Literature Review to Support the Development of a Database of Contemporary Material Properties for Fire Investigation Analysis

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https://dx.doi.org/10.54206/102376/WMAH2173

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June 29, 2020

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Acknowledgments

This project was supported by Award No. 2019-DU-BX-0018, awarded by the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice. The opinions, findings, and conclusions or recommendations expressed in this publication/program/exhibition are those of the author(s) and do not necessarily reflect those of the Department of Justice.

To ensure the database is of the most use to the fire investigation, fire protection, and general fire modeling communities, UL FSRI assembled a technical panel comprised of representatives from public, private, academic, and research sectors. The individuals below provided direction for the project.

Project Technical Panel

Name	Affiliation
Vyto Babrauskas	Fire Science and Technology Inc
Ernest Barile	Philadelphia Fire Department
Nicole Brewer	Portland Fire & Rescue
Morgan Bruns	Virginia Military Institute
Steve Carman	Carman & Associates Fire Investigation, Inc
Paul Claflin	Bureau of ATF, Fire Investigation & Arson Enforcement Division
Jason Dress	Bureau of ATF, Fire Research Laboratory
Adam Friedman	Jensen Hughes, Inc., ATF Fire Research Laboratory Contractor
Brian Geraci	Maryland State Fire Marshal
Barry Grimm	International Association of Arson Investigators
Brian Lattimer	Virginia Polytechnic Institute and State University
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Tom Sabella	Fire Department City of New York
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Abstract

The NIJ Technology Working Group's Operational Requirements (TWG ORs) for Fire and Arson Investigation have included several scientific research needs that require knowledge of the thermophysical properties of materials that are common in the built environment, and therefore likely to be involved in a fire scene. The specific areas of research include: adequate materials property data inputs for accurate computer models, understanding the effect of materials properties on the development and interpretation of fire patterns, and evaluation of incident heat flux profiles to walls and neighboring items in support of fire model validation. These topics certainly address, in a concise way, many of the gaps that limit the analysis capability of fire investigators and engineers.

Each of the three aforementioned research topics rely, in part, on accurate knowledge of the physical conditions of a material prior to the fire, how the material will respond to the exposure of heat, and how it will perform once it has ignited. This general information is required to visually assess a fire scene. The same information is needed by investigators to estimate the evolution and consequences of a fire incident using a computer model. Data sources that are currently most commonly used to determine the required properties and model inputs are outdated and incomplete.

This report includes the literature review used to provide a technical approach to developing a materials database for use in fire investigations and computational fire models. A summary of the input from the project technical panel is presented which guided the initial selection of materials to be included in the database as well as the selection of test measurements.

1 Introduction

For the past several years, the NIJ Technology Working Group's Operational Requirements (TWG ORs) for Fire and Arson Investigation have included several scientific research needs that require knowledge of properties of materials that are common in the built environment, and therefore likely to be involved in a fire scene. The specific areas of research include: adequate materials property data inputs for accurate computer models, understanding the effect of materials properties on the development and interpretation of fire patterns, and evaluation of incident heat flux profiles to walls and neighboring items in support of fire model validation. These topics certainly address, in a concise way, many of the gaps that limit the analysis capability of fire investigators and engineers. Each of the three aforementioned research topics rely, in part, on accurate knowledge of the physical conditions of a material prior to the fire, how the material will respond to the exposure of heat, and how it will perform once it has ignited. This same general information is needed to visually assess a fire scene, as well as if the investigator would like to estimate the evolution and consequences of a fire incident with a computational model.

At the first International Symposium on Fire Safety Science in 1986, Howard W. Emmons summarized the state of knowledge and research needs for the future of fire science. At the time, Emmons noted, "it has become broadly accepted that the way of the future in Fire Engineering is through various levels of modeling, aided by a modern computer." He went on to emphasize the need for a handbook of the material properties for the fuels in the model scenario over the range of temperatures expected in the fire environment to use as inputs to fire models [1]. A 2002 Fire Protection Research Foundation Advisory Council on Post-Fire Analysis emphasized the need for better understanding of the materials found at fire scenes, fire test data on products that more closely reflects the end-use configuration, and a burning rate database [2]. Materials properties and test data as well as the archiving of these data were identified as research priorities for fire dynamics, investigations, and building fires by the Society of Fire Protection Engineers (SFPE) Research Roadmap Working Group in 2018 [3]. The same working group conducted a survey of the fire safety community to identify research needs and a web-based library or database of test data and input properties for models was a frequent response.

Fire models can be valuable in understanding how a fire may have occurred and evolved. The data from models may be used to produce graphical representations that can help to explain complicated fire phenomena and cause and origin hypotheses to persons with no technical background in fire science. While this can be beneficial, it is not without risk. Concerns have been raised within the fire investigation community that when the physics underlying the models being used are not completely understood, investigators may be trading one form of “junk science” for another in the form of misused or misunderstood fire model results [4].

In a section titled *All Models are Wrong but Some Are Useful*, George E.P. Box wrote, “Now it would be very remarkable if any system existing in the real world could be exactly represented by any simple model. However, cunningly chosen parsimonious models often do provide remarkably useful approximations ... For such a model there is no need to ask the question ‘Is the model true?’.

If ‘truth’ is to be the ‘whole truth’ the answer must be ‘No’. The only question of interest is ‘Is the model illuminating and useful?”’ [5]. Computational fire models approximate the fundamental physics involved in fires and fire-induced flow fields. It is imperative that investigators that utilize models in forensic investigations understand the scenarios in which these approximations are accurate enough to be illuminating and useful.

While the physics of fire are well understood by scientists under given sets of conditions, the general application of the science to actual investigations currently has significant limits and uncertainties. One of the major limitations on the use of fire models in investigations and elsewhere is the lack of appropriate input data for the fire models. The utility of computational and non-computational fire models in fire research, fire protection, and fire investigations has been demonstrated in many studies. Fire models can only provide useful information when the input properties and parameters accurately depict the scenario to be simulated. Investigators that utilize simple, non-computational fire models in investigations must also have an understanding of the materials and products at a fire scene and use the appropriate property values to yield accurate conclusions.

Currently, data for fire investigations and fire modeling can be found in a variety of sources that have been developed since Emmons publicized the need for widely available materials property data for model inputs [1]. The more traditional sources are handbooks, which include publications like the Ignition Handbook [6], the National Fire Protection Association Fire Protection Handbook [7], and the Society of Fire Protection Engineering Handbook of Fire Protection Engineering [8]. Some of the handbooks provide significant context with the numerical material data provided, but most handbooks do not include this important contextual information that provides model practitioners with confidence that the material data accurately describes the scenario. Text books also contain tables of materials data that have usually been sourced from papers and reports for the use of the readers.

With the support of NIJ, the National Center for Forensic Science (NCFS) of the University of Central Florida (UCF) and Department of Fire Protection Engineering at the University of Maryland College Park (UMCP) created a Burning Item Database and Thermal Properties Database. However, these databases were developed with data from textbooks and other literature sources, all of which were more than 10 years old when the databases were developed. Additionally, the data available from the existing sources left portions of the database incomplete, or the lack of material identification made the data difficult to use with any confidence. With the development of new materials and products and the rapid introduction of these new materials to the general public and the built environment, test data that is a decade old or older may be of limited use to fire investigators. The fire investigation, fire research, and fire protection communities need a materials property database populated with data from rigorous testing of the most common contemporary products and materials found in the built environment.

The primary objectives of this project include:

1. To measure material properties and fire test data on a combination of at least 70 construction materials, interior finishes, and furnishings for use as fire model input.
2. To develop an online database which provides adequate detail to enable accurate use of the

data as input to a fire investigation analysis.

3. To demonstrate the use of the database for hypothesis testing.

This review identifies and highlights the current status of “published” data available for use in fire analysis and fire models. The technologies available to develop a cloud-based database are briefly discussed and the models and required input data are presented. This information is offered as a platform for the fire research, fire protection, and fire investigation communities to assist with determining the materials to be included in this study, the most important data, the preferred methods of measurement, and the best method of presenting the data.

1.1 Existing Property Databases

Several efforts have been made to compile the results of standard fire tests and thermo-physical properties required in fire investigation analyses or as inputs for fire models. One of the earliest examples of such an undertaking is attributed to Gross, who collected data from a variety of technical reports, research publications, handbooks, and product specification sheets published over the period from 1972 to 1985 [9]. The collection of data presented by Gross was published in response to the need for inputs to the state-of-the-art predictive computational fire models of the time. Thermo-physical properties were presented for a range of materials commonly encountered in the built environment as well as non-combustible materials commonly used in experimental fire research. These properties were presented as a function of temperature when available and as measured at room temperature otherwise. Mass loss rate (MLR) and/or heat release rate (HRR) data collected through tests in which typical combustible furniture items and fuel sources for fire experiments were burned in the open or in a compartment were also collected and presented by Gross. Accompanying these data were basic descriptions and a single photograph or drawing of the furniture items. With this publication, Gross set a standard for presentation of a collection of data for fire model inputs, but the relative lack of images and detailed descriptions of the tested objects and materials left uncertainty in the use of the data by model practitioners.

In an attempt to standardize fire test data such that model practitioners and researchers in all countries would be able to share and access data between each other, researchers from the National Institute of Standards and Technology (NIST) and the UK Fire Research Station developed a data standard and database called the Fire Data Management System (FDMS) [10]. As proposed and executed, the FDMS was a data organization format system as well as a relational database that stored vector (time-dependent) and scalar (single-value) data in tabular format under standard headings and allowed users to search and filter results according to the headings and values in the columns. The test data that were stored in the original FDMS were primarily collected using oxygen consumption calorimetry with bench-scale samples and full-scale single object samples (see Section 5.1). Further development of the FDMS resulted in a more general format to store information and data collected through any test method as well as a central data repository to which researchers could submit data and from which researchers, investigators, and model practitioners could export data [11, 12]. The major accomplishment of the FDMS was a detailed discussion of the functions necessary for management of fire test data to yield maximum usefulness of the data by researchers, model practitioners, and others that require access to the data. The FDMS did not incorporate, but emphasized the need for future developments that included integration between the database and computational models as well as drawings or other images of the test articles [10].

The NIST Chemistry WebBook, first published in 1996, is an open access, online database that provides gas- and condensed-phase chemistry and thermodynamics data as well as phase change data for pure substances [13]. The data are presented in tabular form with the option to plot thermodynamic data as a function of temperature. The database features a robust search function that allows the user to search among the chemicals according to chemical formula, name, International Union of Pure and Applied Chemistry (IUPAC) identifier, Chemical Abstract Services (CAS) number, reaction, molecular weight, ion energetics properties, vibrational and electronic energies, or structure, or the option to search through the database according to author. The database is periodically updated, with the most recent update taking place in October 2018. These data may be useful in forensics analyses, but of limited use as inputs to fire models because pure substances are not often encountered in realistic fire scenarios.

The Ignition Handbook is a collection of information designed to educate readers on a range of basic to advanced topics relating to ignition of explosions and fires [6]. The handbook provides a scientific background on chemistry, ignition, combustion, and the characterization of the ignitability and flammability of materials and products with a focus on forensic investigations. Also included in the handbook are descriptions of the ignition hazard of hundreds of materials and products as well as a collection of tables that provide a wide range of ignition-related properties and standard fire test results from studies conducted throughout the 1900s and early 2000s. The information collected in the Ignition Handbook is useful for general knowledge when conducting investigations, but may lack the specificity required when modeling actual fire events.

In 2005, the SP Swedish National Testing and Research Institute began compiling the results of standard and custom fire tests that were conducted over the course of large experimental programs conducted in Europe in an open access online database [14]. The database includes the time-dependent or temperature-dependent results of tests conducted from 1989 to 2012, ranging in scale from milligram-scale to full-scale on products including upholstered furniture, cables, surface materials encountered on ships and railcars, and other products and materials from the built environment. The entries in the database include labels of up to four constituent materials, product, object, and scenario descriptions, the test method, and the reference study. The database includes a search function that allows the user to filter database entries according to the labels. The database also allows the user to view all data provided for the specific entry, export the data in text or xml format, or access an interactive plotting tool to visualize the data. Although the database provides data from hundreds of tests on materials and objects, there are no images of the test articles in the database and the references are not easily retrievable, resulting in vague labels and uncertainty about the test samples.

The Forest Products Laboratory of the U.S. Forest Service has published the results of cone calorimeter tests conducted on myriad wood-based materials and typical building materials in an open access database [15]. Standard cone calorimeter data sets include the heat release rate per unit area (HRRPUA), mass loss rate per unit area (MLRPUA), effective heat of combustion, specific extinction area, carbon monoxide and carbon dioxide yield, smoke production rate, and extinction coefficient as a function of time. Several entries in the database also include photographs of the sample to provide a better understanding of the structure of the sample for the database user. The database may be filtered according to the type of material and the set point heat flux in the cone calorimeter tests. The Fire Research Branch of the U.S. Federal Aviation Administration (FAA) Technical Center [16] has developed an open access database of cone calorimeter results for polymeric materials. The database provides the CAS number, the material trade name, the chemical name, and the material type (thermoplastic, thermoset resin, epoxy resin, composite, etc.) for the test as well as a file that contains the cone calorimeter output data. The dates of the tests conducted to collect these data range from 1997 to 2015. The data contained in these databases may be useful for analyses related to investigations and fire modeling, but of limited use.

In 2009, the National Center for Forensic Science at the University of Central Florida, in collaboration with the University of Maryland, and funded by the U.S. National Institute of Justice began a project titled “The Creation of a Thermal Properties Database” to collect fire test data and thermal properties in an online database [17, 18]. The database features two distinct components that include a data set for material properties and a data set for object properties. The Material Thermal Properties Database includes ignition temperature, thermal conductivity, density, specific heat capacity, and heat of gasification at room temperature and at ignition temperature for metals, polymers, woods, and other miscellaneous materials, but lacks information related to mass lost during burning. The material properties data presented in the database were drawn from technical reports, research publications, handbooks, and text books published between 1984 and 2007, few of which were primary sources.

The Burning Item Database is divided according to the type of object for which HRR data are available. The designations include beds, chairs, curtains/draperies, electronics, furniture, miscellany, and sofas. For each entry in the data set, a combination of the materials and mass fractions of each material included in the object, total weight, flammable mass, maximum HRR, and effective heat of combustion are provided. Select entries also provide photographs or drawings of the object, and time-dependent charts and tabulated values of the measured HRR of objects for which data were available. Data in the object properties database were collected in tests conducted with the furniture calorimeter or a similar experimental method. These data were sourced from research publications from all over the world that presented data collected over several decades up until 2005. In many cases, the research publications did not provide images or a complete description of the tested object.

The 5th edition of the Society of Fire Protection Engineers (SFPE) Handbook [8] contains several chapters with collections of material properties and object burning data that may serve as input to fire models for a fire investigation analysis. A chapter by Witkowski et al. [19] focused on thermal decomposition of polymers provides a collection of data including polymer chemical names, glass transition, melting, and decomposition temperatures, as well as reaction kinetics for select polymers. Kodur and Harmathy present a collection of thermal and mechanical properties of typical building materials, composites, and insulation materials [20]. The molecular weight, boiling point, heat of gasification, heat of combustion, flashpoint, flammability limits, and autoignition temperature for many liquid fuels have been collected by Drysdale in a chapter that explores ignition of liquids [21]. Much of the data presented in the SFPE Handbook shares sources with previously mentioned efforts and pre-date the Handbook by 40 years.

