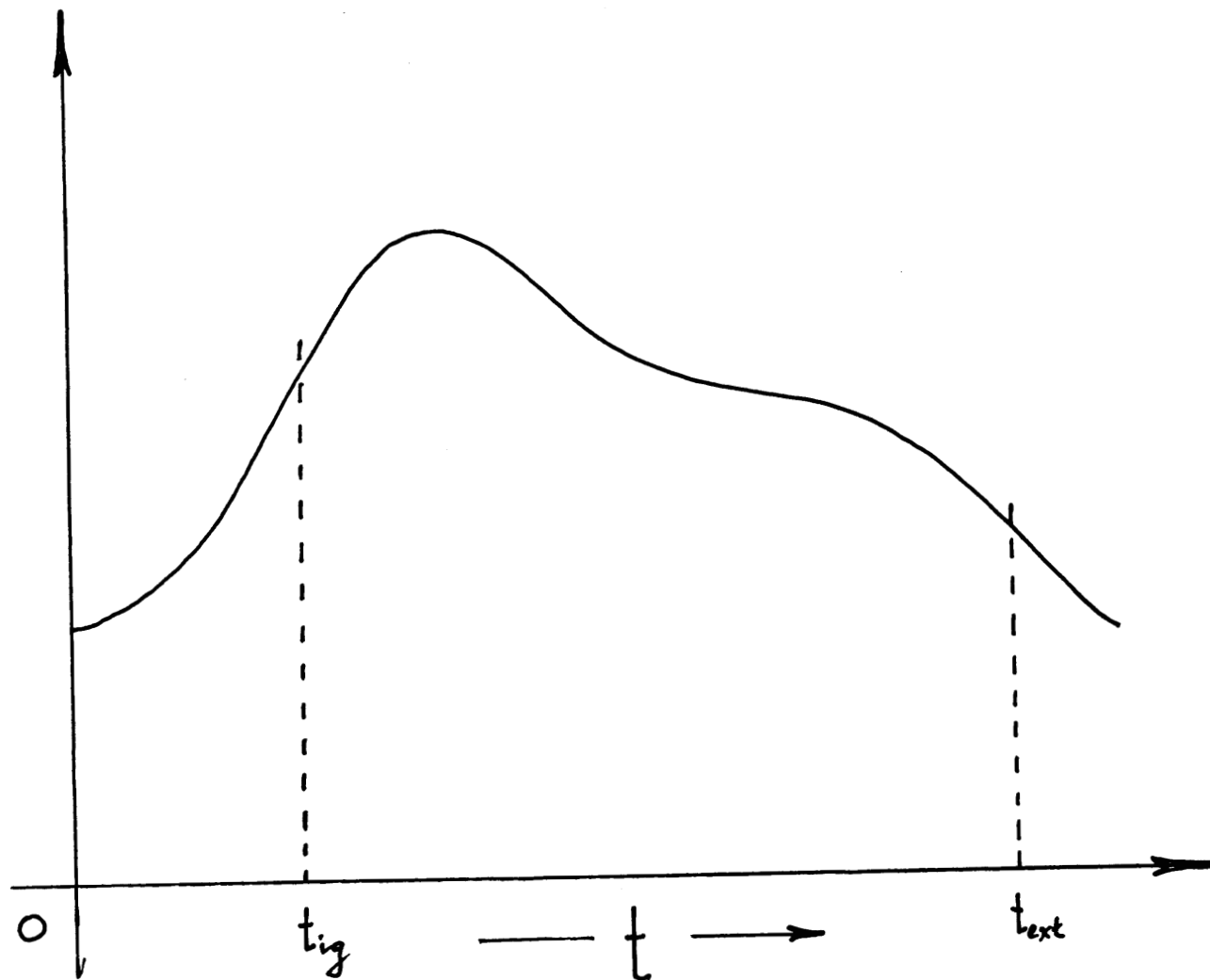


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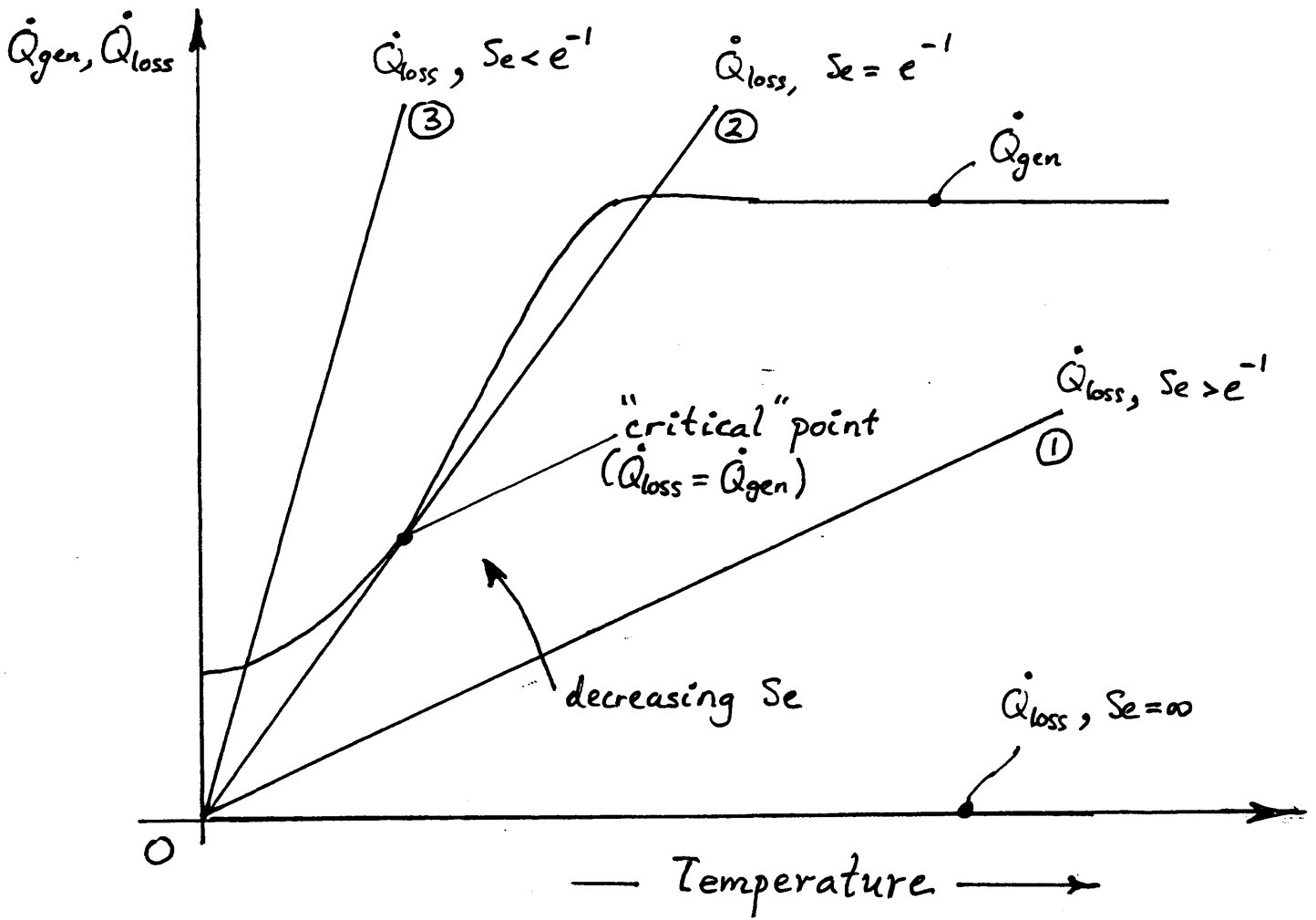


