

# **COMBUSTION RESEARCH STUDIES AT THE NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY**

by

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**NIST**

**National Institute of Standards and Technology**  
Technology Administration, U.S. Department of Commerce

研究所紹介

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### 1 Introduction

The National Institute of Standards and Technology (NIST) is a federal agency within the Technology Administration of the Department of Commerce. NIST's primary mission is to develop and apply technology, measurements, and standards to promote economic growth by working with U.S. industry. Established in 1901 as the National Bureau of Standards (NBS), the institute was renamed in 1988. NIST carries out its mission through four interwoven programs: (1) the Measurement and Standards Laboratories, providing vital components of the nation's technology infrastructure needed by U.S. industry to continually improve products and services; (2) the Advanced Technology Program, providing cost-shared awards to industry for development of high-risk, enabling technologies with broad economic potential; (3) a grassroots Manufacturing Extension Partnership with a nationwide network of local centers and business assistance to smaller manufacturers; and (4) a quality outreach program associated with the Malcom Baldrige National Quality Award that recognizes business performance excellence and quality achievement by U.S. manufacturers and service companies.

NIST employs about 3,300 scientists, engineers, technicians, and support personnel and hosts about 1,250 visiting researchers each year. Fiscal year 1998 operating resources from all sources totaled about \$790 million. The Institute maintains research facilities at its Gaithersburg, MD (234 hectare campus about 30 km northwest of Washington, DC with about 2,700 employees) and Boulder, Colorado (84 hectare campus about 42 km north west of Denver with about 600 employees). There are seven Measurement and Standards Laboratories. They are

- Electronics and Electrical Engineering Laboratory
- Manufacturing Engineering Laboratory
- Chemical Science and Technology Laboratory
- Physics Laboratory
- Materials Science and Engineering Laboratory

- Building and Fire Research Laboratory
- Information Technology Laboratory

These laboratories produce high-quality measurement tools, data, and services extending from science and medicine to industry and commerce, and from public health and the environment to law enforcement and national defense. More detailed information on the research activities of these laboratories can be found at [www.nist.gov](http://www.nist.gov). Combustion related research is being conducted in two of the laboratories: the Fire Science Division and Fire Safety Engineering Division of the Building and Fire Research Laboratory (BFRL), and the Process Measurements Division and Physical and Chemical Properties Division of the Chemical Science and Technology Laboratory (CSTL).

## **2 Combustion Related Research Programs at NIST**

### **2.1 Fire Science Division**

#### **2.1.1 Advanced Fire Measurements Group**

The group's name was recently changed from the "Smoke Dynamics Research Group" to reflect that its principal mission within BFRL is the development and characterization of experimental approaches for quantifying fire behavior. A major focus is the assessment of the uncertainties associated with such measurements. In addition to research funded directly by NIST, a number of projects are performed under the sponsorship of such organizations as the United States Department of Defense (DoD) and the National Aeronautics and Space Administration (NASA).

Even though the focus of in-house projects is fire, there is much which should interest the general combustion community. A current project involves the characterization of the uncertainty in experimental measurements associated with large fires. Recent work has considered the response of thermocouples in fire environments. It has been shown that significant errors in gas-phase temperatures can result from the neglect of radiative effects and the limited time response of thermocouples<sup>(1)</sup>. A modeling effort has complimented the experimental findings<sup>(2),(3)</sup>. A second part of this effort has focused on the development of an approach for measuring the generation of smoke by fires based on laser extinction measurements. The development of this technique was made possible by the experimental finding that the specific extinction coefficient for overfire soot is nearly independent of fuel type<sup>(4)</sup>. Our most recent effort involves the quantification of the uncertainty associated with the measurement of fire heat release rates based on oxygen consumption measurements.

Efforts are also underway to develop new diagnostics for recording species concentrations in fire environments. One approach which is being assessed is the use of near-infrared tunable diode lasers as sources for absorption measurements<sup>(5)</sup>. Due to rapid developments in the telecommunication industry, tunable lasers are becoming widely available over the 1.4  $\mu\text{m}$  to 1.63  $\mu\text{m}$  range. The use of associated fiber optics allows transport of these beams from remote locations to the measurement region. The potential to multiplex a number of laser outputs onto a single fiber offers the exciting possibility of simultaneously measuring temperature and concentrations for a number of important fire species.

Dr. Kermit Smyth (now retired) and coworkers spent many years making detailed measurements of concentration, temperature, and velocity within steady laminar diffusion flames on a two-dimensional Wolfhard-Parker burner and an axisymmetric Santoro burner as

part of an effort to understand soot formation in fires. Recently, these studies have been extended to time-varying flickering flames generated by acoustically forcing the fuel flow in a Santoro burner<sup>(6)</sup>. Experimental results for a number of fuels have recently been made available on the World Wide Web for both steady and time-varying flames<sup>(7)</sup>. Techniques used to characterize these flames include laser-induced incandescence for soot characterization,<sup>(8)</sup> laser-induced fluorescence for characterizing polyaromatic hydrocarbons,<sup>(9)</sup> and thin-filament pyrometry for time-resolved measurements of temperature along a line,<sup>(10)</sup> to name a few.

