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Summaries of Center for Fire Research In-House Programs and Grants - 1987

Sonya M. Cherry, Editor

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Engineering Laboratory
Center for Fire Research
Gaithersburg, MD 20899

October 1987

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U.S. DEPARTMENT OF COMMERCE, Clarence J. Brown, *Acting Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

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Summaries of Center for Fire Research In-House Programs and Grants - 1987

Abstract

This report was prepared for distribution at the Combined Meetings of the Eastern Section: The Combustion Institute and the Annual Conference on Fire Research, November 2-5, 1987. It contains descriptions of the internal programs of the Center for Fire Research as well as extended abstracts of grants for fire research sponsored by the Center for Fire Research.

Key words: Cellulose; charring; combustion; fire models; flame spread; ignition; polymers; smoke; soot; toxicity

Alphabetical Listing of Center for Fire Research Grants

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CFR PRIORITY PROJECTS

This year the Center for Fire Research has focussed its in house research effort on a series of priority projects considered key to meeting its central technical objective of providing practical quantitative tools for fire safety. Many of these projects have involved the coordination of the efforts of professional staff from different organizational groups within the Center. The projects could be divided into three categories, those with short term products, longer term projects to produce engineering tools, and those that lead to a better understanding of fire.

Specific reports on the priority projects are not included in this volume. Technical progress is reported instead in the organizational group technical reports.

FY 87 Priority Projects and their objectives are listed below:

CATEGORY 1 - SHORT TERM OUTPUTS

Cone Calorimeter Development

To organize an ASTM Round Robin evaluation of the Cone in order to gain acceptance of the Cone as an ASTM and ISO Standard. To establish two working Cone Calorimeters in CFR.

Model Accuracy Assessment

Provide the users of fire models the information needed to (1) furnish required inputs to the model, (2) use the model without detailed knowledge of the internal workings of the model but with some understanding of the physics involved, and (3) understand that the degree of confidence that the physics behind the model and its output are realistic for the use intended.

Simulation Laboratory

To transfer the hazard assessment technology to the user community through formal courses and presentations at appropriate meetings.

CATEGORY 2 - ENGINEERING TOOL DEVELOPMENT

Engineering for Fire Protection Applications

Development and transfer of tools the practicing fire protection engineering professional can use to incorporate applied science as a major force in his work.

Fire Hazard Assessment

To deliver a unified and verified fire and smoke hazard assessment method.

Consolidated Compartment Fire Model

Develop generic and applications-specific software modules for a well-documented, user-friendly, modular and easily updated CFR Consolidated Compartment Fire Model (CCFM) Computer Code. Use these modules to implement versions of the CCFM which address particular needs of CFR and the Fire Science and Technology communities.

Transport Physics

To continue the development and incorporation of the physics of transport-related phenomena into models. The selection of phenomena to be addressed takes into account the needs of the user communities and the applications for the models such as hazard and risk assessment.

Toxic Potency Measurement

Produce a technically sound position paper on the proper combustion/animal test methodology for measuring smoke for the N-gas model; expand N-gas data base to include $HC\ell$ and TDI.

CO/Soot Empirical Prediction

To produce a report on best estimates of CO and soot production for the hazard model based on analysis of small and large scale burns.

CATEGORY 3 - BETTER UNDERSTANDING OF FIRE

Wall Fires

To develop an algorithm which predicts the behavior of a burning wall in a room, and to embed this algorithm in a zone-type compartment fire model.

CO Prediction: Turbulent Flames and Smoldering

To develop an understanding of CO production in flames as a basis for establishing a predictive model for CO production in pre and post flashover fires. To develop, for common, smolder-prone residential materials, a data base and a verified theoretical model for CO evolution rates.

Extinguishment

Develop an understanding of fire suppression processes in compartments.

Flame Spread with Radiation

Develop means to predict flame spread on vertical surfaces utilizing laboratory test methods.

Mass Burning Rate/Fuel Generation

Develop a predictive model of mass burning rates of polymeric materials in a pool burning configuration after understanding and characterizing fire plume, heat feedback mechanism and gasification processes of the materials.

Soot Formation and Evolution

Broaden comparisons of detailed species profile measurements in hydrocarbon diffusion flames with existing models of chemical growth; identify fastest steps which produce intermediate hydrocarbons; identify key intermediate hydrocarbons in chemical growth processes. Calculate and measure the size distribution, friction force, and optical properties of soot.