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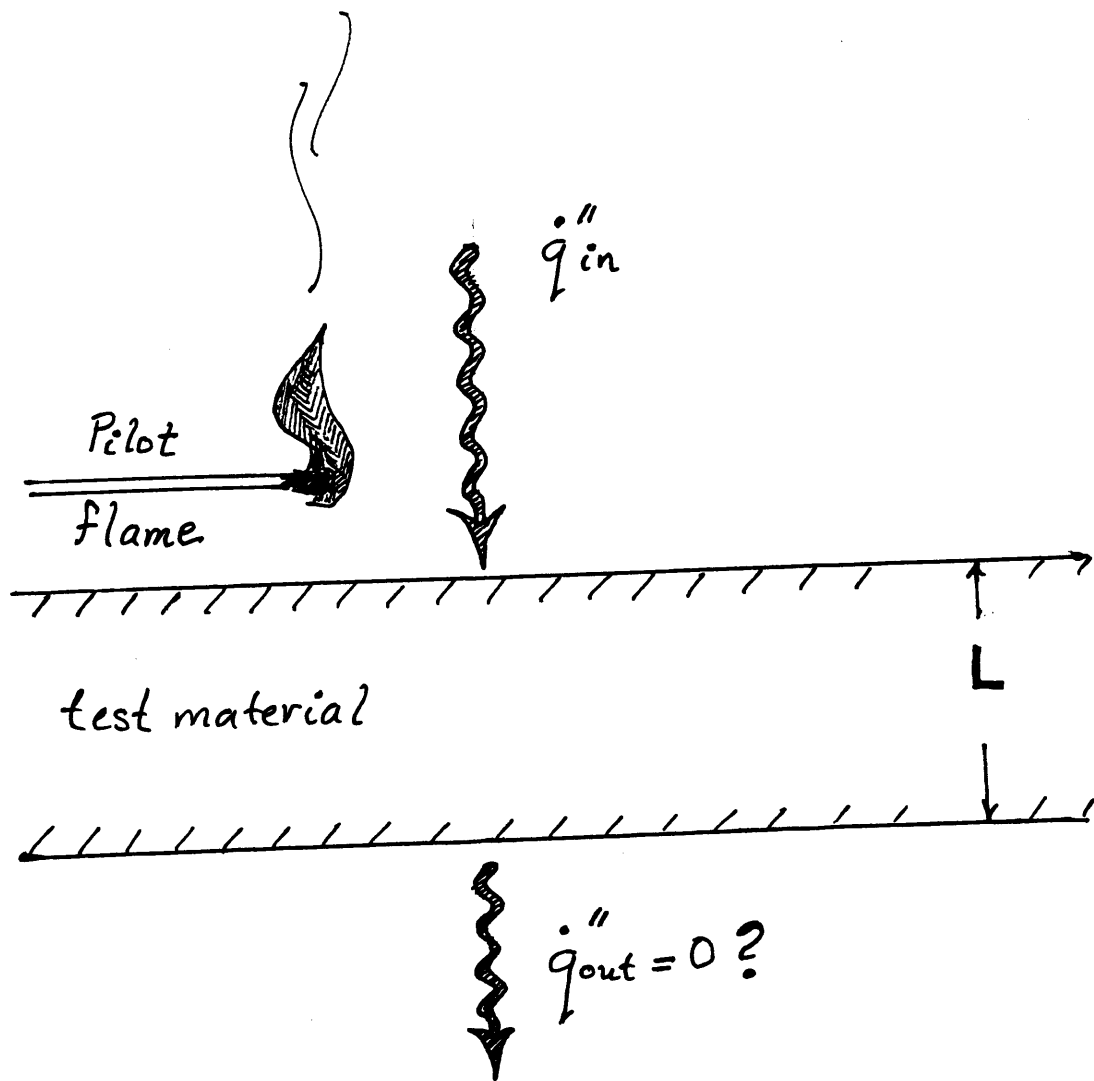