A chapter of the SFPE Handbook authored by Babrauskas presents a wealth of experimental studies published between 1975 and 2013 in which HRR for a wide array of objects and scenarios were collected or inferred from collected data [22]. In the chapter, a multitude of graphs and tables summarize the peak or time-dependent HRR for these objects and scenarios. Khan et al. present a collection of calculated quantities, including the heat of gasification, for polymers and composites tested by FM Global. The handbook also features appendices filled with tabulated thermo-physical properties and fuel properties for combustible materials [23, 24]. These data may be useful when modeling fire scenarios, but full descriptions of the materials and objects tested are generally lacking from the handbook. This lack of specificity may lead to confusion among model practitioners and inaccurate predictions and conclusions from the models.

1.2 Motivation

The data contained in the aforementioned resources and databases was collected in tests conducted from as long ago as 50 years. Over the course of the past 50 years, the constituent materials and design of typical furniture items and construction assemblies has changed significantly with the ongoing development of engineered polymers, composites, and fire retardants over this time period. As the materials involved in fires have become more complicated, the fire investigator also needs a better understanding of the ignition parameters and heating and burning behavior of these materials.

An example of a material that has been misconstrued in the fire protection literature over the years is gypsum. Gypsum is the mineral calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), which is a major component of both plaster and gypsum wallboard. Early measurements for thermo-physical properties were made on the mineral gypsum and published in research articles and handbooks. These published properties were proliferated through other handbooks and persisted and was used by model practitioners in lieu of gypsum wallboard long after plaster and lath construction was largely displaced by wallboard construction. Even after the thermo-physical properties of gypsum wallboard were measured and published, myriad compositions of gypsum wallboard were introduced to the market (The U.S. Gypsum website lists at least 38 different varieties of gypsum wallboard in thicknesses ranging from 1/4 in. to 1 in. available to consumers [25]). Data for the thermal conductivity of gypsum board at room temperature published from 1985 to 2019 ranges from 0.16 W/m·K to 0.355 W/m·K and specific heat capacity at room temperature ranges from 884 J/kg·K to 1540 J/kg·K [9, 26–32]. The uncertainty in the thermo-physical properties of gypsum wallboard, which is encountered in most contemporary construction, may lead to inaccurate conclusions in fire investigation analyses and fire models.

The chemical makeup and configuration of component materials in upholstered furniture items that are commonly found in residential occupancies has changed significantly over the past 50 years. Synthetic materials like polymers and foams have displaced natural materials like cotton in a transition from so-called legacy furniture to modern furniture. These synthetic materials more readily allow flame spread than natural materials and it has been noted that modern furniture may lead to a more severe fire and more rapid transition to flashover than legacy furniture in a residential setting [33, 34]. Although experimental campaigns are periodically undertaken to test furniture typical of the time period to update the information available in handbooks and other resources, the technology for upholstered furniture is rapidly changing as new polymers, flame retardants, barrier fabrics, and furniture configurations are introduced.

This rapid rate of change ensures that upholstered furniture tested a few years prior may not be representative of the present furniture trends. As an example, since July 2007, the design of all mattresses sold in the U.S. has changed to meet peak HRR limits per 16 CFR Part 1633. This change means the construction and composition of mattresses produced after 2007 may be significantly different from those produced prior to 2007 [35].

2 Database Technologies

The two predominant database models are relational and non-relational. Relational databases store information in tables structured into rows and columns. This structured format makes defining relationships between data straightforward and typically uses the structured query language (SQL) for queries. The use of SQL and the relational nature of the tables allows for complicated queries that may be useful to model practitioners. The format of entries in a relational database generally requires the format of the data to be pre-determined and generally consistent between all entries.

Non-relational databases offer more variability in the defined data types (including documents, key-value pairs, graphs, etc.). Because non-relational databases are not required to have a structured format and they do not use a declarative query language (they are often called NoSQL or non-SQL databases). The inherent variability in database entry formats available in NoSQL databases may allow for each entry to be tailored to the measurement or analysis method for the specific material or product. Time-series and temperature-series data may be stored in either type of database.

3 Fire Models

Fire models have become more sophisticated over the past few decades and these models may require more input parameters and more detailed information than is currently available in the resources to attain the desired level of accuracy. Novel test methods have been developed over the past few decades that provide more control in characterizing the reaction-to-fire and thermophysical properties for materials and products.

A myriad of models with a range of complexity have been introduced to the fire protection, research, and fire investigation communities since the 1950s [36]. These models approximate actual physical phenomena and have been developed with empirical and physical bases. The models specifically developed to describe fire-driven physical phenomena range from simple algebraic relations to complicated computational fluid dynamics codes. Increasing the sophistication of the model used to predict a given phenomenon or scenario also increases the number of input parameters and properties required to fully define the model to ensure accurate characterization.

Analytical and semi-empirical models have generally been formulated for specific scenarios and may be used to calculate a single aspect of steady-state conditions, thus they are limited in application, but require fewer input parameters and may be used without the help of a computer. Several chapters of the SFPE Handbook provide detailed descriptions of and the input parameters that they require [8]. This section focuses on computational methods for fire modeling because they require the largest breadth of input properties and parameters.

There are two classes of computational models that are most commonly used in fire research, fire protection engineering, and fire investigation. These classes are zone models and field models, which are also known as computational fluid dynamics (CFD) models. Zone modeling was first introduced to the fire research community in the 1970s and is still widely in use today. Zone models are constructed with the assumption that the atmosphere within a computational domain may be divided into two control volumes that are well-mixed and that generally may be described by a single temperature and composition. The two control volumes are defined as an upper volume zone and a lower volume zone, formed through buoyant stratification driven by the fire source [37].

Some zone models divide the computational domain into an arbitrary number of zones and maintain the assumption that the temperature and concentrations within each zone are uniform [38]. The fire is represented through empirical fire plume correlations as a mass and enthalpy source term. Figure 3.1 shows a schematic of a fire in a compartment as represented in a zone model. In the figure, the dashed lines indicate the boundary between zones CV_1 and CV_2, $\dot{m}_s$ is the mass flux of fuel into the computational domain, $\dot{m}_e$ is the mass flux of air entrained by the plume, $\bar{w}$ is the velocity of the zone boundary, $\bar{V}$ is the fluid velocity, $\dot{m}$ is the mass flux out of the computational domain through a vent, and T and p represent the temperature and pressure of the upper zone, respectively.

The conservation equations for energy and mass are solved for each zone. Pressure is not explicitly

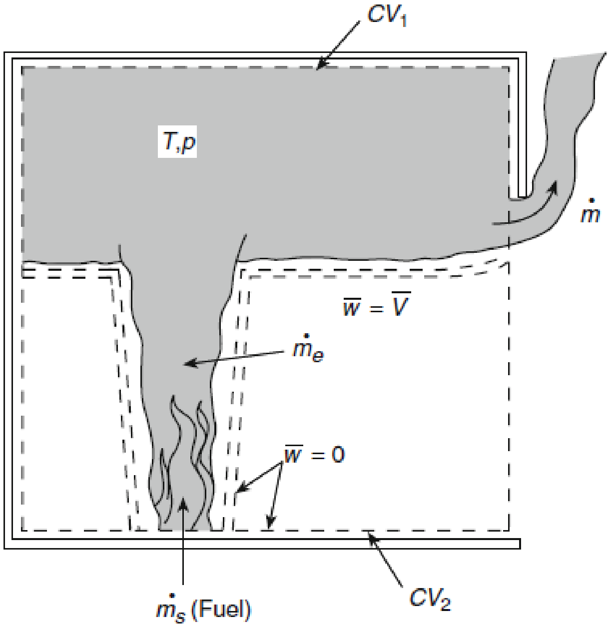


Figure 3.1: Schematic of Zone Model Representation of Fire Compartment [37]

accounted for, but is accounted for implicitly in the energy conservation equations. Because of the formulation of many zone fire models and the disparity between time scales at which pressure equilibrates relative to other variables, compartment overpressures due to fire are generally not resolved.

Submodels available in some zone models may calculate heat transfer to boundary surfaces, structural members, fire and smoke suppression and detection devices, and fuel packages, which require the thermo-physical properties and emissivity of each of the target objects. A submodel may be included that affects the fire source representation due to heat feedback from the hot upper zone or vitiated oxygen conditions in the computational domain to more accurately represent growing fire conditions. The input parameters that may be defined for the fire source are the free burning heat release rate, fuel burning area, heat of combustion, heat of gasification, ignition temperature, critical heat flux, and product yields.

Common zone models include the NIST Consolidated Model of Fire Growth and Smoke Transport (CFAST) [39], The Building and Research Association of New Zealand (BRANZ) B-RISK [40], and the Building Research Institute of Japan BRI2002 [41], among many others [42]. Due to the simplifying assumptions inherent in zone models, they are less computationally expensive than field models, but also suffer from a lack of accuracy when the real conditions deviate from the idealized modeled scenario. A major limitation to zone models is the inability to represent vent flames, transient flow in corridors, and shaft flows [37], although submodels may be developed to represent these phenomena.

CFD fire models divide the computational domain into finite volumes with the assumption that the temperature, pressure, and mass fractions are uniform in each volume and that the velocity and fluxes are uniform over each surface of the volumes. Figure 3.2 displays an image from a simulation of a fire in a compartment with an open door that shows the discretization of the domain and demonstrates the uniformity of temperature over each volume. Equations for conservation of mass, species, energy, and momentum are solved for each finite volume. CFD models are capable of resolving more physical phenomena than zone models as well as transient effects in the development of fire-induced flow phenomena, but do so at a significantly higher computational cost than zone models. CFD fire models also typically include a wide range of submodels that represent phenomena that take place on a length scale smaller than the computational grid or that cannot be explicitly described by the conservation equations.

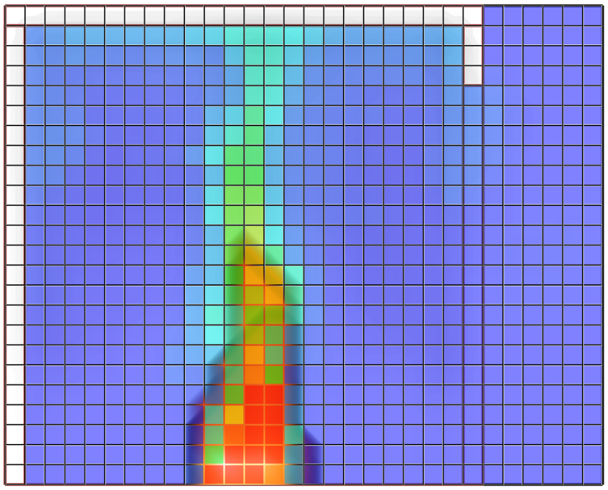


Figure 3.2: Image from CFD Model Simulation of a Fire in a Compartment

The CFD models that are most commonly used in fire research, fire protection engineering, and fire investigation are open source and generalized for the widest possible set of applications. These models include the NIST Fire Dynamics Simulator (FDS) [43] and FM Global FireFOAM [44]. CFD codes that may be useful to fire researchers and fire investigators that employ technologies that have not been considered in this review are ANSYS Fluent and Gexcon FLACS. Fluent is a robust general purpose CFD code that solves the Reynolds-averaged Navier-Stokes (RANS) equations for fluid flow, which are well-suited for steady-state simulations, but are not commonly used to describe fire dynamics or fire-induced flows. FLACS is a CFD code that solves RANS equations and is primarily used to gas dispersion and gas and dust explosions [45].

3.1 Properties Required for Fire Models

Because of the disparity in spatial and temporal scales between the physical processes that occur in the gas phase and the condensed phase, the most sophisticated computational fire models employ a set of coupled submodels that account for chemical and physical phenomena in each phase separately. Within each model, there are varying levels of sophistication based on the submodels employed, and the more sophisticated submodels tend to require more input parameters. The following discussion of fire modeling and submodels are specific to FDS [43], but similar functionality is available in other CFD fire models, and the input properties required in other manifestations are generally the same as those presented in this section.

3.1.1 Condensed Phase Properties

Pyrolysis is the process by which condensed phase materials undergo thermal decomposition and change phase from solid to gaseous vapors. Pyrolysis is typically considered a solid-phase phenomenon, but it is also possible for liquids or solutions to undergo pyrolysis in the process of evaporation. Heat transfer and phase changes from solid or liquid to gaseous fuels are represented in CFD models with a pyrolysis submodel.

Because heat transfer is calculated to and through the material and the boundary conditions may be changing throughout the simulation, an analytical solution to describe heat transfer in the condensed phase is not available. The material must be divided into a grid of cells upon which an energy and mass balance is completed through an iterative solution procedure. To completely characterize objects in the computational domain, the approximate geometry of the object must be defined with materials assigned to each surface of the object. The composition and geometry of each surface of an object of interest must be defined as well as the thermal conductivity, specific heat capacity, and density of each component material. In general, thermal conductivity and specific heat may be defined as functions of temperature. Optical properties including emissivity, refractive index, and absorption coefficient may be defined to quantify absorption and emission of thermal radiation.

The simplest representation of a pyrolysis model requires only that the HRRPUA of a defined surface (obstruction or vent) be specified. This HRRPUA definition may be a single set point, which will maintain a constant HRR, oxygen permitting, or a function of time. In this simple representation, the fire source is instantly burning when the simulation starts and is unaffected by the heat feedback from the flame or surroundings as simulation progresses. In this case, the thermo-physical properties of the materials associated with the fire source surface are not required, but these properties are required for boundary and target object materials.

A more complicated use of the pyrolysis model, which may be employed when the fuel package is a target object, involves assigning an ignition temperature and the heat of vaporization for the surface. In addition to these properties, all of the aforementioned thermo-physical properties must be defined to calculate heat transfer in-depth into the material, which allows the evolution of the surface temperature to be tracked. The definition of the heat of vaporization is optional and accounts for heat absorption by the material as it undergoes thermal degradation and decomposition leading up to ignition, which effectively delays ignition consistent with the actual physics of burning.

A complex representation of pyrolysis may be invoked to couple not only ignition, but also the burning rate, to the material temperature. To invoke this complex model, the reaction mechanism for the material components of the object must be defined. The reaction mechanism requires a reaction scheme, which consists of the number of reactions that occur sequentially or in parallel with the general form shown as Equation 3.1. Also required in the reaction scheme definition are the reactant and product materials or species and the stoichiometric coefficients for each product i' ($\nu_{i'}$). Any intermediate materials that exist in the model between the initial and final state of a material undergoing pyrolysis must also be defined with appropriate thermo-physical properties.

$$Reactant_i \rightarrow \sum_{i'=1}^{N_p} \nu_{i'} Product_{i'} \tag{3.1}$$

The Arrhenius reaction parameters, which include the Arrhenius pre-exponential factor (A_{ij}) and the activation energy (E_{ij}), as well as the reaction order ($n_{s,ij}$), must be defined for the jth reaction. The reaction rate for the jth reaction that involves the ith reactant, as it is represented in FDS is included as Equation 3.2. In addition to these parameters, the heat of reaction may be defined for each reaction and a distinct heat of combustion may be defined for each gaseous product. If the presence of oxygen is expected to affect the rate of pyrolysis or if oxidation is expected to occur, the heterogeneous reaction order ($n_{O_2,ij}$) may be defined as well as the gas diffusion length scale (L_g) as represented in Equation 3.3.

$$r_{ij} = A_{ij} Y_{s,i}^{n_{s,ij}} \exp(-\frac{E_{ij}}{RT_s}) X_{O_2}^{n_{O_2,ij}} \tag{3.2}$$

$$X_{O_2}(x) = X_{O_2,g} \exp(-\frac{x}{L_g}) \tag{3.3}$$

Note that FDS by default uses an nth order reaction model, whereby the reaction rate is a function of the reactant mass fraction ($Y_{s,i}$) raised to the power of the reaction order. Other CFD codes and standalone pyrolysis models provide functionality to define reactions with many possible reaction models [19] that have been derived to describe different physical phenomena or trends visible in the reaction data. A unified theory or standard method of how to best describe the reactions that take place during pyrolysis has not been developed. This means that the model used to describe a pyrolysis reaction is at the discretion of the scientist or engineer that analyzes the experimental data to determine the reaction kinetics as well as the model practitioner in implementing the kinetics in the model. A more detailed discussion and review of analysis techniques is provided in a later section.