The Advanced Fire Measurements Group has worked on approaches for characterizing and describing soot structure. A recent example is a paper by Mountain and Mulholland which describes an approach for calculating extinction coefficients and polarization ratios for soot<sup>(11)</sup>.

Two projects funded by the Microgravity Combustion Program of NASA are currently underway. The first is investigating the role of gravity in the behavior of inverse diffusion flames. A particular focus is the formation of soot and carbon monoxide. An experimental rig is being developed for use in the 2.2 s drop tower available at the NASA Glenn Research Center in Cleveland, Ohio. The second project is investigating the formation of superagglomerates in microgravity diffusion flames. An experimental rig for the 2.2 s drop tower is being developed in which silane will be burned to generate silica superagglomerates. Diagnostics to be used for characterizing the superagglomerates include thermophoretic sampling and optical scattering techniques.

Two on-going projects are part of the effort known as the "Next Generation Fire Suppression Technology Program" funded by the Strategic Environmental Research and Development Program, DoD. The overall goal is the development of retrofitable, economically feasible, environmentally acceptable alternatives for the fire-fighting agent halon 1301, whose manufacture has been banned due to its contribution to the depletion of stratospheric ozone. The first of these projects is the development of an instrument for measuring the concentration of an agent released into an enclosure with good spatial and temporal resolution. The instrument is based on the absorption of mid-infrared radiation. The second project is seeking to identify potential replacement agents for halon 1301 which suppress fires primarily by extracting heat, so-called thermal agents. This project involves searches of the extensive molecular data bases of NIST to identify chemicals which absorb large amounts of heat when their temperature is raised, detailed chemical kinetic modeling of inhibited methane/air diffusion flames to identify the mechanisms of inhibition and extinguishment, and characterization of the effectiveness of potential thermal agents for extracting heat from solid and liquid fuel surfaces<sup>(12)</sup>.

Members of this group have been investigating turbulent mixing for several years with the goal of improving the understanding and modeling of turbulent combustion<sup>(13),(14)</sup>. Recently an internal report has been prepared which summarizes measurements of scalar dissipation in an isothermal, turbulent axisymmetric jet of propane flowing into air<sup>(15)</sup>. Scalar dissipation is recognized as a key parameter in turbulent flame modeling, but experimental characterization, even in isothermal flows, has been very limited.

### **2.1.2 Fire Sensing and Extinguishment Group**

Minimizing the impact of unwanted fires and the negative aspects of the suppression process are the goals of the Fire Sensing and Extinguishment Group. Research is conducted into (1) identifying and measuring the symptoms of pending and nascent fires; (2) devising and adapting monitors for these variables and the intelligence for timely interpretation of the data; (3) developing methods to characterize the performance of new approaches to fire

detection and suppression; (4) determining mechanisms for fire suppression by advanced agents and principles for their optimal use; and (5) modeling the extinguishment process. The current research program discussed below is categorized under three headings: fire detection, transport of suppressants, and chemical inhibition of flames.

### ***Fire detection***

The objective of the fire detection research program is to permit fire sensor designers to demonstrate the feasibility of new concepts, to provide the critical link between sensor input and output required for meaningful numerical simulations, and to improve the reliability and performance of fire detection systems. Applications are to vehicles and to residential, commercial, and industrial structures. To improve detection sensitivity and reduce inappropriate responses, the new sensor designs are based on the measurement of different aspects of the fire source, or on specific combinations of sensors that can help in distinguishing a real fire from an interfering background signal. A standard means for evaluating fire sensors is being developed<sup>(16)</sup> which addresses all of the following questions: what is the nature of the fire in its earliest stage? how are the products transported from the source to a potential sensor location? how does the sensor respond to these products when installed in the field? and is the system immune to nuisance stimuli? The gas and particulate species and the temperature increases produced early in these fires are assumed to be transported from the fire source to the detector at time-varying levels that are predicted using a large eddy simulation. The emulation of the fire and evaluation of the detector response are conducted in the NIST Fire-Emulator/Detector-Evaluator developed for this purpose. Efforts are aimed at demonstrating the advantages of multi-function sensors and multi-sensor detection, with the objective of using such sensors for improving the reliability and performance of fire detection systems through earlier detection of small fires, and for reducing both false negatives (unreported fires) and false positives (reported fires which don't exist)<sup>(17)</sup>.

### ***Transport of suppressants***

Environmentally benign fire suppressants are sought for use in aircraft, ships, computer rooms, telecommunications equipment, and other applications previously protected by halon 1301 (CF<sub>3</sub>Br). The effectiveness of halons is attributable not only to the potent H-atom scavenging of bromine, but also to the physical properties that cause them to flash to a gas and quickly disperse throughout the volume being protected. The development of new technologies to replace halon-based fire suppression systems is hampered by a lack of understanding of the physical processes controlling dispersion, and by the absence of metrics for determining fire fighting agent effectiveness.