Figure II.3

Figure II.4

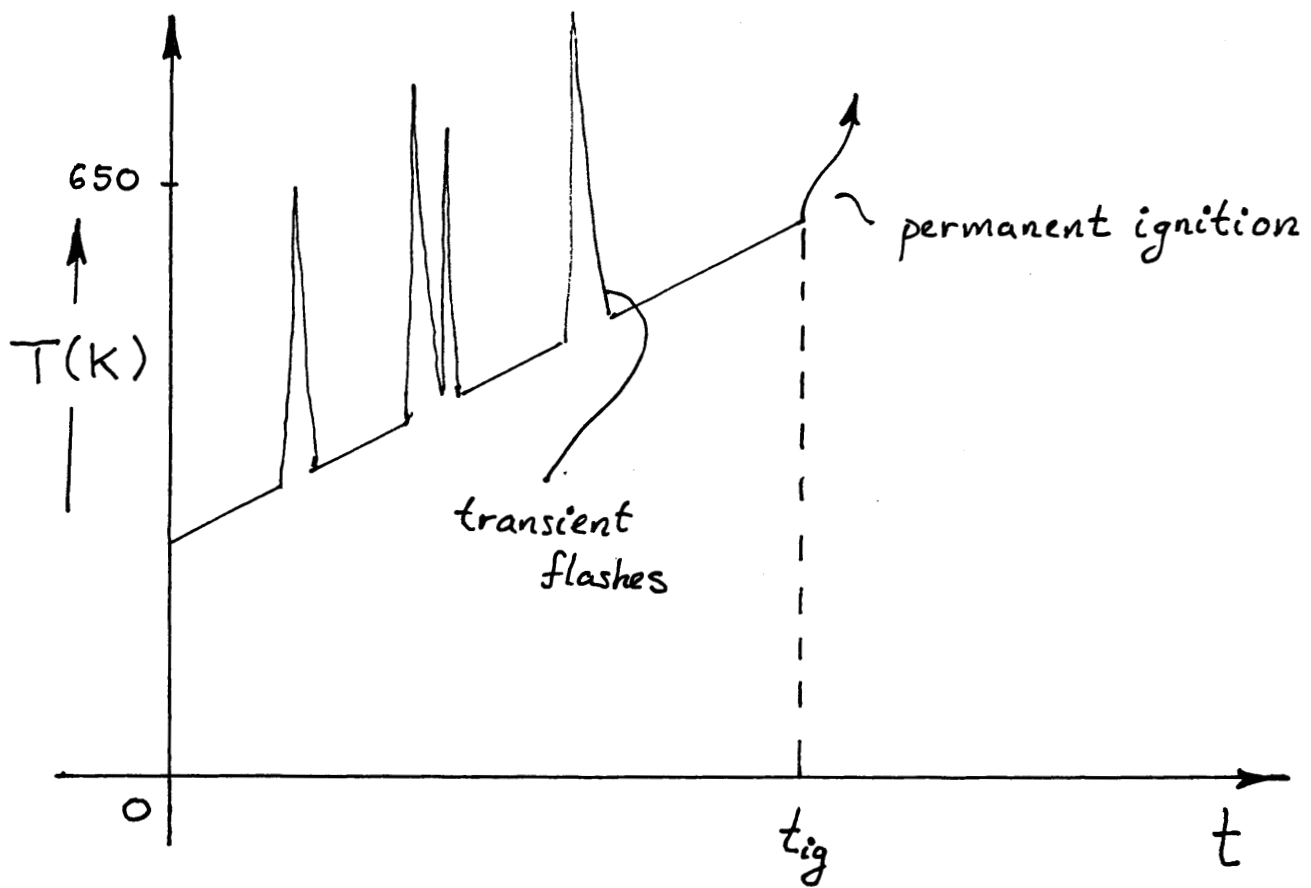
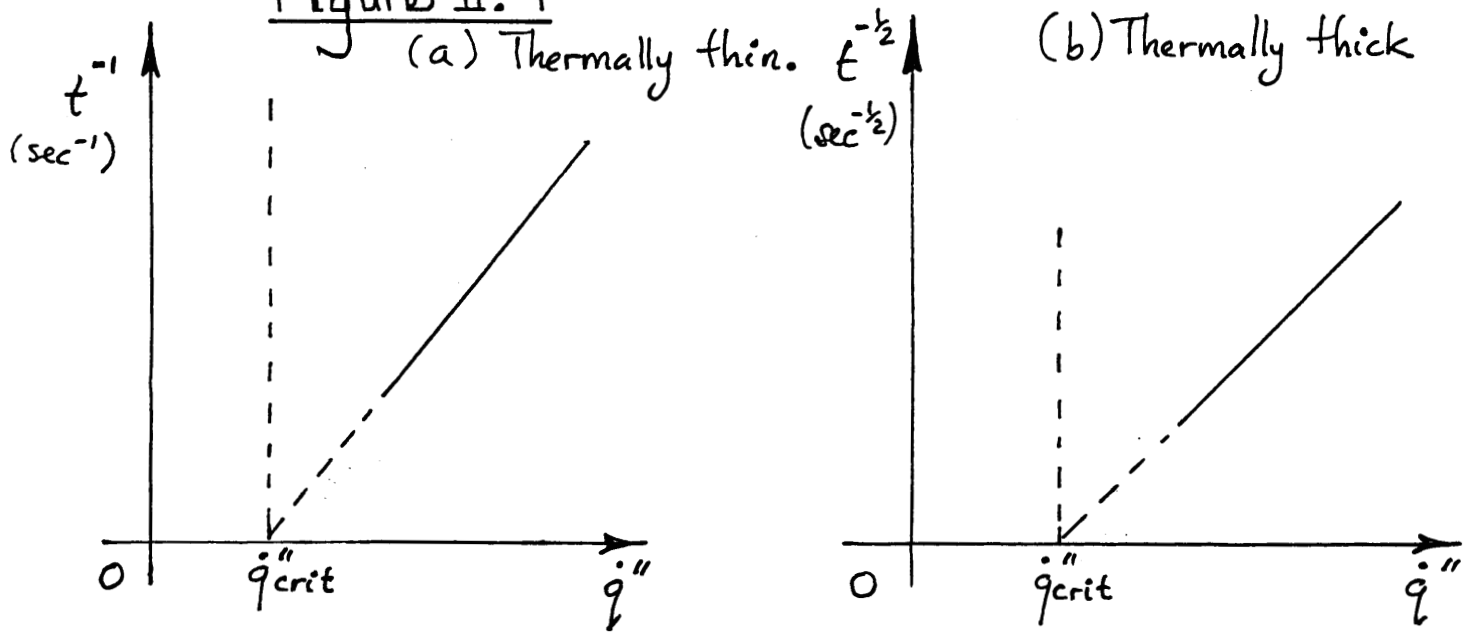