When attempting to accurately represent a material or object in a CFD fire model, the shrinking/swelling behavior of materials is important to understand. Shrinking and/or swelling of a material affects heat transfer through the material, and may affect the burning rate of a object involved in a fire scenario. Shrinking of a material may be accounted for by defining the density of the intermediate and final solid products of degradation such that they have an equal or higher density than the initial reactant relative to the mass of the sample. Swelling may be accounted for in the same way by defining lower densities relative to the initial reactant density.

Liquid fuels require definition of the same set of thermo-physical properties as solid fuels (thermal conductivity, specific heat capacity, density, absorption coefficient, and emissivity). In addition to the thermo-physical properties of the liquid fuels, the boiling temperature and heat of reaction must also be defined to calculate the change in vapor pressure as a function of temperature. For liquids that are introduced to the computational domain as droplets, additional properties that must be defined are the melting temperature, viscosity, coefficient of thermal expansion, and the heat of formation of the vapor.

3.1.2 Gas Phase Properties

Gas phase phenomena are represented by a host of submodels in CFD codes. Each distinct gas species is defined by its molecular weight, enthalpy of formation, thermal conductivity, diffusivity, enthalpy, viscosity, and absorptivity. As an alternative to definition of these properties, the Lennard-Jones potential parameters may be defined to calculate the thermal conductivity, diffusivity, enthalpy, and viscosity of the gaseous species. In some cases, the Prandtl number may also be defined for a gas species.

An important component of CFD codes for fire modeling is the combustion submodel. Similar to the representation of pyrolysis, there are a range of models with varying degrees of complexity that may be invoked depending on the amount of control required by the model practitioner. When this combustion model is defined, a balanced chemical equation for the combustion reaction is assumed. This model requires definition of the fuel species, the chemical formula of the species, the yields of carbon monoxide and soot, and the chemical composition of the soot.

A more complicated representation of combustion chemistry allows species to be assigned and the stoichiometric coefficients to be defined for the reactants and products in each reaction. The heat of formation or the heat of combustion must also be assigned to each reaction when this model is employed.

By default in FDS, the combustion reaction takes on an infinite reaction rate, which means the reaction is controlled by the rate of mixing between the fuel and air. When the model practitioner has knowledge of the reaction kinetics and needs to dictate the reaction rate for the combustion reactions, a finite rate combustion model may be used. By invoking finite rate kinetics, the reaction rate is determined as a function of temperature and the concentration of gaseous species in Equation 3.4. The kinetic parameters required for each reaction are the activation energy and the pre-exponential factor for the jth reaction. Gas phase kinetic parameters also include a temperature exponent (N_T) and concentration exponents ($N_{s,\alpha}$) that affect the reaction rate in proportion to the temperature and reactant concentrations, respectively.

$$\frac{dC_i}{dt} = -A_j T^{N_T} \exp(-\frac{E_j}{RT}) \prod_{\alpha=1}^{N_s} C_\alpha^{N_{s,\alpha}} \tag{3.4}$$

Equation 3.4 accounts for rate of change of the ith species, which is dependent on the concentration of all species (including species i), denoted as species α raised to the power $N_{s,\alpha}$. For many of the species defined in the model, the exponent $N_{s,\alpha}$ may be zero, which renders the rate of reaction independent of the corresponding gas species. If a reaction is defined as reversible, the Gibbs free energy of the reaction may be defined to calculate the equilibrium constant.

The radiation submodel is an integral piece of a CFD fire model because radiation is the main mode of heat transfer in many fire scenarios. A simple method of modeling the fraction of energy from the flame that is radiated to surroundings is by defining the radiative fraction of the fuel involved in the combustion reaction. This is an important simplification because the grid resolution of the computational domain is usually such that the average cell temperature does not capture the actual flame temperature. Because radiative heat transfer is dependent on the fourth power of temperature, the difference between the flame temperature and the average cell temperature can make a significant difference.

Optical properties of gaseous species must also be defined to account for absorption and emission of radiation by participating media. Absorption coefficients for gas species may be defined if they are known to account for radiative absorption and emission. A more sophisticated radiation model that represents absorption and emission does not require absorption coefficients or radiative fractions, but requires the definition of the wavelengths that correspond to limits of spectral bands. To account for radiation absorption and scatter by particles, wavelength-dependent values of the refractive index may be defined.

4 Test Methods

Efficient and effective standard methods are required to measure properties and parameters required for fire models to populate the material properties database. Methods that have been defined in consensus standards and in the scientific literature to measure each of the input properties have been described in this section. This review is focused on determination of solid-phase properties and does not include information pertaining to characterization of liquid or gas-phase properties.

The solid phase thermo-physical properties required as inputs to FDS and other similar CFD models are the density, thermal conductivity, and specific heat capacity. The optical properties required to define solid phase materials are the emissivity, absorption coefficient, and index of refraction. The HRR, HRRPUA, and heat of combustion of materials and objects may be defined in the simplest representation of pyrolysis. The more complicated representation with the simple pyrolysis model requires the ignition temperature and heat of vaporization for the material. When the complex pyrolysis model is invoked to describe material burning, the reaction mechanism must be defined as well as the heat of reaction for each reaction. In all pyrolysis model representations, the heat of combustion may be defined for each combustible gaseous product.

4.1 Density

The density of a solid material must be defined for accurate representation of heat transfer in a fire model. The density is defined as the ratio of the mass of a material to its volume. For prismatic noncellular materials, measurement of density is as straightforward as directly measuring the mass and volume of a sample. There are a multitude of other methods for measuring the density of materials.

Direct measurement of prismatic samples is referred to in standards as "Volume by Measurement." An alternative method to measure volume is by water immersion [46, 47]. This method involves immersing the sample specimen in a known volume of water and measuring the volume or mass of the displaced water to infer the volume of the specimen.

The density-gradient technique [48, 49] involves a graduated column filled with a mixture of two miscible liquids of different densities that is allowed to settle such that a known density gradient is formed. A test specimen is added to the column and allowed to reach equilibrium. The density is calculated based on the location of the center of volume of the test specimen in the column.

The density of glass and other nonporous solids in the range of 1100 kg/m^3 to 3300 kg/m^3 may be measured through a comparative immersion technique [50]. The specimen and a standard material of known density are immersed in a column of standard solution. The solution is heated to change its specific volume in a well-defined manner relative to temperature, and the position of the specimen relative to the position of the reference standard is used to determine the density of the specimen.

The density of in-place wood elements or large logs may be measured using a forstner-type bit to bore a sampling hole in the element [47]. The volume of the sample is determined based on the geometry of the bit. All chips produced from the bore are collected and the mass is measured. A similar method for measuring the density of standing trees or wood structural elements is the use of increment cores [47]. A standard increment bore is used to collect a sample from the element and the volume and mass of the sample are directly measured.

4.2 Thermal Conductivity

It is desirable to characterize the thermal conductivity (k) as a function of temperature in computational fire models. Measurement of thermal conductivity can be difficult and is further complicated when the material undergoes thermal degradation or decomposition when exposed to temperatures typical of a fire environment. Several standard methods and apparatuses as well as non-standard experimental methods exist for the measurement of thermal conductivity, although each method is limited in its scope. Further discussions of methods for measuring thermal conductivity are provided in reviews conducted by other researchers [51].

The guarded-hot-plate (GHP) apparatus [52], the hot box apparatus [53], and the heat flow meter (HFM) apparatus [54] are used in steady-state methods to measure the thermal conductivity of homogeneous samples with parallel sides and dimensions that do not change during the tests. The guarded heat flow meter technique [55] and the guarded-comparative-longitudinal heat flow technique [56] are steady-state thermal conductivity measurement methods that utilize similar apparatuses and methodologies to measure thermal conductivity.

The GHP apparatus consists of a heating element sandwiched between two identical material specimens. The unheated surface of each specimen is in contact with a cold isothermal assembly. The heating element, specimen, and cold assembly are surrounded by guard insulation that limits heat loss to the surroundings to create a condition that approaches an ideal adiabatic system. The thermal conductivity is calculated using the power supplied to the heating element and the temperatures of the cold surface assembly. The GHP is suitable for materials with a thermal conductivity in the range of approximately 0.001 W/m·K to 2 W/m·K. A rendering of the GHP measurement concept is provided in Figure 4.1.

The hot box apparatus includes a climatic chamber and a metering chamber with a sample specimen installed between the two chambers. Sample specimens are typically larger than those used in the GHP and are representative of building construction assemblies that may homogeneous or composite. Tests conducted using the hot box apparatus are typically intended to characterize the thermal resistance of building assemblies under non-fire conditions, so temperatures in the climatic chamber are typically lower than the temperature range required for a pyrolysis model.

The HFM apparatus consists of a single isothermal hot plate and single isothermal cold plate with the specimen positioned between the plates. At least one heat flux transducer is positioned adjacent to the sample specimen in the HFM apparatus to measure heat flux through the specimen.

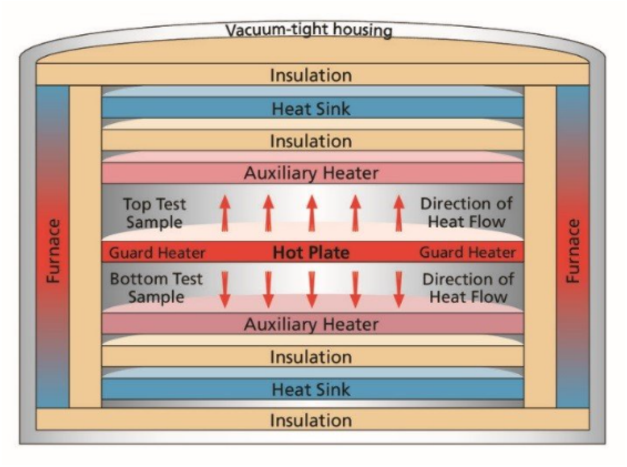


Figure 4.1: Rendering of Guarded-Hot-Plate Concept [57]

The thermal conductivity is calculated with the heat flux through the sample, and the temperatures of the hot plate and the cold plate. The HFM is suitable for measuring the thermal conductivity in the range of 0.005 W/m·K to 2.5 W/m·K at temperatures ranging from approximately 80 K to 800 K. The guarded HFM method utilizes an apparatus similar to the HFM apparatus that is modified to allow smaller test specimens with a wider thermal conductivity range and incorporates guard insulation to minimize heat loss that leads to error in characterization. The guarded HFM test method is considered suitable for measuring thermal conductivity in the range of 0.1 W/m·K to 30 W/m·K over the temperature range 150 K to 600 K. A rendering of a commercially available HFM is provided in Figure 4.2.

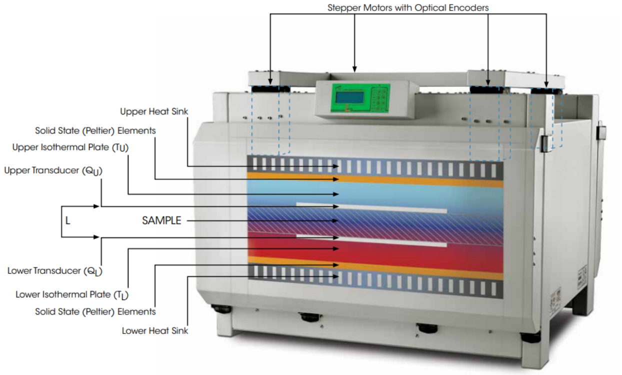


Figure 4.2: Rendering of a Commercially Available Heat Flow Meter Apparatus [58]

The guarded-comparative-longitudinal heat flow (GCLHF) technique involves an apparatus similar to the guarded HFM that incorporates a heater and a heat sink surrounded by guard insulation or a guard heater to eliminate heat loss. The sample is sandwiched between reference material samples in the GCLHF technique. Two temperature measurements are collected from each of the reference samples and the sample specimen that are spaced a known distance from each other in the direction parallel to the flow of heat. The thermal conductivity of the sample specimen is determined based on the heat flow through the reference materials and the temperature difference across that sample specimen. The test method is considered suitable for materials with thermal conductivity in the range of 0.2 W/m·K to 200 W/m·K over the temperature range 90 K to 1300 K.

The standard procedures used to measure thermal conductivity with the GHP and hot box apparatuses are both considered primary methods, and the procedure used with the HFM, the guarded HFM method, and the GCLHF technique are considered comparative methods because thermal conductivity is determined relative to a reference or calibration material. Each of these steady-state test methods can take several hours to ensure the sample attains the steady-state conditions required for accurate measurement. When thermal conductivity values are required over a range of temperatures, tests must be conducted at several temperatures, which compounds the amount of time required to collect meaningful data. This also implies that the thermal conductivity of the materials may not be measured as the material degrades.

Transient thermal conductivity measurement methods may be capable of directly providing the thermal conductivity of a material as a function of temperature. The thermal capacitance (slug) calorimeter [59], the transient-source line (TLS) technique [60], and the platinum resistance thermometer (hot wire) technique [61] are transient methods for measuring thermal conductivity. The flash method [62–64] and the transient plane source (TPS) technique [65] are methods of measuring thermal diffusivity ($\alpha = k/\rho\ c_p$), from which thermal conductivity may be determined. Thermal diffusivity and thermal conductivity may also be determined using a modulated temperature differential scanning calorimeter [66]. The modified transient plane source (MTPS) technique [67] may be used to measure thermal effusivity, from which thermal conductivity may be determined.

The slug calorimeter consists of a well-characterized, metal block (slug) that is sandwiched between two identical sample specimens. The stack of the specimens and the slug are pressed between two retaining plates and the entire system is placed in a temperature-controlled environment. The temperature of the environment and the slug are recorded as the temperature is increased at a defined heating rate. The thermal conductivity is calculated as a function of the apparent mean temperature of the sample specimens. The slug calorimeter is suitable for materials with thermal conductivity in the range of 0.02 W/m·K to 2 W/m·K over the temperature range 300 K to 1100 K. Bentz measured the thermal conductivity of fire resistive materials at elevated temperatures using slug calorimetry [68]. A schematic and photograph of the slug calorimeter from the work of Bentz are displayed in Figure 4.3.