Research has been underway at NIST for the past seven years to establish scientifically defensible test methods for evaluating the dispersion and suppression of gaseous and aerosol alternative agents. In the dispersed liquid agent fire suppression apparatus<sup>(18)</sup>, a steady flow of liquid agent aerosol with drop diameters in the range of 1  $\mu\text{m}$  to 50  $\mu\text{m}$  is produced using a nebulizer located along the center of a low turbulence intensity wind tunnel. The drops are suspended in the air stream and transported to a 15.8 mm diameter, 31.8 mm long, cylindrical porous stainless steel burner. A propane flame is the target for the suppressant. When the droplet loading is sufficient, the stabilization of the flame changes abruptly from the forward stagnation point to the wake, as seen in Figures 1a and 1b. A phase-Doppler particle analyzer is used to measure droplet size and velocity distributions near the flame zone at conditions

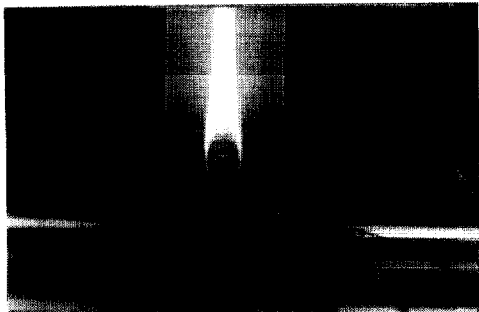


Fig. 1a. This is a view (along the axial direction) of the cylindrical porous burner with an enveloped flame established in the forward stagnation region using propane and air.



Fig. 1b. An example of a wake flame which is obtained (at a fixed fuel injection rate) by increasing the air flow with and without fire suppressant to blow-off the enveloped flame.

before and at blow-off. Fluids examined in this device include pure water, aqueous acetate and lactate solutions, fluoroethers, and various dendrimer solutions. The effectiveness of these materials vary from worse than water to almost four times better than water on a mass fraction basis.

Current bench-scale suppression effectiveness screens, including the one just described, are limited to quasi-steady applications, and are unable to evaluate adequately the highly transient effects of sudden agent addition. The presence of a recirculating flow and hot surface in the fire region can lead to situations more difficult to control, and the possibility of the fire re-lighting. A project has been undertaken to simulate this situation, and to accommodate different transient suppression approaches. A 90 mm by 180 mm porous bronze burner is located in a 90 mm square cross-section duct, downstream of a 25 mm high baffle which creates a stable propane/air flame. A hot surface downstream of the fire is included to act as a re-ignition source. Computational fluid dynamics modeling has been performed and benchmarked against velocity, temperatures and the general flame shape, and a stability map of the flame as a function of geometric and flow parameters has been generated. The required mass, rate and duration of agent delivery to extinguish fires under standard conditions have been determined for  $\text{CF}_3\text{Br}$ ,  $\text{N}_2$  and  $\text{C}_2\text{HF}_5$ . Similar experiments are planned using solid propellant gas generated agents, with particular emphasis placed on the agent's susceptibility to re-ignition on the hot surface.

### ***Fire Suppression Chemistry***

There exists a continuing need for better suppressants and suppression methods, but limited scientific understanding of existing chemical inhibitors hinders development of new agents. Research in this laboratory<sup>(19)</sup> has shown that  $\text{Fe}(\text{CO})_5$  is an extraordinarily effective inhibitor at low mole fractions, but that the effectiveness diminishes at inhibitor mole fractions above about  $100 \times 10^{-6}$ . A detailed chemical kinetic mechanism for the gas-phase chemistry of flame inhibition has been developed and used in numerical calculations of the flame structure to explain the strong effect<sup>(20)</sup>. These calculations show that there exist limits to the effectiveness of any agent which acts to catalytically recombine radicals present at super-equilibrium levels, since the radical mole fractions are not likely to be lowered past the

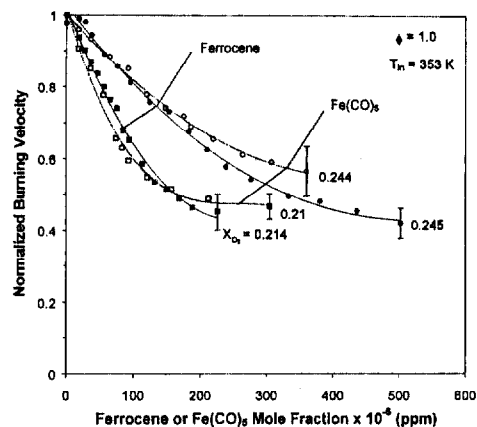


Fig. 2. Normalized burning velocity of premixed  $\text{CH}_4/\text{O}_2/\text{N}_2$  inhibited by ferrocene and  $\text{Fe}(\text{CO})_5$  for several values of the oxygen mole fraction in the oxidizer  $\text{XO}_{2,\text{ox}}$ . The error bars represent typical 95% confidence intervals for the data.

equilibrium values<sup>(21)</sup>. Using laser scattering and extinction measurements, data have been collected to show that formation of particles in the flame is correlated with the loss of effectiveness, indicating that loss of active species to condensation is likely occurring. Research is continuing into the mechanism of iron, with ferrocene [ $\text{Fe}(\text{C}_5\text{H}_5)_2$ ] chosen as a less toxic alternative to iron carbonyl.