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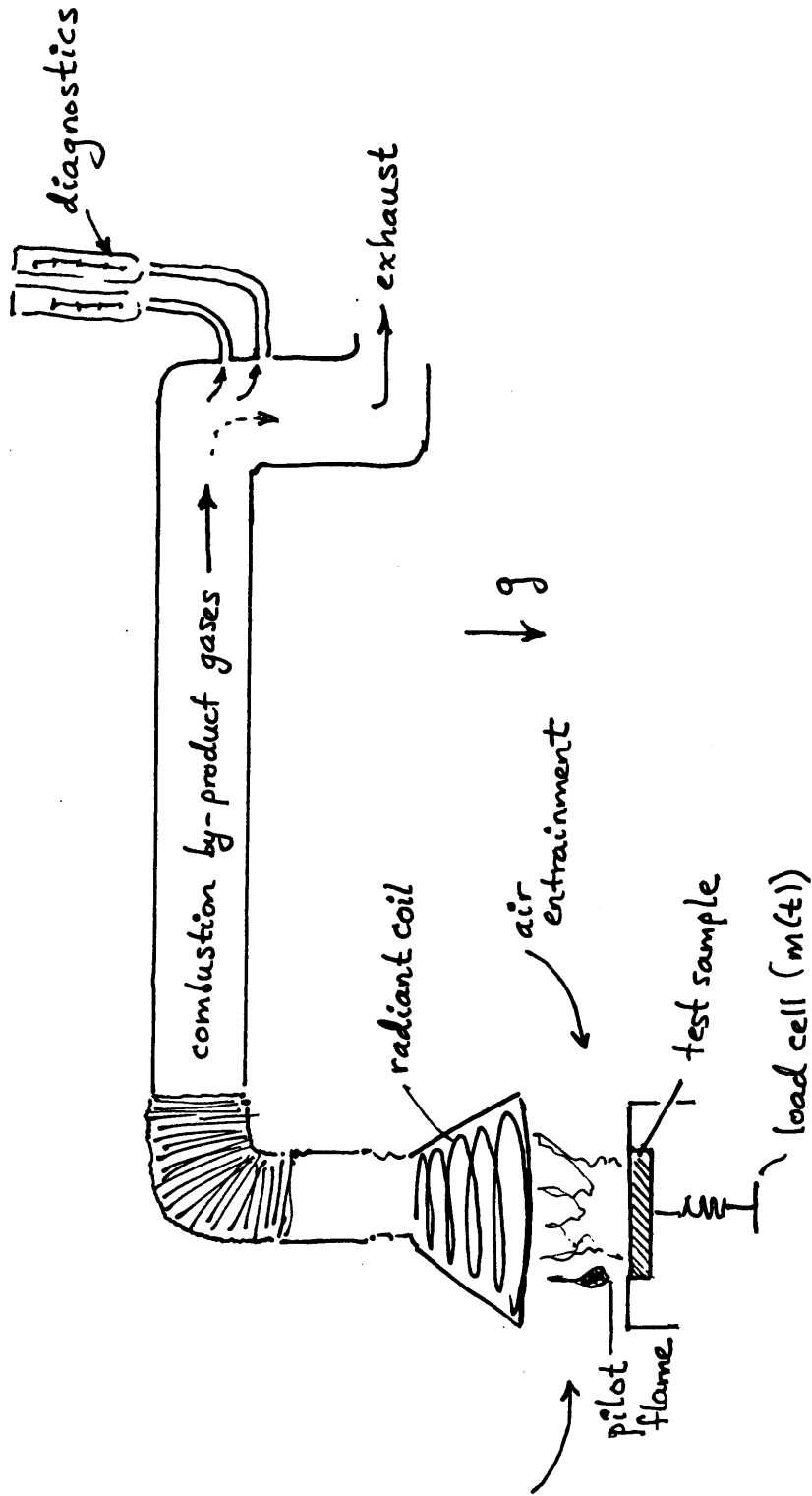