The TLS technique involves embedding a line-source probe, which acts as a heat source and temperature sensor, into the sample specimen. The specimen with the embedded probe may be placed in a temperature controlled environment to measure the thermal conductivity of the specimen at a specific initial temperature or to render the specimen as a melt. A defined amount of energy supplied is supplied to the probe and the probe measured the change in temperature over time to provide the thermal conductivity relative to a calibration material. The TLS technique is suitable for measuring thermal conductivities of thermoplastics, thermosets, soft solids, and viscous liquids in the range of 0.08 W/m·K to 2 W/m·K over the temperature range 300 K to 1100 K.

The hot wire technique of measuring thermal conductivity is similar to the TLS technique. A platinum wire is placed between two bricks of refractory material and a constant electrical current

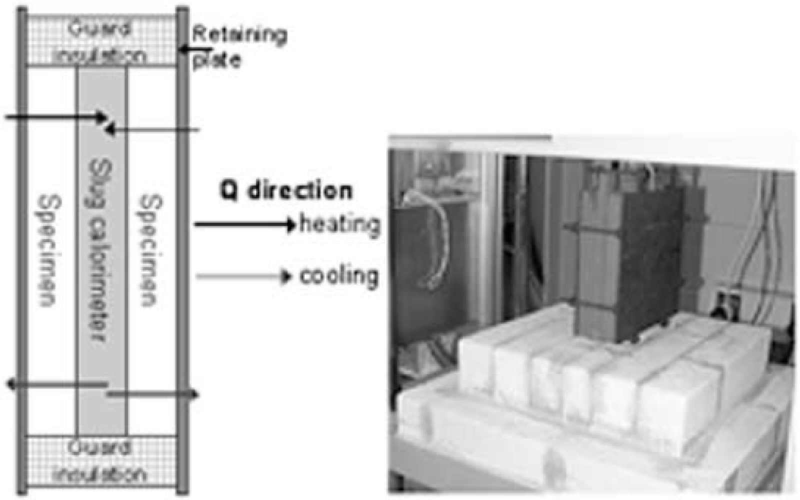


Figure 4.3: Schematic and Photograph of the Slug Calorimeter [68]

is supplied to the wire. The temperature of the wire is determined by monitoring its resistance as it heats. The rate at which the wire heats is directly proportional to the rate of heat flow into the bricks. The test standard recommends that the temperature of the refractory specimen be increased at a set heating rate with a furnace during the test. The hot wire test method is suitable for non-carbonacious, dielectric refractory materials in brick, blanket, or powdered form with thermal conductivity up to 15 W/m·K at temperatures up to 1750 K.

The flash method was designed to measure the thermal diffusivity of non-porous, homogeneous, isotropic materials that are opaque to thermal radiation. This method allows determination of the thermal conductivity from the diffusivity. It may also be used to measure the heat capacity of a material relative to calibration materials. A thin disk specimen is subjected to a short duration radiant energy pulse produced by a flash lamp or a laser and the back surface temperature is measured over time to determine the rate of heat flow through the material. The sample temperature may be increased or decreased during a test along a defined temperature program, usually with a constant heating rate. Thermal conductivities may be measured in the range of 0.1 W/m·K to 2000 W/m·K over a temperature range as large as 75 K to 2800 K. Harada et al. used the flash method to determine the thermal conductivity, heat capacity, and thermal diffusivity of wood up to 543 K for the purpose of studying the charring process for the wood samples [69].

The TPS instrument consists of a flat coil of heating wire which acts as both the heating element and temperature sensor. The sensor is clamped between two identical planar samples with known dimensions and a known amount of heat is introduced to the specimen. The thermal conductivity can be calculated from the voltage and resistance measurements over the surface of the sensor as a function of time. The specimens and the sensor may be located in a temperature-controlled environment to measure the thermal conductivity and thermal diffusivity at higher temperatures. The TPS technique is suitable for measuring thermal conductivities in the range of approximately 0.01 W/m·K to 500 W/m·K at temperatures over the range of approximately 50 K to 1000 K. The TPS may not be suitable for measuring thermal conductivity and thermal diffusivity at temperatures consistent with thermal degradation and decomposition due to the expected geometric changes in the sample structure.

The TPS technique has been used by Grauers and Persson to measure the thermal conductivity of concrete at temperatures up to 873 K [70] and by Suleiman et al. to measure the thermal conductivity and diffusivity of wood at temperatures up to 373 K [71]. Bentz measured the thermal properties of fire resistive materials at room temperature using the TPS technique [68]. Quintiere et al. measured the thermal conductivity of a carbon fiber aerospace composite from room temperature to approximately 900 K using a method similar to the TPS technique [72]. The authors estimated that the uncertainty in the measurement was approximately ± 20% and recommended that a more rigorous measurement be made.

A differential scanning calorimeter is an instrument that measures the rate of heat flow to a material relative to a reference as the temperature of the material is increased over a well-defined temperature program. The sample size required for a test is typically on the order of a few milligrams to minimize temperature gradients within the sample. The temperature program may include linear ramps, isothermal soaks, or may be oscillatory. When an oscillatory temperature program is utilized, the method is called modulated temperature differential scanning calorimetry (MTDSC). MTDSC has been used to determine the thermal conductivity and thermal diffusivity of homogeneous, non-porous solid materials. Sample sizes for the method are larger than typical DSC samples and typically range from 10 mg to 100 mg and must conform to a strict form factor to ensure adequate thermal contact with the crucible that holds the specimen. This method is suitable for measuring thermal conductivity over the range of approximately 0.1 W/m·K to 1.0 W/m·K in the temperature range of approximately 270 K to 380 K.

A MTPS instrument is a modification of the TPS apparatus that includes a one-sided planar heat source that produces a short duration heat impulse that flows into the specimen. Because it is a one-sided heat source, there is no need to surround the probe on both sides with the specimen. The heat source also acts a temperature measurement point and the thermal effusivity of the specimen may be determined as the inverse of the temperature increase. Figure 4.4 displays a TPS and MTPS probe and the methods materials interface with each probe. The ASTM standard for measuring effusivity with the MTPS instrument is intended for fabrics, but may be applicable to many other materials [73]. The thermal effusivity is the positive square root of the product of thermal conductivity, density, and specific heat capacity. Thermal effusivity may be measured in the range of 35 $\mathrm{W{\cdot}s^{1/2}/m^2{\cdot}K}$ to 1700 $\mathrm{W{\cdot}s^{1/2}/m^2{\cdot}K}$.

The transient methods of measuring thermal conductivity typically require smaller geometric sample sizes and significantly less time than the steady-state methods because data are collected while heat flow through the specimen changes over time. A disadvantage of the transient methods is that an additional furnace or oven is generally required to measure thermal conductivity at temperatures significantly elevated above room temperature. The time required to heat the samples in a furnace may be comparable to the times required for the steady-state methods. These transient methods also rely on thermal contact between the sample specimen and the sensor, which makes it unlikely that they are suitable for measuring the thermal conductivity of samples as they undergo thermal degradation or decomposition. Several researchers have developed experimental methods

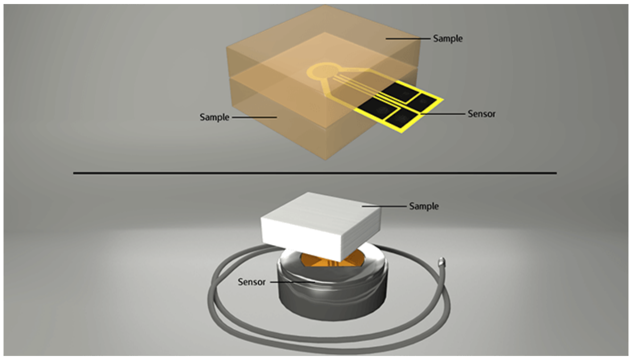


Figure 4.4: Schematic of Transient Place Source and Modified Transient Plane Source [68]

and analyses to determine the thermal conductivity of materials.

Myllymäki and Baroudi demonstrated the use of an inverse analysis to determine the thermal conductivity of a steel plate covered in fire-protective insulation [74]. The researchers showed that a direct measurement is not always necessary to determine the thermal conductivity of a material, and that the number of measurement locations required to assess thermo-physical properties may be decreased when the boundary conditions are well-characterized. Lattimer and Ouellette demonstrated the use of inverse analyses to determine the thermal conductivity and other thermo-physical properties of a glass reinforced vinyl ester composite over a temperature range up to 1073 K [75]. Thermal conductivity was determined using surface temperatures collected when the sample specimen was exposed to a well-defined heat flux in a well-characterized gas atmosphere in a custom-built gasification apparatus.

A research group from the University of Maryland has developed an inverse analysis procedure using a custom-built gasification apparatus called the Controlled Atmosphere Pyrolysis Apparatus (CAPA) in which the thermal conductivity is determined as a function of temperature through the process of thermal degradation [76]. A sample specimen is subjected to a radiant heat flux in a well-defined gas atmosphere and allowed to decompose while the back surface temperature is measured through non-contact infrared thermometry. An advantage of the inverse analysis methodology is that it utilizes a pyrolysis model to minimize error between the prediction and the experimentally measured back surface temperature, which directly yields the input property required to defined the material in a fire model. A rendering of the gasification apparatus developed at the University of Maryland is shown in Figure 4.5

Because of the distinct temperature, thermal conductivity, and sample material limitations of each method, no single method has emerged as the most popular among researchers. The more recently developed transient methods generally require less time and smaller specimen sizes and have wider thermal conductivity ranges, so many recent studies have favored these methods. Experimental methods that are capable of characterizing thermal conductivity through thermal decomposition and degradation have shown promise, although measurement of thermal conductivity through this method requires validation.

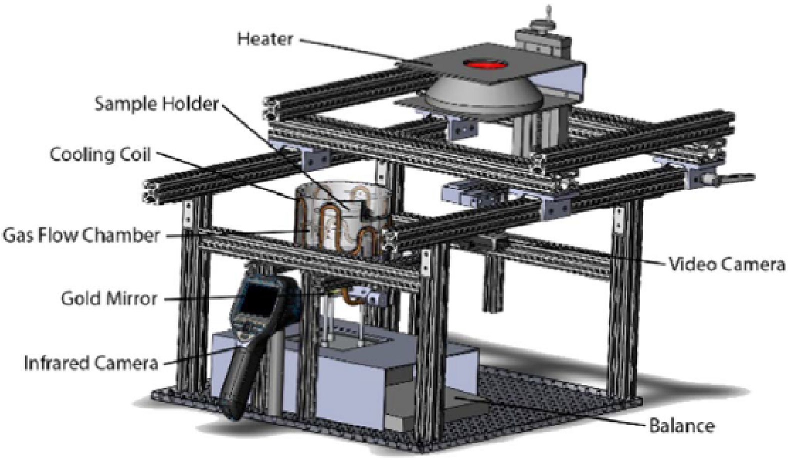


Figure 4.5: Rendering of the Controlled Atmosphere Pyrolysis Apparatus [76]

4.3 Specific Heat Capacity

The specific heat capacity must be defined for all material components through all phases of degradation to fully characterize pyrolysis of a material. The specific heat capacity is dependent on temperature and may be defined as such in pyrolysis models. Measurement of heat capacity as a function of temperature in the range of temperatures at which degradation or decomposition occurs is complicated due to difficulty maintaining thermal contact with the specimen and isolating and identifying partially degraded components.

Differential scanning calorimetry (DSC) [77, 78] derives its name from measuring the differential between the heat flow rate to a sample and a reference as the temperature of the atmosphere is scanned along a well-defined program. All DSC apparatuses consist of a twin measurement system in which changes to the temperature and gas atmosphere affect the sample and the reference. The sample mass must be small (3 mg to 10 mg) to reduce temperature and concentration gradients to eliminate heat and mass transfer within the sample and facilitate the assumption of equilibrium between the specimen and the atmosphere at all times. The reference is most commonly an empty crucible although any well characterized material may be used. Figure 4.6 shows a schematic of a simultaneous thermal analyzer, which is capable of differential scanning calorimetry.

There are two common types of DSC apparatus that are differentiated by the method used to measure the heat flow rate differential. In a heat flux DSC apparatus, the sample and reference are both contained in the same sample chamber during a test. The primary measurement for a heat flux DSC is the difference in temperature between the sample and the reference. The temperature difference is related to the heat flow rate to the sample relative to the heat flow rate to the reference.

A power-compensation DSC apparatus consists of two identical furnaces in which the sample and the reference are positioned to maintain thermal isolation. The difference in power delivered to the sample and reference are directly measured in power compensation DSC [80]. The two furnaces provide an identical heat flow, but as the sample absorbs sensible enthalpy or enthalpy associated

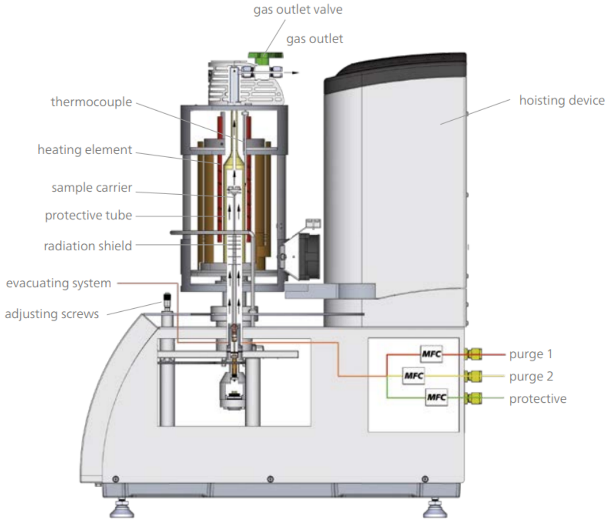


Figure 4.6: Rendering of a Commercially Available Simultaneous Thermal Analyzer [79]

with a reaction or phase change, the temperatures of the furnaces diverge, which provides a signal to the control mechanism to supply more power to the furnace containing the sample.

The standard test method for measuring heat capacity through DSC [77] involves heating the sample specimen at a linear heating rate of 20 K/min through the temperature of interest. The differential heat flow rate between the specimen and an empty reference is compared to the differential heat flow rate between a standard calibration material (typically synthetic sapphire) and the same reference. The specific heat capacity of the specimen is determined relative to the calibration material. The range of temperatures at which specific heat capacity values may be determined is limited by the crucible material and the calorimeter furnace.

When MTDSC is used to determine the specific heat capacity of a material, an oscillatory temperature program is applied to the sample chamber [81]. The temperature program may consist of oscillations about a linear ramp (typically with a heating rate of 3 K/min) or oscillations about a constant temperature. The use of MTDSC to measure specific heat capacity does not require a standard calibration material against which the specific heat capacity of the sample specimen is referred.

Although many fire scientists have used DSC as a standard method to determine the heat capacities of materials and the energetics of heterogeneous reactions at temperatures comparable to those in fire environments [82–87], the validity of DSC to determine heat capacity through the temperature range at which thermal degradation or decomposition may take place has been questioned. Criticism of the method stems from the lack of standard procedures for evaluating calibrations, the uncertainty in the limits of applicability of the measured data, and the sources of uncertainty and systematic errors. The standard heating rates used in the test methods to measure specific heat capacity do not necessarily correspond to fire conditions. These factors must be kept in mind by the researcher conducting tests and analyzing DSC data to ensure accurate parameter measurements. Since DSC provides a direct measurement of the heat flow rate to the sample as a function of temperature, interpretation of the data is dependent on knowledge of the sample material and the discretion of the practitioner.