The work to date indicates that Fe is the precursor that is responsible for strong inhibition by both compounds, as shown in Fig. 2. Other materials containing metals and phosphorous have been demonstrated to have a capability to inhibit flames to an extent surpassing halon 1301. The thermochemistry of many of these compounds and the kinetic mechanisms under which they react in hydrocarbon flames are, at best, not well established and in many cases virgin territory for research. A data base has been developed of experimental results on the combustion related properties of tin compounds, organo-phosphorus compounds, metallic halides and phosphonates.

Many of the hydrofluorocarbons (HFCs) under consideration for fire fighting agents also have properties that make them suitable for refrigerants. To increase the performance of a refrigerant, hydrogen atoms may be substituted for fluorine atoms in the HFC molecule, which can make the refrigerant flammable. HFC-32 ( $\text{CH}_2\text{F}_2$ ) is one example. NIST has studied the flammability limits of  $\text{CH}_2\text{F}_2/\text{air}$  mixtures using a twin flame, premixed counter-flow burner<sup>(22)</sup> and the effect of adding a non-flammable component (e.g.,  $\text{C}_2\text{HF}_5$ ) on the flammability limits of the mixture.

### 2.1.3 Materials Fire Research Group

This Group performs research to facilitate the development by industry of new, less-flammable materials and end products. This capability is based on a fundamental understanding of the mechanisms that control the ignition, flame spread, and burning rate of materials and the chemical and physical characteristics that affect these aspects of flammability. This includes (1) developing methods of measuring the response of a material to fire conditions that facilitate prediction of the full-scale performance of the final product, (2)

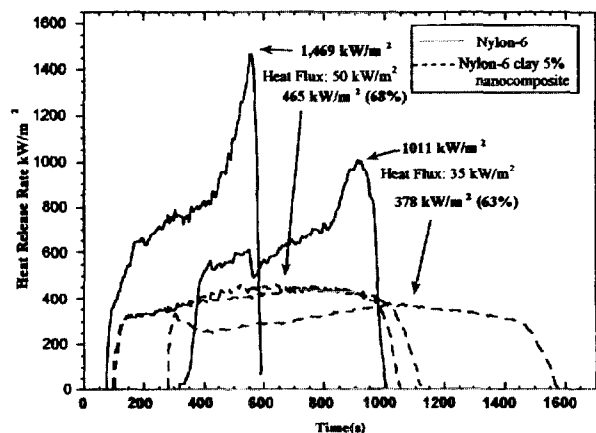


Fig. 3. Comparison of heat release rate between nylon 6 and nylon 6 nanocomposite measured in a Cone Calorimeter.

pursuing computational molecular dynamics modeling and other mechanistic approaches to understanding flame retardant mechanisms and developing new, effective, environmentally-friendly flame retardant approaches, and (3) characterizing and modeling the heat release rates of commodity polymers with and without flame retardant additives and also of fiber reinforced composites.

Our flame retardant approach is to utilize silicon-based additives for large volume commodity polymers such as polyolefins instead of developing new, high temperature polymers. Gas phase flame retardants using halogens, e.g., radical scavenging of H and OH by bromine or chlorine, tend to increase the amount of soot particles and CO. An additional concern is the potential formation of dioxin during incineration of such halogenated compounds. Therefore, our approach is to retain carbon in the condensed phase as much as possible by enhancing the formation of char or to form a protective barrier/insulation surface layer during burning to reduce the transport rate of thermal degradation products to the gas phase.

One promising Si-based flame retardant approach is based on a polymer-clay nanocomposite. Nanocomposites consist of a small amount of layered clay compatibilized by surface modification. A clay layer is a thin flake whose thickness is about 1 nm with an aspect ratio of from 100 to 1,000. With an appropriate organic treatment of the clay surface for the compatibilization, polymer chains can enter into the space between clay layers and thus the interface area between the clay surface and the polymer increases drastically. It appears that this large interface area modifies the physical properties of the polymer and its physical strength and heat distortion temperature increase significantly under certain conditions. The addition of a small amount of treated clays (less than a mass fraction of 5 %) into various polymers such as nylon 6, polystyrene, and polypropylene significantly reduces the heat release rate of these polymers as measured in a Cone Calorimeter<sup>(23),(24)</sup>. An example with nylon 6 is shown in Fig. 3.

There are no significant differences between the specific heats of combustion of the pure polymers and the clay- nanocomposite polymers. This indicates that the mechanism of the observed reduction in heat release rate tends to be mainly in the condensed phase. This



hypothesis was tested by measuring mass loss rate of these samples in a nitrogen atmosphere at an external radiant flux simulating fire conditions using our radiative gasification device. The observed significant reduction in mass loss rate of the clay-nanocomposites as compared with the pure polymer samples confirms the hypothesis because gas phase reactions did not participate in these tests. Recorded video pictures during the tests indicate the formation of a continuous protective char surface layer for the nylon 6 nanocomposite sample compared to a more fragile char layer which was broken into many fragments during the test of the pure nylon 6 sample. This formation of the protective surface layer appears to be the reason for the reduction in mass loss rate and in heat release rate; it acts as a barrier layer for the degradation products and also as a thermal insulation layer. We are currently working to understand the effects of clay characteristics such as aspect ratio, type, organic treatment, end treatment, and others on flammability properties. A theoretical study using molecular dynamic modeling of polymer chains at high temperatures with and without flame retardant additives including clays is being conducted in close collaboration with the experimental studies to understand the flame retardant mechanisms of the additives and to improve further their effectiveness<sup>(25),(26)</sup>.