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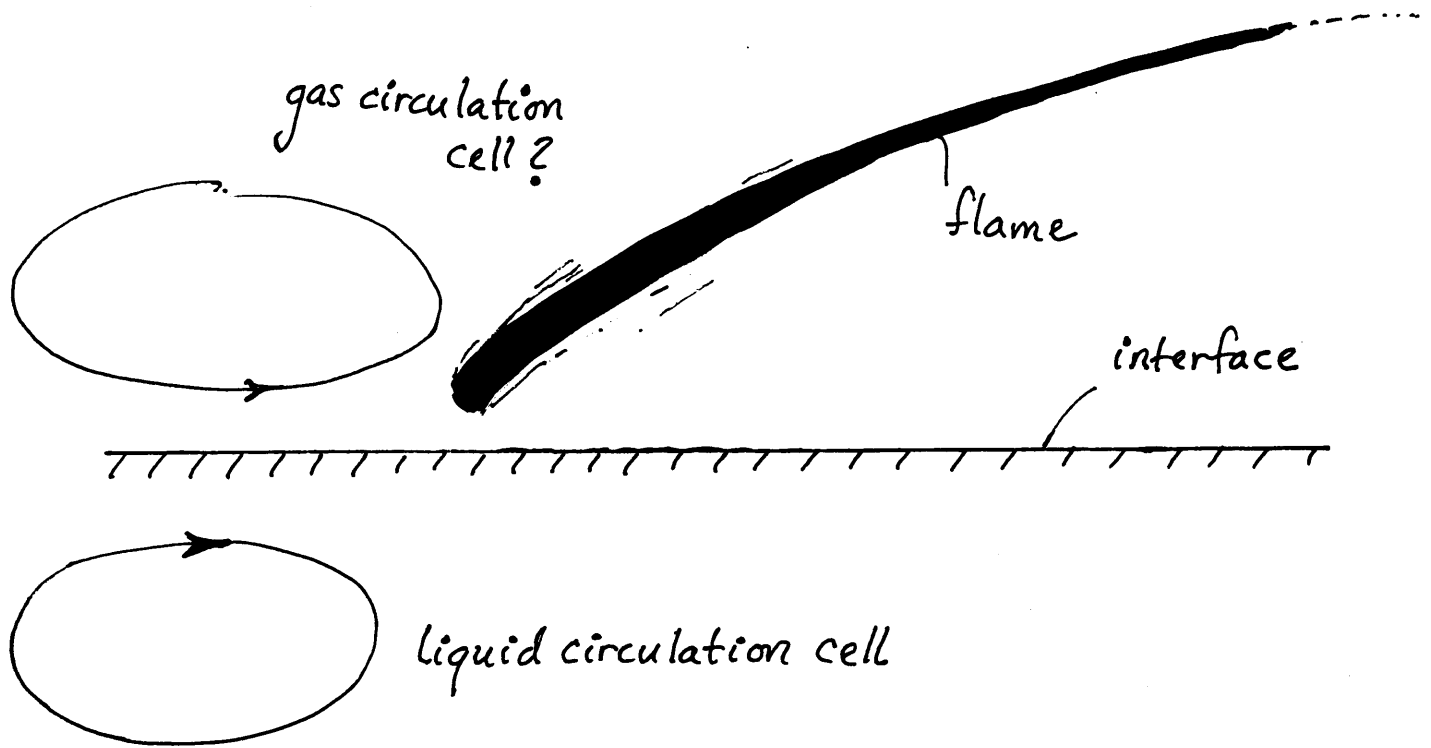