Specific heat capacity may also be determined from the standard test methods used to measure thermal diffusivity [62–65] or thermal effusivity [67]. Thermal diffusivity is the ratio of thermal conductivity to the product of density and specific heat capacity (also called the volumetric heat capacity) ($\alpha = k/\rho \, c_p$). Thermal effusivity is the square root of the product of thermal conductivity, density, and specific heat capacity ($e = \sqrt{k\rho \, c_p}$). If the density and thermal conductivity of the tested material are known, the specific heat capacity of the material may be determined from either the thermal diffusivity or the thermal effusivity.

Alternative methods for measuring specific heat capacity have been used in past fire research and pyrolysis studies. The heat capacity of a material may also be extracted from the Thermal Response Parameter ($TRP = (T_{ig} - T_{\infty})\sqrt{\frac{\pi}{4}\, kc_p\rho}$) [88], the inverse of which acts as the proportionality constant that relates the incident heat flux to the time to ignition. The TRP is generally measured in one-dimensional radiant heating tests. To effectively determine the heat capacity from the TRP requires an extensive experimental and analytical effort relative to DSC tests. The methods for measuring thermal diffusivity, thermal effusivity, and TRP require knowledge of the thermal conductivity and density to provide the heat capacity of the material, which may require additional test methods or apparatuses.

4.4 Emissivity

The emissivity (used interchangeably with ‘emittance’) of a material directly affects the quantity of radiant energy absorbed, reflected, and emitted by a surface, which may have a significant effect on the temperature distribution and burning rate predictions from a pyrolysis model. The optical properties have been measured directly and indirectly through several standard and non-standard test methods.

Analysis of radiant heat transfer may be simplified by assuming material surfaces are opaque or participating media are optically thick. This simplification leads to the assumption that transmission is negligible and allows for the following relationship between the absorptivity (a) and reflectivity (r) of a surface: $a + r = 1$. By assuming the material surfaces are gray emitter-absorbers, Kirchhoff’s law may be invoked to equate the absorptivity to the emissivity (ε) of the material, resulting in the following equation: $\varepsilon + r = 1$ [89].

A standard absolute test method [90] for measuring the total hemispherical emissivity of metal, graphite, and coated metal surfaces up to 1673 K consists of directly heating a sample in an evacuated chamber using an electric current. The temperature of the sample specimen, the chamber surface, and the power supplied to the specimen are used to calculated the emissivity of the specimen.

The emissivity of a specimen surface may be measured using an infrared imaging radiometer [91].

Standard methods are described in which the radiometer is used to measure the surface temperature of the sample while an accurate contact measurement is made in the same location. A second standard method is described in which the surface temperature of the specimen is measured with the radiometer and, then the radiometer is focused on a portion of the specimen with the surface modified to achieve a known emissivity. The emissivity is determined relative to the known emissivity surface.

Three different types of standard inspection-meter comparative methods for measuring emissivity have been published [92]. Method A consists of irradiating a surface and measuring the reflected radiance over the complete hemisphere. The emissivity of the specimen is determined relative to a calibration standard. Method B consists of measuring the radiant energy emitted from the specimen surface via a thermopile. An additional test method for measuring the total hemispherical emissivity of materials near room temperature relies on a portable differential thermopile emissometer [93]. In the test method, the emissometer is calibrated against a low emissivity (reflective) surface and a high emissivity (black) surface and the emissivity of the specimen is determined relative to the high emissivity surface. Hubbard et al. measured the surface emissivity of carbon fiber composites using a portable directional hemispherical reflectometer [94]. While the sample was irradiated, the reflectometer allowed the directional total emissivity to be measured at two angles of incidence as well as the hemispherical total emissivity.

Method C [92] consists of measuring the emittance or reflectance from a sample using a Fourier transform infrared (FTIR) emissometer/reflectometer. A reflectometer is a form of spectrophotometer that measures the radiant energy reflected from a material usually within a specific spectral band. The instrument must be equipped with an integrating sphere, ellipsoid, hemi-sphere, or hemi-ellipsoid. An additional standard test method to measure near normal-hemispherical absorptance, reflectance, and transmittance of materials utilizes a spectrophotometer equipped with an integrating sphere [95].

An integrating sphere is a device used to collect reflected or transmitted radiation from a sample to a hemisphere. The electromagnetic radiation gets captured in the hemisphere and the entirety of the energy is measured by spectrophotometers on the sphere. The test method is suitable for a wide range of materials that generally have a flat sheet form factor. Fire researchers have used an integrating sphere to characterize emissivity of materials. Spectrophotometers and integrating spheres have been used in several research efforts to measure the optical properties of materials for pyrolysis models [96–100]. Figure 4.7 displays schematics of two different integrating spheres used to measure spectral reflectivity by Chaos [100].

A standard method for measuring the reflectivity of transparent materials involves a light source with a known luminance and a photometer [101]. The light source and photometer are positioned at known angles with respect to each other and with respect to the specimen surface. The luminance transmitted through and reflected by the specimen are measured by the photometer relative to the luminance from the source to determine the reflectivity, from which the emissivity may be inferred.

In addition to the aforementioned standard methods to determine emissivity, El Bakali et al. provide a survey and review of calorimetric, direct, and indirect experimental methods for measuring

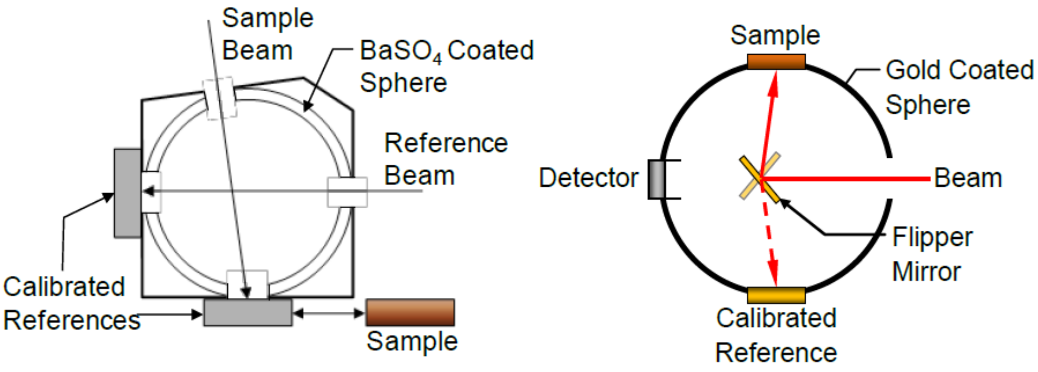


Figure 4.7: Two Examples of the Use of Integrating Spheres for Spectral Reflectivity Measurements Used by Chaos [100]

emissivity [102]. The specialized equipment used in these standard methods and experimental studies generally cannot withstand large temperatures, so it is evident that the changes in the optical properties that occur due to elevated temperatures and thermal degradation or decomposition of the sample may not be assessed with these methods. El Bakali et al. have recently devised a novel apparatus for measuring emissivity of materials at temperatures above approximately 673 K [102]. The method consists of irradiating a sample with an ellipsoid furnace while the emitted energy is measured by a near-infrared spectrometer or one of two mid-infrared cameras. The signal from the detectors is compared to the signal measured from a blackbody at the same temperature and the spectral emissivity is calculated as the ratio of the two signals.

4.5 Absorption Coefficient

The absorptivity of a material surface is a property equal to the ratio of the heat flux absorbed by the material to the heat flux incident to the material [89]. The absorption coefficient of a material is the fraction of incident radiation that is absorbed by the material per unit depth below the material surface, and the absorption coefficient is defined analogously for a non-solid participating medium [97]. Due to application of Kirchhoff's law, the absorptivity is assumed to be equal to the emissivity of a material surface, which generally precludes the need to explicitly define the absorptivity of the surface. The absorption coefficient of a material must be defined when in-depth absorption and emission of radiation is represented by the pyrolysis model.

Many of the methods described in Section 4.4 may be used to measure spectral or diffuse transmittance of materials. Because the absorption coefficient is measured with units of reciprocal length, it is also dependent on the optical path length through the material (the thickness of the specimen). Standard methods used to measure transmittance of materials with the use of an integrating sphere and a spectrophotometer may be used to measure absorption coefficient, given accurate specimen thickness measurements [92, 95]. Linteris et al. used an FTIR spectrometer with an integrating sphere to directly measure transmitted and reflected spectral intensity for polymer specimens of several thicknesses, from which the absorption coefficient was calculated [97].

Jiang et al. used a non-standard method in which a polymer was exposed to radiation from a heater with a well-defined emission spectrum to measure the transmitted radiation with a heat flux gauge to determine the absorption coefficient [103]. Similar methods have been used by other researchers to determine the effective broadband absorption coefficient [97, 104, 105]. Care is taken when measuring the broadband absorption coefficient with this method to only measure the heat flux on the unheated side of the the material prior to the material heating to the point where the back surface of the specimen radiates heat.

4.6 Index of Refraction

The model representation of in-depth radiative absorption and emission may also require definition of the index of refraction for the sample material. Index of refraction may only be measured for transparent or semi-transparent materials. Two standard methods for measuring the index of refraction are generally used. One method utilizes a refractometer [106, 107] and the second is an immersion method that requires a microscope [107].

A refractometer is a device specifically designed to measure the index of refraction of materials. A common laboratory refractometer (Abbe refractometer) uses a prism to scatter light to illuminate the specimen and a prism with a high index of refraction to refract the light after it has passed through the specimen. The operating concept of an Abbe refractometer is displayed in Figure 4.8. After the operator adjusts the position of the refractive prism, a detector on the instrument indicates the index of refraction. Refractometers typically use white visible light to determine the index of refraction, but some instruments are capable of measuring index of refraction at wavelengths more pertinent to fire conditions. Refractometers are suitable for solid non-opaque materials that may be isotropic or anisotropic.

The second method is typically used for powdered or granulated transparent material. The specimen is immersed in a liquid with a known index of refraction and placed on the stage of a microscope. The microscope is focused on the particle or granules of the material and then brought slightly out of focus to form a bright halo around or within the image of the particle. The direction of the halo indicates when the immersion liquid or the granulated material has a higher refractive index. The process is repeated with other immersion liquids until the index of refraction of the material specimen is determined.

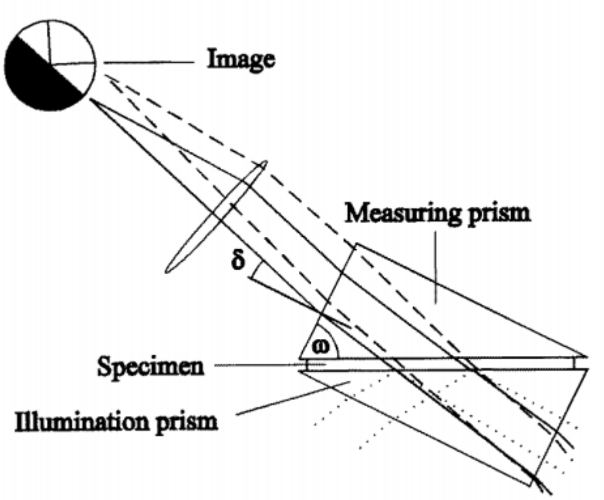


Figure 4.8: Schematic of Abbe Refractometer Concept [108]

5 Characterization of Burning

The simplest representations of burning in fire models rely on an assignment of the HRRPUA to material surfaces and obstructions in computational fire models. A more complicated representation requires the ignition temperature and the heat of gasification. The most complicated representation requires definition of the reaction mechanism and effective reaction kinetics of the pyrolysis reactions.

5.1 Heat Release Rate

The state of the art in measurement of HRR is the use of oxygen-consumption calorimetry to relate the decrease in oxygen (O_2) concentration when a fuel is burning in a well-ventilated scenario to the heat released from combustion of the volatile pyrolyzate or flammable vapor. Oxygen consumption calorimetry was developed in the late 1970s as the result of research primarily conducted by Parker [109] and Huggett [110]. Oxygen consumption calorimetry is based on the concept that the heats of combustion per unit mass of O_2 consumed for many organic fuels fall in the range of 13.1 kJ/g O_2 ± 5% [110]. With a well-known volumetric flow rate of air and the products of combustion into a calorimeter, the HRR of the burning material may be determined. Oxygen consumption calorimetry has been applied to many standard fire test methods to determine the HRR. These methods are presented here in order of increasing scale.

Microscale combustion calorimetry (MCC) [111] is a standard thermal analysis method that is capable of measuring the heat release rate due to complete combustion of a material as a function of temperature. In MCC, the sample is contained in an open, ceramic crucible to ensure the gaseous pyrolyzate escapes the pyrolysis chamber with no resistance to flow. The sample is pyrolyzed in an inert atmosphere (typically nitrogen) at a well-defined heating rate generally between 12 K/min and 120 K/min. The gaseous pyrolyzate is allowed to mix with excess O_2 at a relatively low temperature in a mixing chamber and flows to a combustion chamber at a temperature of 1173 K where complete combustion takes place. The heat release rate due to combustion of the pyrolyzate is measured using oxygen consumption calorimetry. The mass of the sample is typically in the range 3 mg to 5 mg to minimize the formation of temperature gradients within the sample and to ensure the reduction in O_2 concentration is within the limits of the O_2 sensor. MCC has been used by fire researchers to determine the effective kinetics of the pyrolysis process [112–114] and to assign heats of combustion to the gaseous products of pyrolysis [112, 115, 116].

The cone calorimeter [117, 118] is a standard apparatus that may be used to measure time to piloted ignition or autoignition, as well as HRRPUA, MLRPUA, effective heat of combustion, specific extinction area, carbon monoxide CO and carbon dioxide CO_2 yield, smoke production rate, and extinction coefficient as they evolve over time. Tests are typically conducted on coupon-sized samples (10 cm by 10 cm), which are subjected to a well-defined heat flux generated by an electrical resistance radiant heater. An igniter may be used to measure time to piloted ignition at the given heat flux, or tests may be conducted without the igniter to determine the conditions required for autoignition. An exhaust system maintains a constant volumetric flow rate to collect the products of combustion via an exhaust hood as the sample specimen burns. The mass is measured as the sample specimen burns. A pump collects gas samples from the exhaust system which are analyzed in real time to measure concentrations of O_2, CO_2, and CO. A laser-based smoke obscuration measurement system installed in the exhaust duct provides the extinction coefficient and specific extinction area of the smoke and products from the sample specimen. The cone calorimeter has been used extensively for fire research, to assess the burning hazard of materials, and to measure properties for input into fire models.

In many studies, researchers have modified the cone calorimeter from its standard configuration to expand the measurement capabilities. Because cone calorimeter tests are conducted in an open atmosphere, results are only available for well-ventilated scenarios in ambient air. To study vitiated or oxygen-enriched conditions or to promote pyrolysis without a flame to ensure boundary conditions do not change over time, researchers have modified the cone calorimeter to control the atmosphere in the vicinity of the specimen surface [119–122]. Urbas and Parker installed an infrared pyrometer on the cone calorimeter to measure the specimen surface temperature up to the time of ignition [123]. The researchers also mounted a thermocouple to the specimen surface to indirectly determine the surface emissivity.