Developing new principles for reducing the flammability of polymeric materials requires knowledge of the detailed processes these materials undergo during burning. A series of degradation/gasification experiments on commodity polymers such as polypropylene (PP), polyethylene (PE), and polystyrene (PS) was conducted to study the condensed phenomena in the radiative gasification apparatus without any influence of gas phase reactions (flaming). Specimens were exposed to a radiant flux of 40 kW/m<sup>2</sup> in a nitrogen atmosphere, and the gasification (mass-loss) rate and temperatures within the specimens were measured. Direct observation of these tests revealed the formation of numerous bubbles and boiling phenomena of molten polymers. However, addition of a small quantity of silica gel (for example, 5 mass %) into PP suppresses the liquid-like behavior without any formation of bubbles except at the very early stage of the gasification and reduced the gasification rate about 50 %. The sample behaved more or less as a solid and it appears that the transport process of the molten degradation products generated inside the specimen is by capillary flow through the solid-like layer. These results show the importance of the transport process of the degradation products through the specimen. A modeling study to describe the observed behavior in the specimen is in progress. A one-dimensional model that includes in-depth gasification, a melting phase change, a vigorous bubbling layer, radiative and convective heat losses at the surface, and substrate thermal properties has been completed<sup>(27)</sup>. Inclusion of the transport of evolved degradation products through the specimen and the impact of bubbles on thermal conductivity is under way. The condensed phase gasification model is coupled with a gas phase model based on the large eddy simulation, LES, method to calculate burning rates of polymer samples in a Cone Calorimeter, including radiative transfer from flame to the sample surface.

When the heated surface of a burning thermoplastic is not horizontal, the molten layer will have a tendency to flow downward; this can have a profound effect on the gasification and burning rate behavior since heat and, possibly, burning material are being transported (and the protective layer-- one of the most promising approaches being pursued here- may be lessened in its effectiveness). These flow phenomena have been observed frequently in real fires, but, presumably because of their complexity, have been ignored almost completely by the fire research community. However, this is becoming a more critical fire-growth issue due to the significant increase in the daily use of thermoplastics. The flow behavior of the polymer melt, particularly its effective viscosity, is the most important property needed to predict these changes in shape. These materials are non-Newtonian in behavior with viscosities which

depend significantly on shear rate and strongly on temperature. The dependence of the viscosity of each polymer of interest on these two parameters is now being measured to provide a vital input to first cut models that predict the flow which will result from fire-level heat fluxes impinging on a simple vertical slab polymer geometry. At the same time, an apparatus has been constructed with which to check these model predictions. The apparatus permits quantitative study of the behavior of a polymer slab subjected on one surface to a uniform radiant flux of varied intensity. Melt flow velocity, melt surface temperature and overall weight loss measurements are being made for comparison with the model predictions. The materials chosen have a wide range of melt flow properties. Thermal stability is also varied since it too can affect melt viscosity. Burning experiments with these same materials are planned as a prelude to modeling the burning process.

## **2.2 Fire Safety and Engineering Division**

### **2.2.1 Fire Dynamics Group**

The group's mission is to improve measurement and prediction of fire phenomena to reduce the human and economic losses resulting from fires and related hazards. In addition, the group supports U.S. industry through the development and application of measurement methods, standards, and predictive models.

The research conducted by the Fire Dynamics Group falls into two general categories - experimental measurements and predictive modeling. Measurements support the modeling efforts in two ways. The measurements generate physical parameters that cannot be obtained easily by theoretical means, and the measurements also verify the accuracy of the predictive models. These models predict the growth, spread, suppression, and emissions from fires ranging in size from tiny laboratory flames on the order of a millimeter in thickness to large-scale fire plumes on the order of kilometers. The computer models attempt to bridge the gap between basic research and practical applications, while maintaining high standards of scientific rigor.

A number of on-going projects include the following:

- Computationally efficient radiation models are being developed for implementation in computational fluid dynamics, CFD, computer simulations. Radiation is a dominant mode of heat transfer in fires. Existing approaches to the calculation of radiative transport in the fire and combustion research communities are not well suited to the high resolution requirements of the NIST fire codes. Computationally efficient algorithms are therefore being developed for implementation in practical problems.
- Wind/fire interactions are being modeled in an effort to understand the coupled effect of these phenomena. Current understanding of this process is meager. As part of the validation process, prediction of large-scale wind-driven fire experiments such as those being developed for the new test facilities at NRIFD in Japan will be undertaken. One rare, but potentially catastrophic form of fire spread is fire whirls, where organized angular momentum interacts with buoyancy to produce large swirl velocities<sup>(28)</sup>.
- Calculation of hazards presented by large industrial fires, such as oil-storage containers to nearby people and structures. The ALOFT (A Large Outdoor Fire Plume Trajectory) code was developed to follow smoke plume dispersion from a fire as it is transported to downwind targets. The predictions of downwind deposition of potentially hazardous soot particulate matter have been compared favorably with field measurements conducted in collaboration with the Alaska Department of Environmental Conservation, the U.S.