For FY 88 most of these projects will continue with the following new or modified projects added:

Toxicity SRM Development

To develop a material suitable for standard reference material use for combustion toxicity tests.

Fire Data for Materials

To assess the fire performance of materials, components, systems, and assemblies and to develop the protocols for obtaining, assessing, and evaluating input data for fire models used for hazard assessment.

Turbulent Burning Theory

Mathematical modeling of turbulent combustion processes in fires.

Time Dependent Fire Plume Model

Data based fire plume flow model incorporating low frequency large scale eddy structure.

Engineering Analysis System & Fire Reconstruction

The development of separated and assembled fire protection analytical (computerized) tools and the transfer of these tools to practicing professionals. The use of these tools and other resources to recreate and otherwise analyze one of more significant fires. To initiate verification of the results, to evaluate the tools, and to assist decision maker in actions to prevent recurrence.

Expert Systems for Model Codes

To work with model code organization, such as NFPA, to develop a generic form of expert systems that will serve as a model for the replacements of written model codes by expert systems.

Smart Detectors

To examine the feasibility of the application of predictive methods and detector technologies to improvements in the response and selectiveness of detectors.

In addition to these priority projects funded mostly by funds appropriated for the Center, research work has been performed for other Federal agencies. Although these "other agency" projects naturally relate directly to the missions of those agencies, they also supplement the priority project effort and provide a vehicle for transfer of the technology.

FIRE MEASUREMENT AND RESEARCH DIVISION

FIRE PERFORMANCE AND VALIDATION
CENTER FOR FIRE RESEARCH
FY 87

Professional Personnel

Richard D. Peacock, Acting Head
Emil Braun, Physicist
J. Newton Breese, Computer Programmer
C. Lynn Forney, Mathematician
Billy T. Lee, Fire Prevention Engineer
J. Samuel Steel, Physicist

Objectives

The objectives are to develop the generic methodology for assessing the accuracy and limitations of fire models and to design and conduct tests to evaluate the fire performance of components, systems, and structures.

Scope

This work includes two important efforts: first, the conduct of unique, highly instrumented experiments to establish fire behavior on a realistic scale in order to establish performance characteristics and to contribute to model development and, second, the evaluation and verification of fire models by providing a mathematical tool for comparing experimental data with model outputs utilizing expertise in facility fire test experimental design, instrumentation, and data processing and analysis.

Projects

1. **Model Accuracy Assessment**

The objective of this project is to develop the methodology for the evaluation and verification of fire models; it focuses on the development of mathematical and computational techniques for fulfilling this objective. A fully documented, highly instrumented collection of experimental tests was completed in the last year along with the development of algorithms which provide an archetypical set of calculations using experimental data for comparison with zone fire models. Over the next year, the procedure for model validation will be tested and refined on two existing fire models within CFR: ASET, a single room model with few inputs and outputs, and FAST a multi-room model for fire and smoke transport.

Figure 1 shows a comparison of experimental and predicted temperatures as a function of time for two rooms in a multi-room facility. The agreement is quite good, but deviations exist and provide insight into the limitations of the model. Free convection is the mechanism for enthalpy flux between layers and compartments. In the burn room, the plume flow dominates while in adjacent compartments the flow through the vents is most important. In the earlier version of this model, the plume was not treated as a separate zone. Rather it was assumed that the upper layer was connected to the fire by the plume. The implication is that the plume is formed instantaneously. Consequently, early

in a fire, when the energy flux was very small and the plume length very long, the entrainment was overpredicted. This resulted in the predicted interface falling more rapidly than was seen in experiments. Also, the initial temperature was too low but the rate of rise was too fast. The asymptotic temperature was correct. The latter occurred when these early effects were no longer important. The correct sequence of events is for a small fire to generate a plume which does not reach the ceiling or upper layer initially. The fire entrains enough cool gas to decrease the buoyancy to the point where the plume no longer rises. When there is sufficient energy present in the plume, it will penetrate the upper layer. The effect is two-fold: first, the interface will take longer to fall and second, the rate of rise of the upper layer temperature will not be as great. To this end the following prescription has been incorporated: for a given size fire, a limit is placed on the amount of mass which can be entrained, such that no more is entrained than would allow the plume to reach the layer interface. The result is that the interface falls at about the correct rate, although it starts a little too soon, and the upper layer temperature is slightly overpredicted but after the initial phase, follows the experimental data very well. In addition, the implementation of this model has a place to insert an algorithm for forming a plume.