Figure III.1

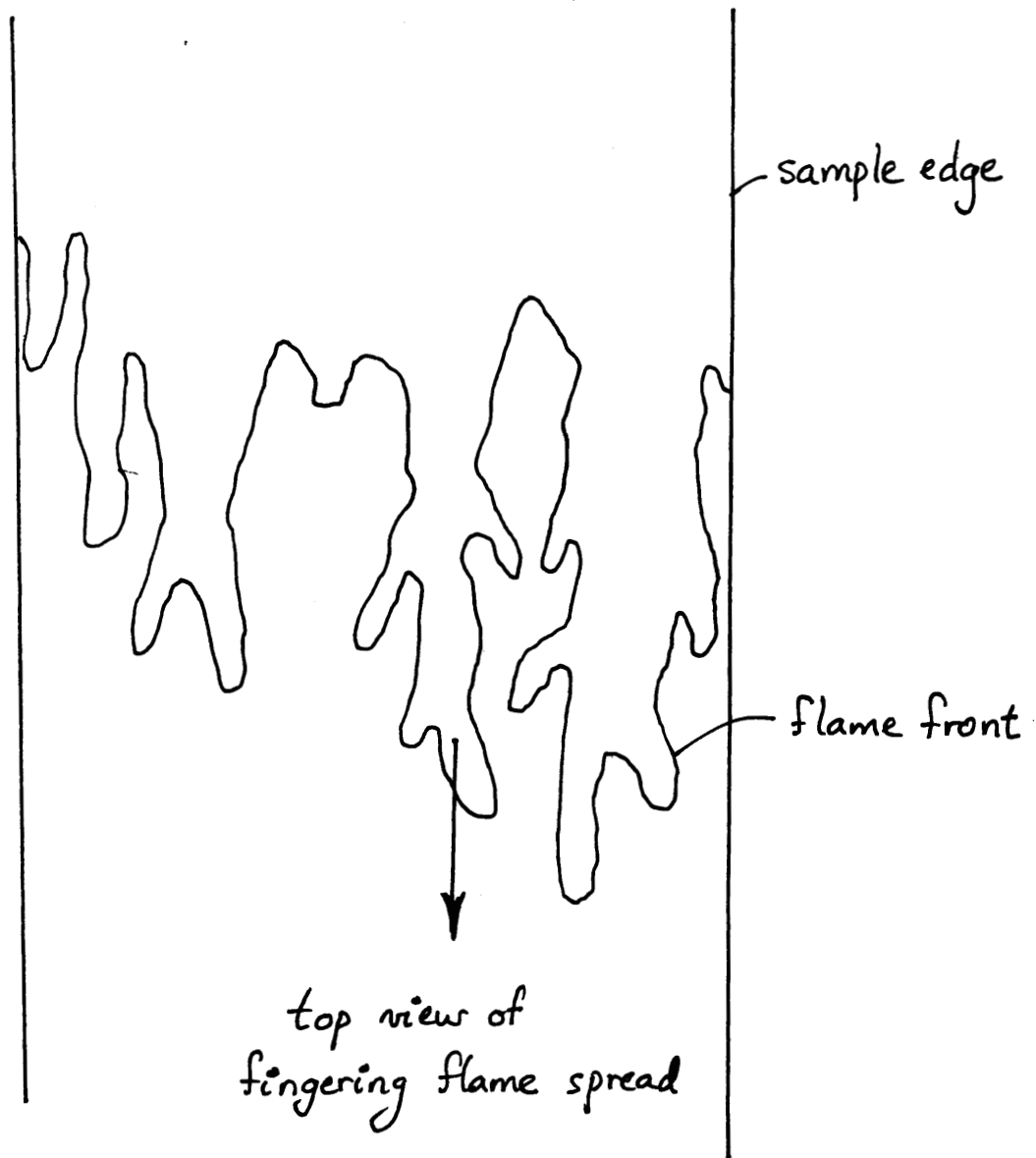


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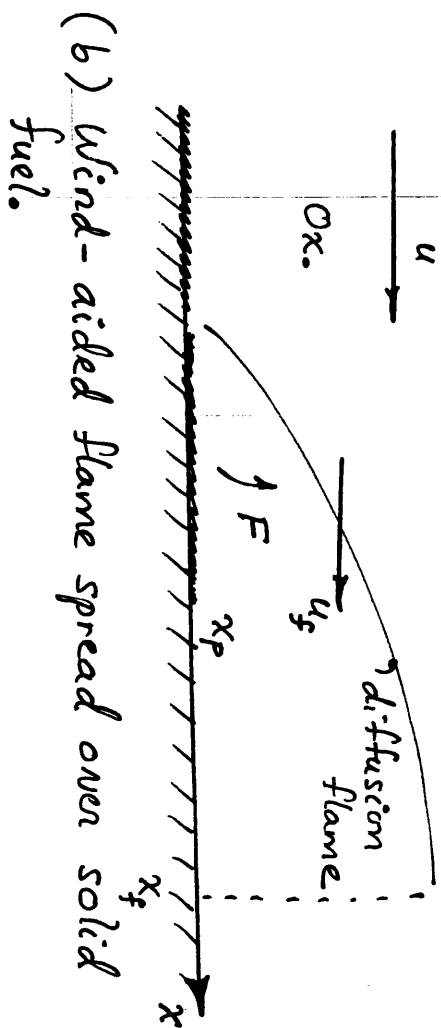
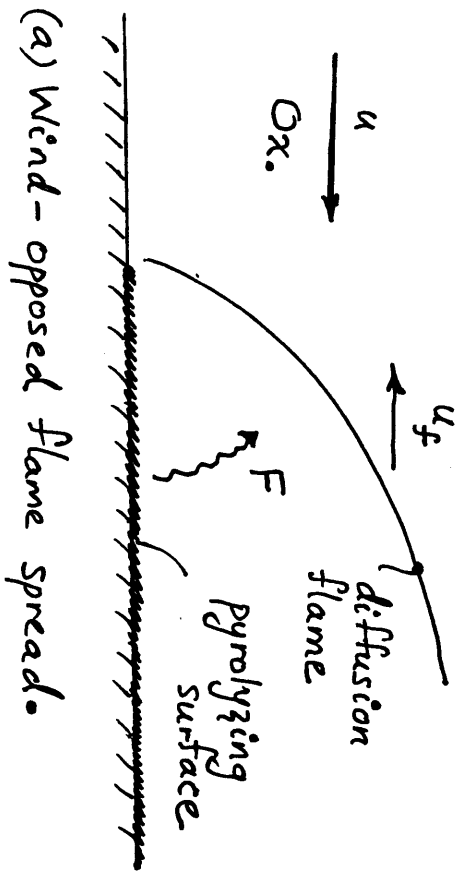
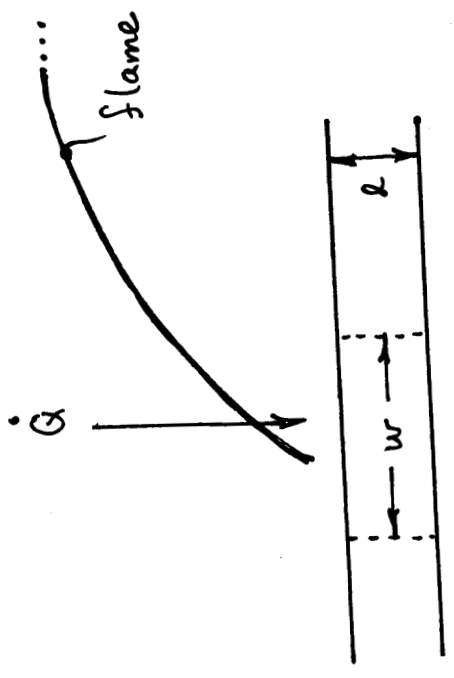
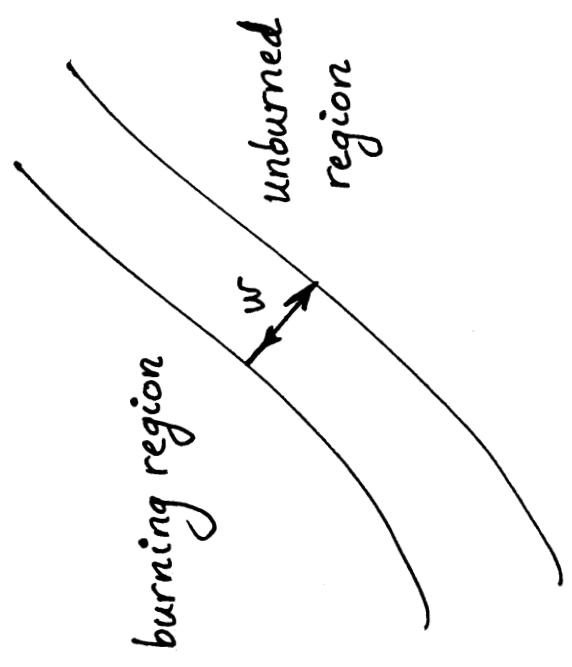