The fire propagation apparatus (FPA) [124, 125] is a standard apparatus that may be used to measure time to ignition, chemical and convective HRR, MLR, and effective heat of combustion as the sample specimen burns. A photograph of the FPA is provided as Figure 5.1. Sample specimens tested in the FPA are typically planar and cut such that they have dimensions of approximately 10 cm by 10 cm in the horizontal orientation and 10 cm wide by 30 cm high in the vertical orientation. During a test, the sample specimen is held in a vertical transparent quartz tube and irradiated by infrared heaters positioned outside of the quartz tube while the sample mass is measured with a load cell. An exhaust system captures the products of combustion and the HRR is determined based on consumption of O_2 and production of CO_2 and CO. A gas flow system is incorporated into the apparatus at the bottom of the quartz tube to facilitate flow through the tube to produce a well-defined gas atmosphere in the vicinity of the sample surface.

Four distinct experimental procedures are associated with the FPA that include an ignition test, combustion test, pyrolysis test, and fire propagation test that each incorporate a different combination of gas atmosphere, incident heat flux, and sample orientation. The ignition test and combustion test are similar to the cone calorimeter (or controlled-atmosphere cone calorimeter) test conducted with the sample in the horizontal orientation, the pyrolysis test is conducted in an inert atmosphere to yield MLR data with no flaming combustion, and the fire propagation test is conducted in the vertical orientation to collect HRR data as the sample undergoes upward flame spread. Marlair, et al. modified the standard FPA to include additional gas analyzers to measure nitrogen oxides NOx, total hydrocarbons (THC), water H_2O, sulfur dioxide SO_2, hydrogen cyanide HCN, hydrochloric acid HCl, and soot in under-ventilated conditions [126]. Chaos described a modification to the FPA that included an infrared pyrometer to measure the surface temperature in gasification tests [100].

Figure 5.1: Photograph of the Fire Propagation Apparatus [125]

The intermediate scale calorimeter (ICAL) [127, 128] is a standard test apparatus that is used to measure HRR, MLR, smoke production rate, and product yields of materials, products, and assemblies subjected to a well-defined incident radiant heat flux. The ICAL may also be used to determine the effective heat of combustion, surface temperature, ignition temperature, and emissivity of the specimen. The ICAL is designed for sample specimens 1 m^2 in size. The specimen is exposed to a radiant flux in the range of 0 to 50 kW/m^2 and the effluent is collected by a hood with a cross section of approximately 2.4 m by 2.4 m. The concentrations of O_2, CO_2, CO, and potentially other combustion products are measured to determine the HRR of the sample. A white light optical system is also incorporated in the exhaust duct to measure the optical density of the smoke. Thermocouples may be installed in the specimen from the unheated side to determine thermo-physical properties.

The Single Burning Item (SBI) test method [129] is intended to determine the burning behavior of construction products when exposed to thermal attack by a single burning item. The SBI test is suitable for sheet products with a maximum thickness of 200 mm, and is not suitable for flooring materials. Figure 5.2 displays a photograph of the SBI test apparatus to show its scale relative to a laboratory technician. The specimen is formed into a corner with a short wing with dimensions 0.5 m wide by 1.5 m high and a long wing with dimensions 1.0 m wide by 1.5 m high. The test is conducted in a structure with a floor area of 3.0 m by 3.0 m and a height of 2.4 m. The structure is built from a noncombustible material and has an opening through which a trolley containing the specimen may be moved. The specimen is exposed to a flame from a burner located in the corner where the two wings of the specimen meet with a total HRR of approximately 30 kW. The HRR is measured using oxygen consumption calorimetry and the smoke production rate is determined through smoke obscuration measurements.

Figure 5.2: Photograph of the Single Burning Item Test Apparatus [130]

The Room Corner Test [131, 132] is a standard method to test interior finish materials under specified fire exposure conditions. The test is conducted in a structure with a floor area of 3.6 m by 2.4 m and a ceiling height of 2.4 m. The construction of the structure is noncombustible and the structure contains a door opening in the center of one of the 2.4 m long walls. The ceiling and all of the walls, with the exception of the wall that contains the door opening, are covered in the sample specimen sheets. A burner with a specified HRR is placed in one of the corners on the side of the structure opposite the door opening. The combustion products exhausting from the through the door opening are collected by an exhaust hood and the HRR is measured using oxygen consumption calorimetry. Gas temperature, material surface temperature, gas velocity and flow rates through the door opening, and radiant heat flux through the door opening may also be measured during the standard test.

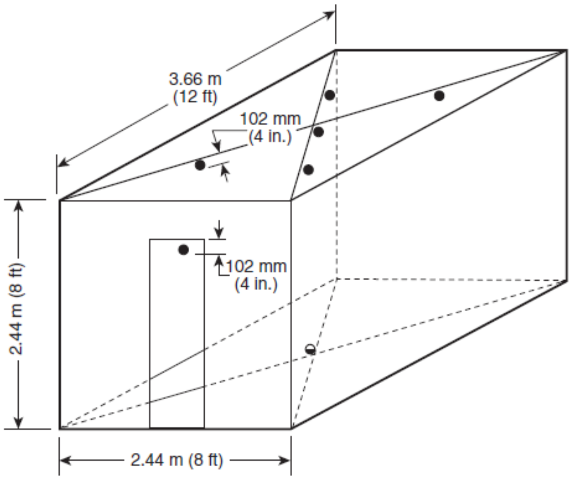


Figure 5.3: Schematic of the Room Corner Test Structure [132]

Standard test methods to measure the HRR of upholstered furniture [133] and mattresses [134] may be conducted in a structure identical to that in the Room Corner Test method, a larger structure with floor area 3.6 m by 3.0 m, or may be conducted in an open calorimeter. The gaseous products of combustion are collected by an exhaust duct and the HRR is determined through oxygen consumption calorimetry. As with the standard tests at other scales, there is also the capability to measure MLR and evaluate smoke obscuration in the exhaust duct. The major difference between these test methods and the aforementioned methods is that these methods are intended to evaluate full consumer products whereas the other methods are intended to evaluate materials and sheet configurations of construction assemblies. The standard methods specify a propane burner as the ignition source, although several researchers have investigated the sensitivity of the measured HRR, rate of flame spread, and overall reproducibility to other, more realistic, ignition sources [135–138].

5.2 Radiative Fraction

The radiative fraction is an important consideration that dictates the radiant heat flux incident to target objects from a burning fuel. It is defined as the ratio of energy radiated from the flame to the surroundings and back to the fuel surface to the total energy released in the flame. Typically the radiative fraction is determined by directly measuring radiant heat flux at a specific distance from the flame while simultaneously characterizing the total amount of heat released from the flame. Radiative fraction has most often been quantified in the literature for liquid pool fires because of the relative ease of generating steady burning conditions as well as the knowledge of the heat of combustion for these liquid fuels.

Research that included measurement of the radiative fraction for liquid fuels has been conducted at NIST starting in the 1990s. Experiments involved pool fires in pans ranging in diameter from 0.1 m to 1.0 m with a radiometer directed radially in toward the center of the fire plume and a radiometer flush with the bottom pan surface directed upward parallel to the central axis of the fire plume [139, 140]. Recent work has included a larger array of heat flux gauges to measure the radiative heat flux with greater resolution and, by association, the radiative fraction of the fuel [141].

A relationship between smoke point and radiative fraction was described by deRis, who detailed the design of an apparatus to measure the radiative fraction of solid-phase materials [142]. The described apparatus was an early conception of the FM Global Fire Propagation Apparatus, which was used by Tewarson to characterize the smoke point of a variety of solid materials [143]. Quintiere et al. demonstrated a method for quantifying the radiative fraction of solid-phase materials with a mass and energy balance of a sample in the cone calorimeter [144]. Hamel developed a novel method for measurement of the radiative fraction of axisymmetric laminar flames from gaseous and solid fuels. The method utilizes a novel apparatus called the Milligram-Scale Flaming Calorimeter to measure total heat release rate and requires a DSLR camera and a heat flux to characterize radiative intensity [145].

5.3 Heat of Gasification

The heat of gasification is the total amount of energy required, per unit mass of a condensed-phase material, to volatilize the material to produce thermally stable products. In the case of liquids, the products are gaseous vapors, and in the case of solids, the products are gaseous pyrolyzate and solid products of degradation (typically called char and/or ash). The heat of gasification includes contributions from sensible enthalpy and heats of reaction (or heats of vaporization) associated with the pyrolysis process. The heat of gasification is evaluated between the initial temperate of the condensed-phase material (typically room temperature) and the highest temperature at which the solid continues to volatilize.

Measurement of the heat of gasification may be complicated because it is dependent on the heat capacity and heats of reaction (heats of vaporization) of a material and must be measured while the material is changing phase during the process of degradation, decomposition, or evaporation (technically identical to the heat of decomposition for a solid and heat of vaporization for a liquid). A test method to measure the heat of gasification of materials that has become common among fire researchers recently is DSC [82, 83, 146, 147]. DSC tests conducted in an inert atmosphere over the temperature range through which the material completely volatilizes provides the heat of gasification.

A commonly used method before adoption of DSC was proposed by Tewarson and Pion and involved measurement of the MLR for the test specimen subjected to several different incident heat fluxes using the FPA. The heat of gasification is determined as the inverse of the slope of the peak MLR in this one-dimensional heating scenario plotted against the incident heat flux [148]. This method is limited in applicability to only homogeneous materials.

Jackson developed an apparatus specifically for measuring the heat of gasification of materials [149]. The apparatus consisted of a cone heater comparable to that used with the cone calorimeter, a pyrolysis chamber through which nitrogen flows to maintain non-flaming conditions, and a radiometer above the heater to measure the energy reflected and radiated from the exposed surface of the sample. The instantaneous heat of gasification was determined as the net heat flux divided by the instantaneous MLR. Lattimer and Ouellette measured the heat of decomposition using a novel gasification apparatus with a ramping incident heat flux as well as DSC [75]. Quintiere measured the heat of gasification of a carbon fiber composite using by cone calorimeter test data and DSC data [72]. Quintiere found considerably different values for heat of gasification by each method.

5.4 Ignition Temperature

The ignition temperature of a material is directly dependent on the ignition and heat exposure scenario. Ignition is typically studied in standard tests that rely on radiant heating of samples prepared to approach one-dimensional heat transfer conditions. These tests may feature a pilot flame or igniter as the ignition source.

Ignition is possible when the concentration of volatiles above the surface of the sample specimen increases to within the flammability limits of the vapor mixture. When the minimum energy required for ignition is transferred to the vapor mixture, ignition occurs and a sustained flame covers the specimen surface. This energy may be densely distributed over a small volume as a spark or open flame (piloted ignition) or may be the result of uniformly increased temperature of the vapor mixture (autoignition). The temperature required for autoignition is typically higher than the temperature required for piloted ignition.

A standard method for evaluating the piloted ignition temperature of a material that was first described by Quintiere and Harkleroad [150] uses the Lateral Ignition and Flame Spread Test (LIFT) apparatus [151]. Specimens for the ignition test using the LIFT apparatus are planar and have dimensions of 15.5 cm by 15.5 cm. The specimen is held vertically in a sample holder in the LIFT apparatus. The apparatus consists of a radiant heating panel mounted at an angle of 15° from the surface of the specimen such that the incident heat flux to the specimen surface is not uniform. The pilot flame is approximately 2.5 cm above the entire upper edge of the specimen. The heat flux incident to the specimen is measured with a heat flux gauge with a dummy specimen is in position. The dummy is replaced by the sample specimen to begin the test, and the time of ignition is recorded. The heat flux to the specimen is increased if ignition occurred and decreased if ignition did not occur, and the process is repeated until the critical heat flux for ignition is determined. The effective ignition temperature is inferred through an energy balance analysis at the surface of the sample.

The test standard for the MCC indicates that the surface temperature at piloted ignition may be approximated by the temperature at which the maximum HRR is measured for a material [111]. A more detailed analysis based on the concept of the critical mass flux required for piloted ignition (CMF) may be conducted on MCC data or data collected through thermogravimetric analysis to determine the temperature at which the CMF is generated for a material. Rasbash et al. [152] and Drysdale and Thomson [153] demonstrated measurement of the CMF using an a precursor to the mass loss calorimeter. The mass loss calorimeter is similar to the cone calorimeter without the incorporation of oxygen consumption calorimetry or a laser for smoke obscuration measurement [154].

Ignition temperature may be directly measured with thermocouples on the surface of the sample or with a non-contact measurement. Measurement of the surface temperature of a sample converging toward ignition using thermocouples is difficult due to the changing properties of the material surface [155]. An infrared pyrometer has been used by several researchers to measure the surface temperature of sample specimens up to the point of ignition in bench-scale burning tests in a non-invasive way [100, 123].

5.5 Reaction Kinetics

The most complicated representation of burning that is currently available in fire models requires definition of reaction kinetics to describe the MLR of a material as a function of temperature. The most straightforward method of collecting data from which the reaction kinetics may be determined involves measuring the evolution of the mass of a sample as a function of temperature. Thermogravimetric Analysis (TGA) [156, 157] is a test method in which the mass of a sample is measured as the environmental temperature is increased along a user-defined temperature program in a well-defined gas atmosphere. TGA tests are completed with various heating programs, generally in an inert atmosphere to gather data on the total sample mass as a function of temperature.

These data may be replicated with mathematical formulae that relate the rate at which the sample mass volatilizes to the temperature and composition of the sample. Sample specimens have masses typically in the range of 3 mg to 10 mg. The total gas flow rate is typically on the order of 100 mL/min, and may be reactive or non-reactive according to the desired test conditions. TGA tests are typically conducted at several heating rates to facilitate determination of reaction kinetics. There are a multitude of methods for determining reaction parameters from thermogravimetric data, and describing the details of all methods is outside the scope of this work. Several articles provide detailed discussions of the possible analysis methodologies [19, 158–161].

TGA has been coupled to infrared spectrometry such that the volatiles evolved during testing flow through a heated gas transfer line to an instrument capable of infrared spectrometry [162]. This coupled test method may allow researchers to identify the chemical components of the gaseous volatiles produced during pyrolysis or burning to better understand the heat of combustion as well as the potential toxicity of the evolved gases and vapors as a function of sample temperature.

Data collected in MCC tests [113] and DSC tests [163] have been analyzed to extract kinetics as an alternative to TGA data. These methods are limited to specific materials that display HRR and heat flow rate curve maximums that correspond to the maximum MLR, which requires a priori knowledge and precludes a large subset of materials. Researchers have applied optimization algorithms to conduct inverse analyses on bench-scale fire test data to infer the decomposition kinetics [164–166]. Inverse analyses and the use of optimization algorithms are reviewed in the following section.

There is no single, universally accepted, standard method in the fire protection community to determine reaction kinetics, which can lead to a disparity between kinetic parameters determined by different investigators using disparate experimental and analytical methods. Part of the argument for defining pyrolysis kinetics in fire modeling is that definition of kinetics effectively decouples the mathematical description of burning from the experimental method, ignition source, or fuel configuration. Kinetics allow the model to be truly predictive by representing the burning rate as a function of temperature only. Without a standard methodology to determine decomposition kinetics, the results of fire models parameterized with reaction kinetics may be less accurate and robust than those defined with less complicated models of burning.