The opposite problem is encountered in the flow through vents. The entrainment is underestimated. The difficulty lies in the use of a plume model well beyond its nominal range of validity. The work of McCaffrey really only applies to a circular plume. In the case of vent flow an extended flat plume similar to a waterfall is encountered. However, there exists no reliable correlation as yet. Thus we must presume to use the former correlation until a better plume model can be developed.

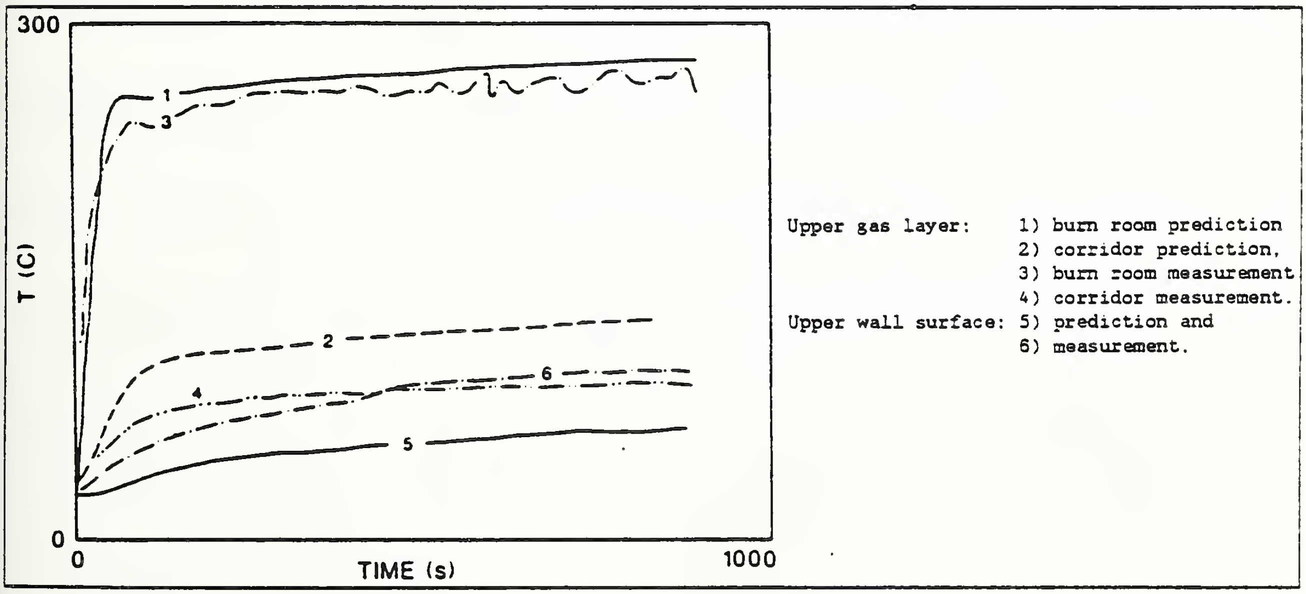

Figure 1. A comparison of the upper gas layer and upper wall surface temperatures in a multi-room large-scale test facility

Davies, A. D., "Some Tools for Fire Model Validation," Fire Technology, Vol. 23, No. 2, May 1987 pp 95-114.

Peacock, R.D., Davis, S., and Lee, B.T., Experimental Data for Model Validation, NBSIR in preparation.

Jones, W. W., and Peacock, R. D., Experimental Verification of a Model for Fire Growth and Smoke Transport, submitted for presentation at the Second Annual Symposium on Fire Safety Science.

Braun, E., Davis, S., Forney, C. L., and Peacock, R. D., Procedure for the Evaluation of Computer Fire Models, NBSIR in preparation.

Davis, S.,and Braun, E., "Validation of Fire Models", paper presented to International Symposium on Mathematical Modeling and Related Fire Test Methods, American Society for Testing and Materials, December 1986. To be published in The Journal of Fire Sciences.

3. Flame Spread on Walls

The objective of this project is to examine flame spread on selected wall materials burning outside of a room and inside a full-size room to provide a data base for the development and refinement of a mathematical algorithm for wall burning. This work complements small-scale work on flame spread (upward, downward, and lateral), both before and after flashover. The ongoing experimental study is designed to analyze flame spread along a combustible wall surface using a controlled ignition source along the floor.

Lee, B.T., and Steel, J.S., Standard Room Fire Test Research at the National Bureau of Standards, NBSIR to be published.