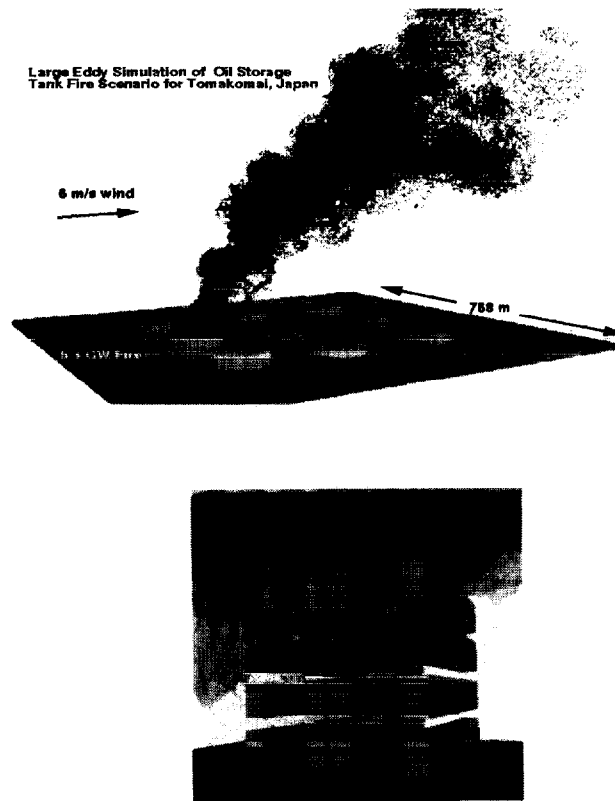


Fig. 4 Simulations of a burning oil-storage container and a rack-storage warehouse fire.

Department of Interior Minerals Management Service, and Environment Canada with technical support from several major oil companies. The model has been used in many applications including its use to characterize the smoke plumes and analyze data from the large-scale oil fire tests conducted in Japan in January 1998 as part of the US/Japan Earthquake Mitigation Partnership<sup>(29)</sup> (see Figure 4). The success of the computer model has led the State of Alaska to embark on a certification of the model for evaluating the hazards posed by the use of in-situ burning of crude oil spills as an environmental remediation procedure.

- Simulations of the dynamics of large pool fires have been developed. The models include the effects of radiation blockage by smoke<sup>(30)</sup>. These simulation tools allow in-depth environmental hazard analyses that are currently addressed with crude empirical tools.
- CFD simulations of fire scenarios with particular emphasis on reconstruction of fire-phenomena in terms of fire-fighting strategies and safety.
- Studies of microgravity combustion include models of flame spread over condensed phase materials and gravitational jitter effects. These models and experiments have relevance to fire safety aboard space platforms.
- Fundamental studies of flame structure and extinction. Experimental measurements and Direct Numerical Simulations (DNS), using simplified chemistry, are being conducted to investigate small well-defined baffle-stabilized and unattached gaseous non-premixed

flames<sup>(31)</sup>. These studies are related to an improved understanding of the mechanisms of flame extinction in an effort to find a new generation of replacements for Halon fire suppressants.

- A major thrust of the Fire Dynamics Group is the simulation of fire growth in industrial facilities. The Industrial Fire Simulator (IFS) model is a CFD model that uses a LES approach to fluid dynamics<sup>(32),(33)</sup>. The IFS model calculates fire growth and spread in a large enclosure to investigate the effect of water sprinklers on the spread and growth of fires burning standard commodities in a well-defined rack storage configuration in a warehouse as shown in Figure 4. A central challenge for the IFS model is to represent fire phenomena like ignition, flame spread, and water suppression in a way that preserves what is known about the underlying physics, but is tractable computationally. Measurements from appropriate small-scale experiments are used within the various fire related IFS sub-models<sup>(34)</sup>. Ultimately, we plan to use the IFS model to also address fire growth and spread in residential structures, which can be used as a design tool for improved fire safety performance of fire protection elements.

## **2.3 Physical and Chemical Properties Division**

### **2.3.1 Chemical and Thermodynamics Group**

The principal thrust of research efforts in this group in the combustion area is directed towards the quantitative understanding of the chemical changes that organic molecules undergo at high temperatures under oxidative or pyrolytic conditions. Particular emphasis is placed on the determination of rate constants and expressions for single step thermal reactions. The aim is to advance the application of the technology of computer simulation through the development of reliable chemical kinetic data bases. The program consists of experimental measurements, development of theory, the evaluation of chemical kinetic data and the simulation of combustion processes.