Figure III.3

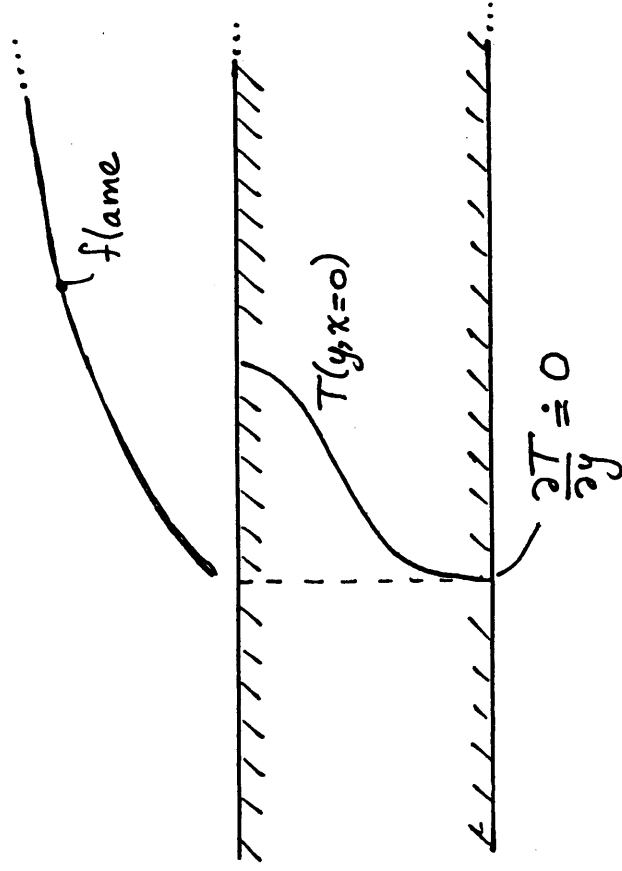


side view of flame spread.

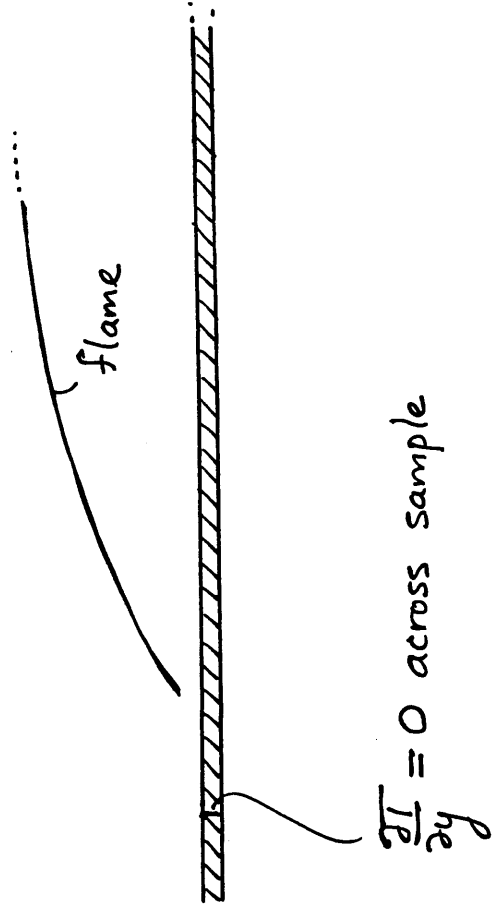


top view of flame spread.