6 Sensitivity Analyses

Because of the large number and wide range of inputs required for computational models, it can be useful to researchers and model practitioners to identify the sensitivity of the predicted quantities of interest to changes in the input properties and parameters. In addition to identifying the affect each parameter has on final predictions, sensitivity analyses may also allow the model practitioner to propagate uncertainty or error from the input properties through a model to the final predictions. Sensitivity analyses conducted on pyrolysis models have been reviewed in this section to help identify the most important measurements in which to invest resources to maximize the usefulness and utility of the database. Nyazika et al. provide additional commentary of sensitivity analyses on pyrolysis models [167].

Stoliarov et al. conducted an analysis to determine the effect of variation of several thermo-physical properties on predictions of fire response parameters for a typical generic non-charring engineered polymer using the ThermaKin pyrolysis model [168]. A survey of literature data that included properties of a wide range of polymers was used to define a mean value as well as an upper and lower bound on the range for each parameter. These bounds served as the range over which each property was adjusted to investigate the sensitivity of each on the time to onset of mass loss (t-ML), the peak MLR (pMLR), the time to peak MLR (t-pMLR), and the average MLR (avgMLR). Simulations of one-dimensional radiative heating of an average polymer sample with four different thicknesses subjected to three different heat fluxes in gasification tests were used to the predict fire response parameters. Charts that summarize the results of the analysis are provided in Figure 6.1.

The charts show the maximum and the mean variation in the response parameters due to variation of the input property normalized by the average polymer response. The properties represented in the chart are the density (ρ), specific heat capacity ($c_{room-dec}$), thermal conductivity (k), reflectivity (r), absorptivity (α), heat of decomposition (h_{dec}), a lumped kinetic parameter representing the Arrhenius pre-exponential factor and the activation energy (E/A), and the char yield. The authors concluded that the kinetic parameters, heat of decomposition, and the char yield are generally most important. The density, heat capacity, and thermal conductivity were found to be of little importance when predicting the peak and average MLR magnitudes, but times to mass loss and peak MLR were found to be sensitive to these parameters. Cross-sensitivities were not investigated in this work, nor was the effect of temperature-dependence of the properties, and the analysis was focused on polymers.

Linteris investigated the effect of variations in model inputs on the time history of the MLR and time to ignition for the thermal decomposition of the non-charring polymer poly(methyl methacrylate) (PMMA) predicted by both ThermaKin and FDS [169]. The input properties that were investigated were varied over a factor of 2 to 2.5 greater than and less than literature values for PMMA. A summary of the results of the sensitivity analysis are provided in Figure 6.2. In the figure, ΔH_{reac} indicates the heat of reaction, S is the sample thickness, c is the specific heat capacity, α is the absorption coefficient, k is thermal conductivity, and E_a is the activation energy. A double check mark indicates a large effect on the metric, single check marks indicate a moderate effect, and no

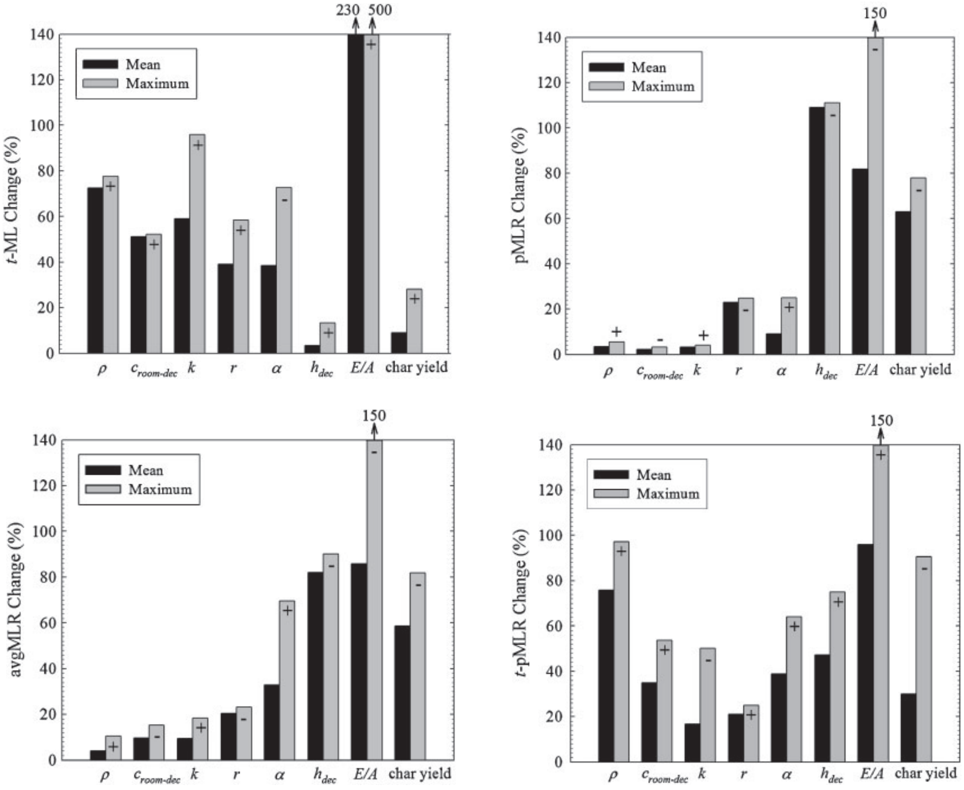
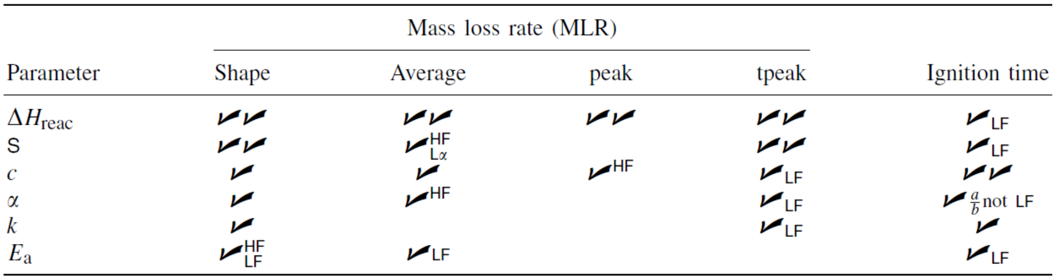


Figure 6.1: Results of Sensitivity Analysis Conducted by Stoliarov et al. [168]

check mark indicates a minor effect. The letters next to the check marks indicate the conditions under which the sensitivity is limited with LF indicating low heat flux conditions, HF indicating high heat flux conditions, Lα indicating low absorption coefficient, and $\frac{a}{b}$not LF indicating all but the lowest heat flux.



	Mass loss rate (MLR)				
Parameter	Shape	Average	peak	tpeak	Ignition time
ΔH_{reac}	✓✓	✓✓	✓✓	✓✓	✓LF
S	✓✓	✓HF Lα		✓✓	✓LF
c	✓	✓	✓HF	✓LF	✓✓
α	✓	✓HF		✓LF	✓ $\frac{a}{b}$not LF
k	✓			✓LF	✓
E_a	✓HF LF	✓LF			✓LF

Figure 6.2: Results of Sensitivity Analysis Conducted by Linteris [169]

Thermal conductivity was found to have a positive correlation with the time to ignition at all heat fluxes. The heat of reaction was found to be the most important factor in prediction of time to ignition and MLR. Adjusting the thermal conductivity of the material resulted in changes in the shape of the MLR curve, but did not significantly affect the average MLR or the peak MLR. Absorption coefficient affected the shape of the MLR curve, and the peak and average values of the MLR decreased with increasing values of absorption coefficient. The heat capacity had little effect on the MLR curve at low heat fluxes and only affected the shape, shifting the peak later in time, while at high heat fluxes, increasing the heat capacity resulted in lower average and peak MLR. It was determined that model results had a low sensitivity to defining average values of thermal conductivity and specific heat capacity as opposed to temperature-dependent values.

Linteris et al. conducted a sensitivity analysis as part of a modeling effort for the gasification of four polymers [99]. The magnitude of the perturbations for each parameter was chosen to reflect the uncertainty in determining the parameter. The parameters that impacted the predictions, in order of sensitivity, were the activation energy, pre-exponential factor, heat capacity, and absorption coefficient. The thermal conductivity had little effect on the MLR profiles for all of the polymers and the heat of decomposition had the most significant effect on the MLR. The analysis concluded that uncertainties in the measured parameters created variations in the predicted MLR curves that were greater in magnitude than the error between the predicted curves and the experimental curves. Since the variations in the parameters were on the order of the expanded uncertainty of each input property, this conclusion implies that an emphasis must be placed on reducing the uncertainty in parameter estimation and measurement.

Bal and Rein conducted a study to assess the complexity required in pyrolysis models [170]. This study was motivated by the trend that models require definition of more parameters as the complexity of the models increases, which requires a more extensive experimental effort and increases the computational cost of modeling. The authors defined the optimal complexity of the model as the number of input parameters that yields prediction errors that equally due to uncertainty in measured properties and to neglecting physical phenomena. Three models for the pyrolysis of PMMA were assessed to illustrate the breadth of variations available to predict the pyrolysis of a single material and each used a different set of governing equations in the pyrolysis model and different methods to determine the parameters to define the sample in the models.

A relatively small error in the surface temperature prediction was achieved with a large reduction in the number of parameters used to define the heat transfer physics and all complexity associated with mass transport within the solid appeared to be negligible. When it was assumed that the heat of decomposition was negligible, the thermo-physical properties had no temperature dependence, and there was no in-depth radiation absorption there were large errors in the surface temperature prediction. It was demonstrated through this study that the chemical mechanism had a significant impact on the MLR, single-step reaction kinetics led to a large increase in the MLR error, and that a good prediction of the energy distribution throughout the solid and any heat losses must be accurately quantified to produce accurate MLR predictions. Though several of these conclusions may be applied generally to pyrolysis models, it must be noted that this study was focused on models for PMMA, which undergoes pyrolysis with the least complicating factors, and it is no surprise that much of the complexity in these models was found to be extraneous.

Chaos conducted a sensitivity analysis using a simplified version of the pyrolysis model GPyro claiming that previous sensitivity analyses examined specific materials or situations and lacked generality [171]. Chaos investigated the model response based on both a non-charring and a charring virtual material with properties representative of common thermoplastics. Figure 6.3 displays a summary of the results of the analysis for the charring material. In the figure, the subscripts v and c represent the virgin and char phases and ε denotes the emissivity, k denotes the thermal conductivity, C_p denotes the specific heat capacity, ρ denotes the density, ΔH_p denotes the heat of pyrolysis, n is the reaction order, and $E_a/\mathrm{Ln}Z$ is a lumped reaction kinetics parameter. The sensitivity coefficient is essentially the partial derivative of the natural logarithm of the model response with respect to the natural logarithm of the input property.

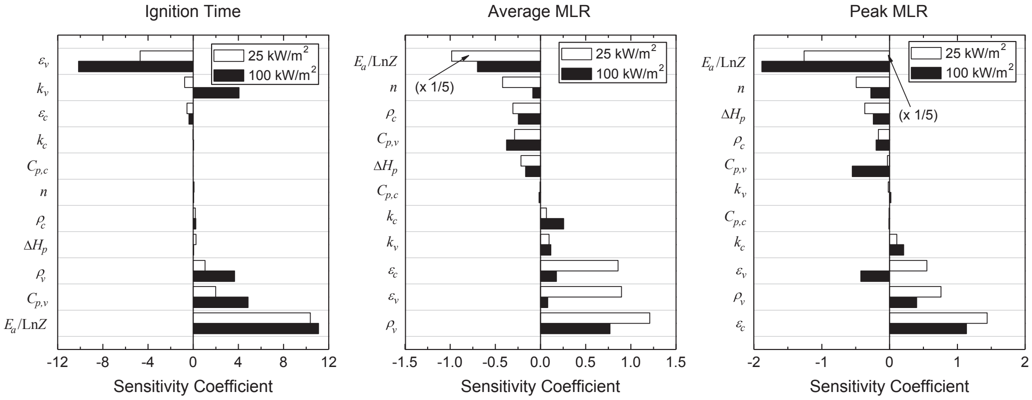


Figure 6.3: Results of Sensitivity Analysis Conducted by Chaos (Modified from [171])

For the charring material, the MLR was most affected by the virgin and char emissivities and the reaction parameters at low heat flux. At high heat flux, the same trends were observed up to the first MLR peak and thereafter the char and virgin thermal conductivities dictated the MLR due to the insulating layer at the top surface. The surface temperature rise was affected by the thermal conductivity, density, and heat capacity of the virgin material and the emissivities of the virgin and char components. For high and low heat flux conditions, the ignition time was most sensitive to virgin emissivity, reaction parameters, virgin heat capacity, and virgin density. The peak and average MLR were most sensitive to the virgin and char emissivities and the virgin density.

All the analyses were in agreement that the reaction kinetics and the heat absorbed during the pyrolysis process had the most significant effect on the MLR curve. The absorptivity and absorption coefficient also tended to have a marked effect on the MLR curve as well as the sample temperature distribution. The time to the onset of mass loss was affected most significantly by the reaction kinetics and the heat capacity of the material. The thermo-physical properties of the virgin material appeared to affect the initial rise of the temperatures throughout the sample, but did not significantly affect the overall MLR curve. Chaos found that for charring materials, the emissivity and thermal conductivity of the char tended to have a profound effect on the MLR after the onset of mass loss [171].

Bal and Rein emphasized the importance of temperature-dependent thermo-physical properties [170] but Linteris concluded that constant values of heat capacity and thermal conductivity, evaluated at the average temperature between ambient and decomposition, and temperature-dependent values of the same properties yielded similar results in bench-scale thermal degradation simulations [169]. Stoliarov et al. made a similar conclusion, stating that density, heat capacity, and thermal conductivity are of little importance when predicting the peak and average MLR and the mean value of these parameters from a literature review may be used in lieu of direct measurement [168].

The range of methods used to conduct these sensitivity analyses and the conflicting conclusions drawn from each demonstrates the complexity and nonlinearity of the mathematics of pyrolysis. It is clear from the review of the analyses in this section that the sensitivity of the pyrolysis process to each thermo-physical property and kinetic parameter is dependent on the test conditions, the sample material, and the structure of the sample. Because of this and because few of the materials investigated in these sensitivity analyses formed char or had complicated composite geometries like many of the materials that are commonly found in the built environment, it is unclear which conclusions may be applied to materials in general.

7 Tools for Analysis of Collected Data

Raw experimental data and material properties are essential to improving fire modeling predictions and improving the reproducibility of fire models from different investigators and laboratories. Tools to analyze raw data and material properties held in the database will make the database easier to use and more valuable to model practitioners. Some of the tools that have been developed and demonstrated as particularly useful for solid-phase fire modeling over the past decade are reviewed in this section.

Investigators have employed inverse analysis techniques to milligram-scale and bench-scale experimental data to determine properties and parameters required for fire models. In the context of fire modeling, inverse analysis involves deduction of unknown properties from experimental data when a mathematical model for the experiment is available. Because milligram-scale fire tests rely on zero-dimensional heating and bench-scale fire tests rely on one-dimensional heating of the specimen generalized comprehensive pyrolysis models can typically be used to model the results of these tests. Inverse analysis is a form of indirect measurement when a direct measurement is not possible. Many researchers have used inverse modeling techniques to determine input properties and parameters for fire models. All of the techniques and studies have not been included here, but several review articles provide an overview of inverse analysis [167, 172].