Huang, D.Y., Evaluation of Quarter-Scale Compartment Fire Modeling for Constant and Stepped Heat Inputs, submitted to Fire and Materials.

4. Flammability of Composites for Naval Ship Use

The objective of this program is to assist the Navy in designing fire-resistant ship components from fiber- and metal-reinforced composites by systematically assembling data on the composites flammability properties. To date, the laboratory work performed has been using the cone calorimeter; this work is being extended to more advanced composite materials. We have found an apparent linear relationship between the average heat release rate during the first minute after ignition and the external flux imposed on a polyester composite and on a polyphenylene sulfide composite; the same was indicated for an epoxy composite. Indications are that similar relationships hold for rate of heat release averaged over periods where the rate is not changing extremely fast. If this observation continues to hold, we may have a means for estimating the heat of vaporization of the resin based on its apparent heat of combustion and heat losses based on the material thickness and depth of material charring and burning. In the coming year, depending on the availability of suitable specimens, flame spread measurements will be made with the IMO apparatus. Fire scenarios, currently being developed by the Navy, will be translated into full-scale experiments to provide large-scale verification of a predictive tool to be developed.

Braun, E., and Brown, J.E., Cone Calorimeter Characterization of Composite Materials, Nat. Bur. Stand., NBSIR in preparation.

5. Fire Safety Aspects of Solid Fuels

The objective of this continuing project is to study the hazards associated with the installation, operation, and maintenance of solid fuel burning appliances used for space heating in single family dwellings and in similar small-scale applications. Fire incidents from the use of solid fuel burning equipment rose from 66,800 to 130,100 between 1978 and 1981. This trend slowed from 1981 to 1982 to slightly less than a seven percent increase. The frequency of fire incidence stabilized between 1982 and 1983 (increasing during this time less than one percent) and actually decreased in 1984 (dropping nearly 11 percent). Positive actions by the Center for Fire Research and others are believed responsible for improving the safety of these appliances and, thus, reversing an increasing fire incidence rate. The overall research program has included typical operating conditions of modern heating appliances, intensity and duration of chimney fires in factory-built and masonry chimneys, clearance reduction systems for protection of combustible walls and ceilings, and wall pass-through systems for connection of appliances to chimneys through combustible walls.

Peacock, R. D., Thermal Performance of Masonry Chimneys and Fireplaces, Nat. Bur. Stand. NBSIR 87-3515 (April 1987).

Peacock, R.D., Wood Heating Safety Research: An Update, accepted for publication in Fire Technology.

Associated Grants and Contracts

James P. Jarvis - Clemson University, " Graphical Presentation and Numerical Analysis of Fire Data for Model Validation."

FIRE PERFORMANCE AND VALIDATION GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution:	Clemson University
Grant No:	60NANB6D0627
Grant Title:	Graphical Presentation and Numerical Analysis of Fire Data for Model Validation
Principal Investigator:	James P. Jarvis, Professor Department of Mathematical Sciences Clemson University O-104 Martin Hall Clemson, SC 29634-1907 Telephone: (803) 656-5214
Other Professional Personnel:	Michael K. Kostreva, Associate Professor Lynn J. Forney, Research Associate
NBS Scientific Officer:	Sanford Davis

Technical Abstract:

Introduction. Over the past several years, the Center for Fire Research (CFR) at the National Bureau of Standards, has been developing mathematical models for predicting the environmental conditions which occur as a fire develops and spreads. Once these models are shown to be "valid", they become a useful tool in determining and solving problems related to fire safety. Currently work is being done to establish a methodology for assessing the validity of the mathematical models developed. It includes four broad steps: (1) conceptual model validity - checking that the theory and underlying assumptions are correct and reasonable; (2) computerized model verification - ensuring that the computer programming and implementation of the conceptual model is correct; (3) operational validity - determining that the model's output behavior has the accuracy required for the model's intended purpose [5, 8, 9]; and (4) data validity.

The effort described here is largely related to operational validity. It has three main components: development of computer software tools for graphical analysis of data, sensitivity analysis of models, and dimensional analysis and determination of core parameters for models. Although much of analysis has been oriented toward ASET, a model for estimating the Available Safe Egress Time from a single room fire [1], it is hoped that the techniques will have more general applicability. An overview of both completed and anticipated results is given below.