Figure III.4
C



(a) Thermally thick.



(b) Thermally thin.

Figure III.5

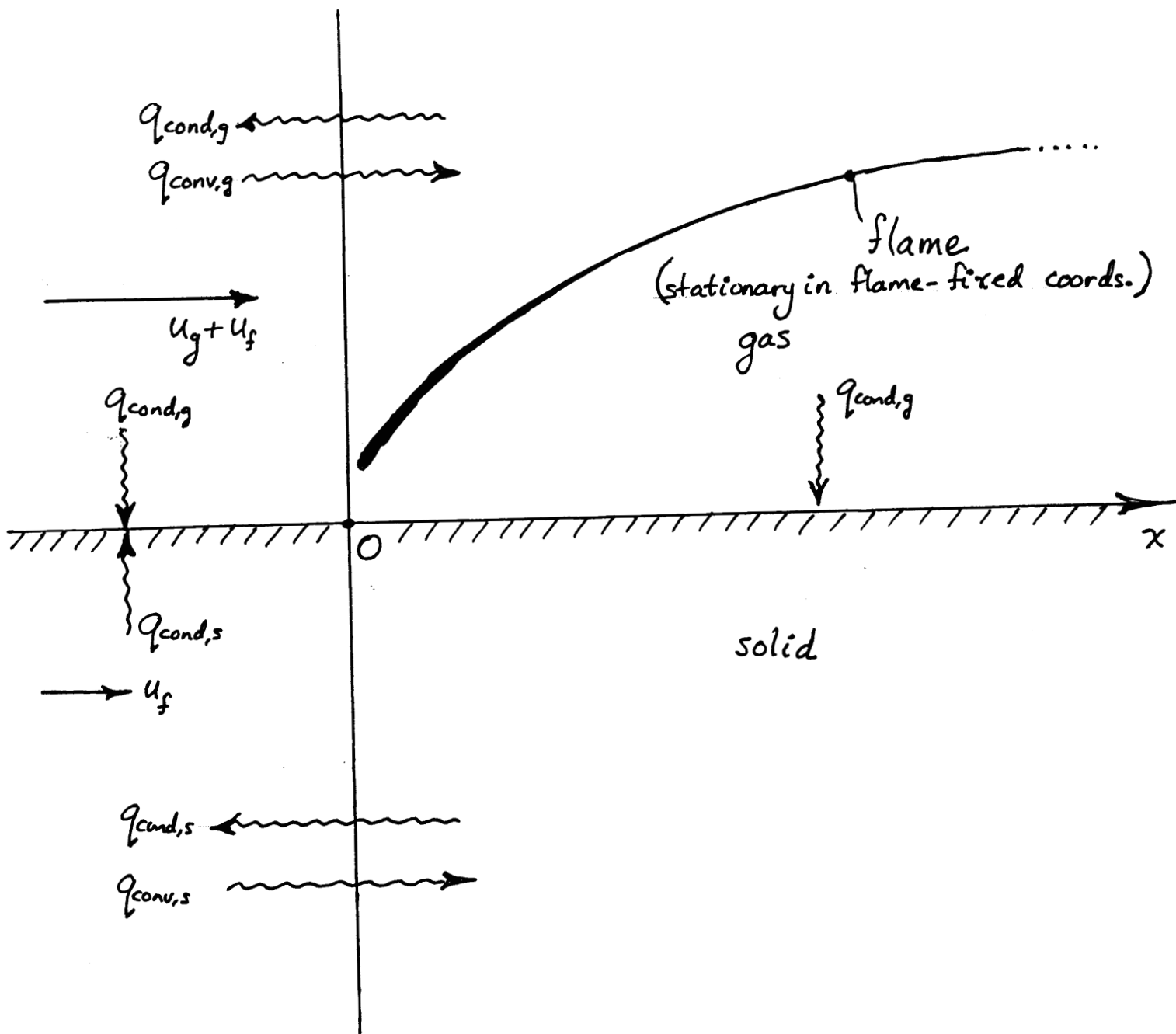


Figure III.6

Name	Chemical Symbol	n	m	α	$\Delta \bar{h}_c$ (kcal/gm-mole fuel)	$\Delta \bar{h}_c$ (kcal/gm-mole O ₂)
methane	CH ₄	1	4	2	-212.7	-106.4
propane	C ₃ H ₈	3	8	5	-530.34	-106.07
n-butane	C ₄ H ₁₀	4	10	6.5	-687.32	-105.74
n-hexane	C ₆ H ₁₄	6	14	9.5	-1002.10	-105.48
n-heptane	C ₇ H ₁₆	7	16	11	-1159.46	-105.41
toluene	C ₇ H ₈	7	8	9	-943.12	-104.79
acetylene	C ₂ H ₂	2	2	2.5	-310.46	-124.19
ethylene	C ₂ H ₄	2	4	3	-337.07	-112.36
benzene	C ₆ H ₆	6	6	7.5	-788.70	-105.16

Table II.1