Optimization techniques used to minimize an objective function are often utilized when conducting inverse analyses. The optimization function is generally a measure of the error between a predicted curve and the measured curve. By minimizing this error, the values of the set of variables that made up the search domain may be defined as the unknown properties that successfully reproduce the experimental result. The most common optimization algorithms for highly dimensional problems like extracting the parameters of the reaction mechanism from a set of thermogravimetric data are evolutionary algorithms that are based on natural selection. These algorithms begin with a diverse group of parameter sets (called individuals) and the sets that produce the best fitness to the experimental curve survive and pass on property values that produce the most accurate prediction to the next population of parameter sets. Over many iterations, all of the property values in the set take on their optimal values. Lautenberger and Fernandez-Pello provide an overview of optimization algorithms used to determine material properties for fire models [173]

Bruns proposed a methodology to determine the kinetic parameters for pyrolysis reactions using Bayesian inference to compute probability density functions (PDFs) from Markov Chain Monte Carlo Simulations intended to fit experimental TGA data [174]. By determining PDFs for the kinetic parameters of pyrolysis reactions, the uncertainty in each parameter was inferred, which facilitated the determination of uncertainty in bench-scale simulations. It was found that the kinetic parameters determined through this method did not always extrapolate well to other heating rates, and this was attributed to overly complicated reaction models. It was found that some of the parameters that fit experimental TGA data tended to provide qualitatively poor predictions for the experimental HRR curves. Evaluation of uncertainty is an important topic in fire modeling and the method proposed by Bruns may form the basis for a useful tool in the material properties database.

Bruns and Leventon recently developed a high efficiency algorithm to determine kinetic parameters from TGA data [175]. The algorithm is fully automated and requires no interaction from the user and requires a time on the order of one second to generate kinetic parameters for a material from TGA data. The algorithm has also been extensively validated against polymer materials [175] and vegetative fuels [176]. A highly efficient method for extracting kinetic parameters and other key properties from TGA data would be a useful tool to incorporate into the material properties database.

A variety of optimization algorithms have been used with varying degrees of success, but because of the high dimensionality of the parameter space in some cases, it is possible to minimize the error between the predicted and experimental curves with a set of parameters that are outside the range of real possibilities. It is also possible that the set of parameters determined through inverse analyses will fit the calibration data well but will not provide the predictive capabilities required for fire modeling [165]. Marquis et al. demonstrated a methodology to directly measure as many properties as possible and use inverse analyses with optimization algorithms to determine the remaining unknown properties [84, 177].

Yang et al. proposed a methodology for material property determination that was focused on minimizing the cost associated with material characterization [178]. The authors concluded model predictions within 20% of experimental data may be yielded through analysis of TGA and cone calorimeter data that involves the SCE optimization algorithm. Fiola et al. recently proposed a methodology to completely parameterize a pyrolysis model through a combination of direct measurement and limited inverse analyses conducted using the hill climbing optimization algorithm [179]. A tool that allows model practitioners to conduct inverse analyses with optimization algorithms on the raw data available in the database may eliminate or minimize the need to directly measure all properties.

It is expected that there will be several user groups that will require different data and properties from the database. A tool to translate from more complex representations of burning to less complex representations ensures all user groups can extract their specific required properties from the same set of data. Such a method should guarantee that the same general results and conclusions are achieved regardless of the complexity of the model. This type of tool may also help to minimize the effort required to extract derived properties from the raw experimental data. As an example, an automated tool may be capable of extracting the melting temperature from TGA data according to the definition of the melting temperature, and automatically populate that property to the database.

Because computational fire modeling requires many property values as inputs and the intention is to make this database easy for fire model practitioners to use, a tool that outputs the lines of code required for common fire models using selected properties from the database will facilitate widespread use of the database. Such a tool may bring the database closer to a state where it is seamlessly integrated with common publicly-available computational fire models. To validate this type of tool and the set of properties that are stored in the database, it is important to demonstrate that common fire models parameterized with the collected properties adequately describe realistic fire scenarios. Through these validation exercises, the most accurate representation of burning that uses the measured properties will be explored to improve the utility of this tool.

8 Methods and Materials

The materials and products to be characterized and tested to populate the database have been selected to maximize the usefulness of the database to fire investigators and model practitioners. A list that includes the materials and products that will be characterized for the database is provided as Table 8.1. The numbers that appear in the leftmost column are intended to keep a count of the individual materials that will appear in the database. The entries that include several numbers in the leftmost column indicate that the product in the rightmost column is composed of several distinct materials that will be characterized individually.

Table 8.1: Materials for the Database

Number	Category	Material/Product
1	Roofing	EPDM Membrane on XPS Rigid Foam
2	Roofing	Roof Felt Underlayment
3	Roofing	Cedar Shake
4	Roofing	Asphalt
5	Roofing	Fiberglass Asphalt
6	Exterior Siding	Composite Decking
7	Exterior Siding	Exterior Insulation and Finish Systems
8	Exterior Siding	Tent Systems
9	Exterior Siding	Vinyl Siding with EPS Foam
10	Exterior Siding	Vinyl siding
11	Exterior Siding	Window Systems
12	Exterior Siding	Pine lap siding (Painted)
13	Exterior Siding	Window Screen Material (Vinyl-Laminated)
14	Exterior Siding	Fiber Cement siding
15	Exterior Siding	Stucco
16	Structural	Exterior Plywood/CLT
17	Structural	Oriented Strand Board
18	Structural	SPF Wood Joist/Stud
19	Structural	Particle Board
20	Structural	Medium Density Fiberboard
21	Structural	Cinder Block
22	Structural	Concrete
23	Insulation	Extruded Polystyrene Rigid Foam (XPS)
24	Insulation	House Wrap
25	Insulation	Polyisocyanurate Rigid Foam
26	Insulation	Polyurethane Spray Foam
27	Insulation	Wool
28	Insulation	Cellulose

Continued on next page

Table 8.1 – continued from previous page

Number	Category	Material/Product
29	Insulation	Fiberglass
30	Interior Finish	Rebond foam carpet padding
31	Interior Finish	Memory foam padding with moisture barrier
32	Interior Finish	Nylon carpeting high pile
33	Interior Finish	Nylon carpeting (low pile)
34	Interior Finish	Wool
35	Interior Finish	Fiber Reinforced plastic panel
36	Interior Finish	Laminate flooring
37	Interior Finish	Polyester carpet (high pile)
38	Interior Finish	Polyester (low pile)
39	Interior Finish	Triexta
40	Interior Finish	Vinyl plank flooring
41	Interior Finish	Vinyl tile
42	Interior Finish	Rayon (Rug)
43	Interior Finish	Cotton (Rug)
44	Interior Finish	Pine board paneling
45	Interior Finish	Rubber carpet padding
46	Interior Finish	Luan Paneling
47	Interior Finish	Solid Oak Hardwood flooring
48	Interior Finish	Basswood bead board
49	Interior Finish	Engineered hardwood flooring
50	Interior Finish	Eucalyptus Hardboard paneling
51	Interior Finish	Ultralite Gypsum Board (2 Coats of Latex Paint)
52	Interior Finish	Standard Gypsum
53	Interior Finish	Plaster
54	Plumbing	Foam insulation
55	Plumbing	Heat-tape Materials
56	Plumbing	Cross linked polyethylene (PEX)
57	Plumbing	Polyvinyl chloride (PVC)
58	Plumbing	Chlorinated Polyvinyl chloride (CPVC)
59	Cable	Solid Romex NM-B (PVC jacket)
60	Cable	Coaxial Cable (PVC Conduit)
61	Engineered Wood	Counter top, Solid acrylic polymer
62	Engineered Wood	Engineered wood cabinets/furniture vinyl over particle board
63	Engineered Wood	Counter top, Plastic Laminate over particle board
64	Engineered Wood	Engineered wood cabinets/furniture vinyl over MDF
65	Upholstered Furniture	Bean Bag Furniture
66-68	Upholstered Furniture	Polyester Microfiber/PUF/Polystyrene
69-71	Upholstered Furniture	Vinyl/Polyester batting/PUF
72	Upholstered Furniture	Cotton Upholstery

Continued on next page

Table 8.1 – continued from previous page

Number	Category	Material/Product
73	Upholstered Furniture	Hemp
74-76	Upholstered Furniture	Polyester Microfiber/Polyester batting/PUF
77	Sleeping Products	Mattress Topper, Latex Foam
78	Sleeping Products	Polyester Sheets
79	Sleeping Products	Microfiber Sheets
80	Sleeping Products	Mattress Topper, Polyurethane Foam
81	Sleeping Products	Mattress Topper, High Density Polyurethane Foam
82-84	Sleeping Products	Innerspring Mattress
85-87	Sleeping Products	High Density Polyurethane Foam Mattress
88	Sleeping Products	Cotton sheets
89	Sleeping Products	Feather Pillow
90	Sleeping Products	Bamboo Sheets
91	General Polymers	High-Density Polyethylene (HDPE)
92	General Polymers	Low-Density Polyethylene (LDPE)
93	General Polymers	Polypropylene (PP)
94	General Polymers	Polystyrene (PS)
95	General Polymers	Polyethylene Terephthalate (PET)
96	General Polymers	Polycarbonate (PC)
97	General Polymers	Polyamide (PA) (Nylon)
98	General Polymers	Acrylonitrile butadiene styrene (ABS)
99	General Polymers	Acrylic (PMMA)
100	General Polymers	Polylactic Acid (PLA)
101	General Polymers	Polyvinyl chloride (PVC)

The history of materials, and particularly aging of upholstered furniture items may be an important factor. Aging or contamination of furniture items may affect the thermo-physical properties and flammability characteristics of the component materials. Because there is a plan to support development and hosting of this database in perpetuity, the sensitivity of properties and the fire response of the materials to these factors is an important consideration to study, but it is outside the scope of the initial period of performance.

There may be significant differences in the components, properties, and reaction-to-fire between materials that are sold under the same trade name due to variations in manufacturing processes, standards, and intended end use. A detailed investigation into all of the scatter in properties and reaction-to-fire or variation in composition for all of the proposed materials is unfeasible for this period of performance. Material from a single manufacturer/production method will initially be investigated with a structure in place to update the entry in the future with data collected from different manufacturers/production methods. Descriptions of the materials and products that appear in the database will provide as much detail as possible, including the date the material was manufactured, the manufacturer, trade name, etc., to specify the characterized material.

One specific variation in preparation that may be investigated is gypsum wallboard with the surface painted and unpainted. Additionally, many of the pure materials from the General Polymers category have been characterized in previous studies and the properties and test data measured during this project may provide a representation of the variability in the properties due to different formulations, manufacturers, and processes. The list of materials presented here should be considered a baseline and starting point, with a structure in place to expand the number of materials and variables investigated after the initial period of performance.

Three major groups that are expected to use the database have been identified: fire investigators, fire protection engineers, and fire researchers. Table 8.2 identifies the sets of properties that must be complete to ensure each user group can effectively use the database. The property denoted as 'HRR' in Table 8.2 includes all heat release related properties, including HRR, total heat released, and heat release rate per unit area (HRRPUA). In the table, an 'X' symbol denotes a property that is expected to be required by that user group as an input to a model, a 'V' symbol indicates data that is expected to be useful for validation of a modeling methodology or modeling results, and no symbol indicates a property that is not expected to be heavily used by that user group.

The Fire Investigators user group is expected to use the database as a reference for ignition temperatures and melting temperatures as well as for inputs to models used to test hypotheses about potential fire scenarios. The models that fire investigators use are generally related to fire spread, ignition, and burning rates. To model these phenomena, investigators may require HRRPUA, HRR, total heat released, time to ignition, ignition temperature, heat of combustion, and the thermophysical properties.

The Fire Protection Engineers user group is expected to use the database for inputs to fire protection analyses and models that predict fire growth and spread and smoke movement in the built environment. These methods generally require the same inputs as those used by the Fire Investigators user group, with the addition of product yields and the radiative fraction of the fuel.

The Fire Researchers user group are expected to use the properties in the database for model development and modeling fire phenomena from first principles. The Fire Researchers user group is expected to use all of the properties in the database because of the breadth of inputs required to describe burning using the most complex model representations. This means the Fire Researchers user group is expected to need the pyrolysis reaction kinetics, heats of reaction/gasification, and the optical properties in addition to the expected properties for the Fire Protection Engineers user group. The HRRPUA, time to ignition, ignition temperature, and full scale HRR data are expected to be used by Fire Researchers to validate models and modeling methodologies.

Although this database has been conceptualized to serve many sectors of the fire protection community, the initial funding for the database comes from the National Institute of Justice (NIJ), which has a vested interest in fire investigations. To ensure the database is effective for the fire investigation community, the properties that correspond to the Fire Investigators user group in Table 8.2 will hold the highest priority.

Table 8.2: Expected Property Requirements for Each User Group

User Group	HRR	Ignition Temperature	Time to Ignition	Soot Yield	CO Yield	Reaction Kinetics	Heat of Reaction	Heat of Combustion	Density	Thermal Conductivity	Specific Heat Capacity	Emissivity	Absorption Coefficient	Radiative Fraction
Fire Investigators	X	X	X					X	X	X	X			
Fire Protection Engineers	X	X	X	X	X			X	X	X	X			X
Fire Researchers	V	V	V	X	X	X	X	X	X	X	X	X	X	X

Some of the properties that are listed in Table 8.2 must be determined from raw data through an analytical method, and the resulting property may be dependent on the method used to determine the property value. Compounding this issue is the fact that several of the properties lack a consensus on the definition of the property or the accepted methods to determine the property. To combat confusion and misuse of the derived properties provided in the database, the definitions of the properties and the equations used to derive the properties will be clearly indicated in the database.

The experimental methods and standard tests that were proposed to measure each of the properties were discussed in the meetings. The proposed experimental methods are presented in Table 8.3 in order of descending priority. The property denoted as ‘HRR’ in Table 8.3 includes all heat release related properties, including HRR, total heat released, and HRRPUA.

The time to ignition is particularly sensitive to the emissivity, but most practical materials have average emissivity values in the range of approximately 0.7 to 0.95. Additionally, there is currently no computational fire model in which the spectral emissivity of a material may be defined. For these reasons, the measurement of emissivity using an integrating sphere was deemed a low priority measurement relative to the other listed measurement methods.

Table 8.3: Properties and Methods for Database

Property	**Method**
HRR	Oxygen Consumption Calorimetry
Heat of Combustion	Oxygen Consumption Calorimetry
Ignition Temperature	Cone Calorimeter
Density	Balance and Direct Volume Measurement
Thermal Conductivity	Heat Flow Meter
Specific Heat Capacity/Heat of Reaction	Differential Scanning Calorimetry
Thermal Diffusivity	Transient Plane Source
Radiative Fraction	Radiometer & Calorimeter
Emissivity/Absorption Coefficient	Integrating Sphere
Reaction Kinetics	Thermogravimetric Analysis

9 Future Work

The next major phase of this project involves conducting additional research to finalize the structure and type of database as well as the format of the experimental data to be stored in the database. It is expected that the tools and functionality that have been proposed will factor into the structure of the database, and that ideas for additional tools and functions will result from the database research. Concurrently, the experimental procedures and protocols proposed to measure each property will be finalized to ensure consistency between experiments. The procedures for securing and storing data and the format of the raw data will also be finalized to facilitate transfer of the data and properties from the laboratory to the database.

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