Graphical Analysis. Data produced from both fire models and experiments typically include a number of variables and their values over time. An important aspect of model validation is the capability of viewing such data in a flexible, robust manner. To this end, a computer graphics system for analysis of fire data is being developed. It will ultimately include both general scientific plotting capabilities and well as numerical techniques, such as smoothing and normalization, specifically developed for application to fire data.

The system is being developed on an IBM PC, but is written in FORTRAN and employs the Graphics Kernel System [6] to facilitate portability to other systems. It is anticipated that the system will be transferred to CFR computers. The system uses a command line interface with extensive error checking and on-line help available. The basic command structure includes capabilities for varying the labeling and scaling of line and scatter plots; attaching boxes, arrows, and text to enhance a plot; saving both data and plotting formats; displaying system status; and changing output devices. Currently, screen, printer, and pen plotter output is supported.

Sensitivity Analysis. Sensitivity analysis of a model is a study of how changes in the model parameters affect the results generated by the model. The parameters through which the model is studied consist of the input and internal variables and the assumptions, logic, and structure of the computational procedures of the model. Our interest here is in the input and internal variables. Some questions of interest to be investigated are: (1) which are the dominant variables? (2) what is the possible output range for a given input? and (3) what is the expected range in output for a given range of an input variable? Because of the number of variables in typical fire data and since each output variable is actually a time series, a full analysis is generally infeasible and the set of variables selected for study must be reduced.

Classical sensitivity analysis examines the partial derivatives of a function (model) with respect to its variables in some local region of interest. A function may be sensitive to changes in a variable in one region and insensitive to the same variable in another region; hence, a function cannot necessarily be classified as either sensitive or insensitive to a particular variable. In performing a sensitivity analysis on a model, a global, as opposed to local, measure of sensitivity may be more desirable.

Three methods for estimating the sensitivity of a model to its variables will be briefly discussed and illustrated using the ASET model. The models is based on a system of two differential equations used to estimate the smoke layer height from the floor and the temperature of the smoke layer as functions of time for a single room in which a fire develops and grows. The equations are denoted as $dz_1/dt=f_1(z,c,t)$ and $dz_2/dt=f_2(z,c,t)$ where z_1 is the layer height, z_2 is the upper layer temperature, t is time, and c is a vector of parameters. The layer height and temperature equations depend on the height and area of the room, the height of the fire base from the floor, the initial heat release, the heat release generation function, the fraction of the heat release lost to the contents and surroundings, the fraction of the heat release radiated from the fire, and ambient conditions.

In general, the sensitivity equations will not be known explicitly. Thus, the sensitivity equations must be solved by numerical techniques. Three such techniques are being examined. First, a finite difference method can be used to estimate the partial derivatives of the model z with respect to each of its variables: $c_1, c_2, c_3, \ldots, c_n$. For this method the derivatives are estimated by $dz_i/dc_j=\{z_i(c_1,c_2,\ldots,c_j+\Delta c_j,\ldots,c_n,t) - z_i(c_1,c_2,\ldots,c_j,\ldots,c_n,t)\}/\Delta c_j$. This method requires that the model z be run n+1 times to obtain estimates of the partial derivative of z with respect to each of its parameters. Since this method is a linear approximation, the choice of Δc_j is important. If Δc_j is selected too large, then the sensitivity estimate obtained may be very poor.

The other two methods are direct techniques but differ in their approaches. The direct method involves deriving the sensitivity differential equations from $dz_i/dt=f_i(z,c,t)$ and then solving the sensitivity differential equations. The general form of these equations will be $ds_{ij}/dt = \partial f_i/\partial c_j + \Sigma_k(\partial f_i/\partial z_k)\cdot s_{kj}$ where $s_{ij}=\partial z_i/\partial c_j$. The solution of the sensitivity equations can be done in two basic ways. One way is to treat $dz_i/dt=f_i(z,c,t)$ and its sensitivity equations as a coupled system and solve the system simultaneously [3]. The work involved in solving the sensitivity equations using the direct coupled method is solving a system of m+mn equations, m original differential equations and n systems of m sensitivity differential equations. A second way is to first solve $dz_i/dt=f_i(z,c,t)$ and then solve the system of sensitivity equations using the solution z(t) and some interpolation scheme [4]. The work involved in solving the sensitivity equations using the direct decoupled method is solving a system of m equations and then solving m sensitivity equations n times.