In the experimental area, thermal rate constants are determined in shock tubes and static reactors. The shock tube work has been focussed on the thermal stability of organic molecules as expressed in terms of unimolecular rate expressions. A comparative rate method has been employed to make high accuracy rate constant measurements for the thermal decomposition of intermediate sized organic molecules. Sufficient data have now been accumulated so that predictions regarding the bond breaking process in most organic fuels can be made<sup>(35)</sup>. This work has also led to the determination of the strengths of the bonds in these molecules and the heats of formation of the radicals that are formed from the breaking of these bonds<sup>(36)</sup>. This in turn leads to measures of the thermal stability of the radicals. Present work is concentrated on the determination of the branching ratios for the decomposition of larger hydrocarbon radicals<sup>(37)</sup>. The general situation is complicated by the possibility of isomerization channels. An additional thrust is the determination of the thermal stability of highly unsaturated, including aromatic, molecules. The aim of this work is to obtain information on the molecules that are intermediates preceding polyaromatic hydrocarbon and soot formation. Work in static reactors has been concerned with the combination reactions of unsaturated radicals. They involve the generation of these radicals using flash or chemical techniques and then monitoring their temporal behavior by laser absorption in real time and with gas chromatography for final product analysis. Particular attention is being placed on propargyl<sup>(38)</sup> and vinyl radicals<sup>(39)</sup>.

The theoretical work has concentrated on the role of energy transfer in high temperature

processes. Special emphasis is placed on multichannel decomposition and isomerizations and chemical activation processes. It is well known that the rate constants for thermal unimolecular processes in the broadest sense are increasingly influenced by energy transfer effects with increasing temperature. The methodology for making such corrections is well established for single step decomposition processes and chemical activation reactions at low temperatures. The general situation involving multichannel reactions and isomerizations is more complex and indeed there is no simple closed expression answer to this problem<sup>(40)</sup>. We are in the process of developing a program to treat the more general situation. This involves solving the time dependent master equation and determining the temporal behavior of the distribution functions. Rate constants (some of which may be time dependent) can then be determined using the RRKM values for the specific rate. It is expected that this program will be an element in a new data base for unimolecular reactions. In combination with the stored transition state structures and energetics, it will become possible to calculate desired rate constants (for unimolecular as well as chemically activated reactions) as needed and thus serve as a modern alternative to the traditional archival data bases.

Considerable effort has been devoted towards the simulation of the fire suppression phenomena. Chemical kinetic data bases for the effect of a number of common suppressants on hydrocarbon flames have been developed<sup>(21),(41)</sup>. Our principal concern has been the simulation of the effect of suppressants on flame velocity. This has led to a more detailed understanding of the role of chemistry in the phenomenon. An interesting concept developed in the course of this work was that of the ultimate limits of chemical inhibition and it would appear that a metallic suppressant such as iron fits into this category<sup>(42)</sup>. An important corollary is the conclusion that suppression with such compounds cannot arise from gas-solid interactions. Our current interest is focussed on the generalization of the rankings from these simulations to fuels in general. This involves reviewing the literature, carrying out sensitivity analysis for a variety of fuels and demonstrating that the same set of reactions are the controlling factors with respect to the flame velocity. This provides justification for a "universal" ranking of fire suppressants.

The present interest in fire suppression properties of halogenated compound is a natural continuation of earlier work on the combustion related properties<sup>(43)</sup> of such molecules in the context of incineration. We are considering the incineration of chlorinated compounds paying special attention to the formation of polychlorinated unsaturated compounds. The initial work has concentrated on the cases where one and two carbon compounds are the fuel. A data base of pertinent reactions has been compiled. Simulations are being carried out. It is clear that in the context of gas phase processes, polychlorinated compounds are a direct consequence of imperfect mixing in the incinerator with chlorine atoms and molecules being formed as a result of lean combustion. The unsaturated combustion products are derived from rich combustion. The mixing of these streams then leads to the formation of chlorinated unsaturated compounds.

## **2.4 Process Measurements Division**

### **2.4.1 Thermal and Reactive Processes Group**

Control of process efficiency and the formation of species byproducts from industrial thermal oxidation systems (e.g., power generation and treatment of liquid chemical wastes) is generally based on a priori knowledge of the input stream physical and chemical properties, desired stoichiometric conditions, and monitoring of a few major chemical species in the

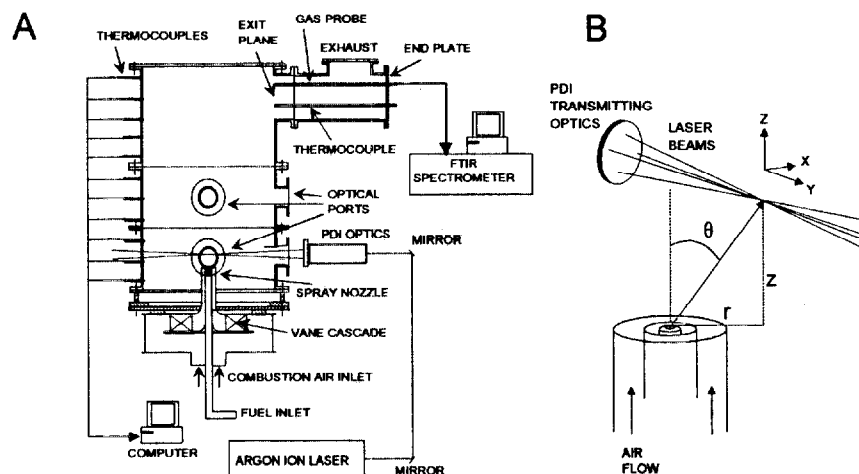


Fig. 5. Schematic of reference spray combustion facility.

exhaust. Optimization of the performance of these systems is relying increasingly on computational models and simulations that help provide relevant process information in a cost-effective manner. In general, there is a dearth of reliable data for specifying model initial/boundary conditions, and a need for experimental/numerical comparative analysis of conditions within the reactor. System performance is dependent on the liquid atomization, aerodynamic design, and the degree of liquid/air mixing within the reactor. The need to provide in-situ, real-time data on the characteristics of the droplet field and flame structure, and its interrelationship with the system operating conditions, heat transfer, and particulate and gaseous byproducts, is crucial for the development and validation of advanced computational models, diagnostics, and instrumentation.

Although CFD offers a cost-effective alternative to experiments, the accuracy of the CFD model must first be assured. This should be accomplished in two ways: verification and validation. Verification involves ensuring the accuracy of the numerical code. That is, determining if the algebraic and differential equations within the model have been accurately solved. In addition to verifying that the numerical code arrives at the correct solution, it is also necessary to determine if the correct model has been solved. This is the validation step. Thus, the focus of this program is to provide experimental data with quantitative uncertainties for CFD model and submodel validation.

The Process Measurements Division of CSTL has constructed a reference spray combustion facility (see Figure 5) and developed a benchmark database to assist in validating multiphase combustion models and submodels. The facility includes a stainless steel enclosure to isolate the reacting fuel spray from the surroundings and provide well-defined boundary conditions for modeling the combustion process. The baseline case, defined together with our industrial collaborators who are involved in multiphase combustion modeling, consists of a swirling methanol spray flame generated with a pressure-jet atomizer. Methanol was chosen as the baseline fuel because of the availability of the kinetic and thermodynamic properties that are required to model the combustion process. The operating conditions for the baseline case are summarized in Widmann et al<sup>(44)</sup>.

The experimental facility includes a swirl burner with a movable 12-vane swirl cascade.

The cascade is adjusted to impart the desired degree of swirl intensity to the combustion air stream that coflows around the fuel nozzle. Recent 3-D CFD modeling of the vane cascade and combustion air passage yields a swirl number of  $S = 0.54$ <sup>(45)</sup>. The liquid fuel is forced through a pressure-jet nozzle and forms a hollow-cone spray with a nominal 60° full cone angle. A parallel program is underway to develop a reference atomizer with well-defined droplet size and velocity distributions. The atomizer will then provide known spray characteristics at the inlet, and define this boundary condition for CFD models.

The burner is enclosed within a stainless steel chamber to provide improved reproducibility and control of the spray flame. The chamber height is 1.2 m and the inner diameter is 0.8 m. Several windows provide optical access, and a stepper-motor-driven traversing system translates the entire burner/chamber assembly permitting measurements of spray properties at selected locations downstream of the nozzle. Additional details on the design of the burner are available in the literature<sup>(46)</sup>.

The spray data are collected non-intrusively using a two-component phase Doppler interferometry (PDI). Details of the PDI arrangement and operating conditions are given by Presser et al<sup>(47)</sup>. Data are provided for the size and velocity distributions of the fuel droplets, the droplet number density, and the volume flux of fuel droplets within the spray. Gas temperature and heat flux profiles are measured along the reactor wall and ceiling boundaries. Gas temperature and species measurements obtained at the reactor exit can be used for boundary conditions or validation of computational results. The inlet combustion air has been characterized using a 3-D CFD simulation to determine the velocity and turbulence intensity profiles, and the simulation has been validated with experimental data obtained using a five-hole pitot probe<sup>(45)</sup>. To complete the baseline data set, gas-phase mean velocity and inlet turbulence intensity measurements are planned using the PDI by seeding the combustion air with spherical salt particles.

Gas-phase species concentrations were measured using Fourier transform infrared spectroscopy. A gas sampling system, consisting of an air-cooled sampling probe, a heated gas line, and a vacuum pump, facilitates the transport of the sample gas extracted from the combustion facility into the single-pass gas cell (10 cm path length) in a continuous manner. The sampling probe was designed to aerodynamically quench chemical reactions occurring within the gasses being sampled. A calibration gas mixing system is used to generate quantitative spectral data for gas/vapor mixtures of known concentration at elevated temperatures (up to 125 °C).

A data set of completed measurements (with associated quantitative uncertainties) has been released<sup>(44),(45)</sup> so that the task of modeling the spray combustion facility may begin. Several industrial partners have or are currently carrying out simulations of this reference facility. Industrial and academic collaborators use the NIST database to validate multiphase combustion models and submodels. Workshops have been used to familiarize the participants with NIST's reference spray combustion facility, assess the information currently provided in the database, review preliminary findings from simulations of the NIST facility, allow modelers to express their data needs, and provide an opportunity for feedback concerning future measurements.

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