Dimensional Analysis and Core Parameters. Model validation and interpretation are two important steps of any application of mathematical models. In order to perform these steps in a systematic and economical manner, it is essential that the mathematical model undergo a simplification process known as dimensional analysis, and that the minimum number of dimensionless parameters be found. Once these parameters, the core parameters of the model, are known, the organization of the validation step and the interpretation of the model follows; e.g., [7]. If the validation is attempted without first determining the core parameters then many additional experiments may have to be performed in validation, with no additional confidence gained in the validity of the model. The reason for this is that the same experiments will be repeated, simply in another parametric description.

For example, suppose two parameters, say a and b, occur in an unsimplified form of a model, always as the product a•b. Then experiments which double the parameter a while halving b will produce the same result as the base case in which both are unchanged. Since validation, including expensive laboratory work, forms a part of fire modeling, it becomes increasingly important to nondimensionalize to the core parameters. With regard to models familiar to fire researchers, Cooper [1] simplified the ASET model from twelve raw physical parameters to four parameters. However, is four the smallest number of parameters needed to specify the ASET model? Are other models of interest in fire research currently formulated in terms of core parameters? Is there a general algorithm for obtaining core parameters? These are some questions currently under investigation.

Mathematical models are seldom used in a manner which exploits all of the information they convey. Whenever differential equation models are applied, such as in fire research, the solution (functions of time and/or space) as well as several derived outputs are available (such as available safe egress time, temperature at hazard, hazardous concentration, etc.). Once core parameters are established, it is possible to gain significant insights into model behavior by plotting the derived outputs against the core parameters for a large collection of model runs. Such graphs, either surfaces or contour plots, are similar to bifurcation diagrams. Knowing regions of parameter space in which large changes in these derived outputs occur can direct attention to areas in which the model is especially sensitive. By the same token, knowing flat regions of these surfaces can be a great timesaver.

Another way in which the information a model contains may be made more accessible is through the use of tables. Users without constant access to computers may derive necessary information from tables which summarize model applications.Tables of previously computed solutions, or values interpolated to them may be used to supplement graphical displays. For example, consider the following: a constant size 1320kW fire may start on the floor of a room with 10,000 feet area and ceiling height of 10 feet. Which design change can increase the available safe egress time the most: a change in height of 1 foot or a change in area of 1000 feet? A glance at the table answers this question. (This example uses data from Cooper and Stroup [2].)

ASET	Area:	9,000	10,000	11,000
Height:	9	99	110	122
	10	210	233	257
	11	315	351	386

Summary. A variety of techniques, including graphical, sensitivity, and dimensional analysis, are being examined for their applicability to the fire validation problem. Although these procedures are being tested in the context of the ASET model, it is hoped that the experience gained can be applied to other fire models as well.

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FLAMMABILITY AND TOXICITY MEASUREMENT
CENTER FOR FIRE RESEARCH
FY87

Professional Personnel

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Richard H. Harris Jr., General Physical Scientist
John F. Krasny, Textile Technologist
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Marc Nyden, Research Chemist
Maya Paabo, Research Chemist
Kay M. Villa, Textile Technologist
Helene Clark, Guest Worker, University of Pittsburgh
Joshua L. Gurman, Research Associate (AISI)
Marc Janssens, Research Associate (Natl. Forest Products Assn.)
Margaret Yoklavich, Guest Worker, University of Pittsburgh

Program Objectives

To develop measurement methods and the underlying principles for characterizing the combustibility of furnishings and building materials and the impact of the combustion products on living organisms.

Scope

Typical efforts of this group include:

- assessing the appropriate applications of the NBS toxicity screening test method
- determining the extent to which a limited number of gases determine the lethality of combustion products
- developing a rationale and the methodology for predicting soot and specific gas production in full-scale fires from bench-scale methods
- exploring possible alternatives to animal testing for measuring the impact of combustion products on people
- generating a valid, detailed model for the burning of upholstered furniture
- producing a data base for Cone Calorimeter measured fire properties
- developing an appropriate measurement methodology for the propensity of cigarettes to ignite soft furnishings
- reinforcing the relationship of combustion in the Cone Calorimeter to large scale burning and aiding the promulgation of the Cone Calorimeter for engineering and code applications

Projects

1. Heat Release Rate and Related Properties of Materials

The focus in this area is measurement of materials properties in the Cone Calorimeter. This instrument was initially developed for heat release rate studies. More recently, the capability was added to do smoke obscuration, soot mass, gas species yield characterizations. In addition, data are regularly taken on ignitability, mass loss rate, and the effective heat of combustion. The Cone Calorimeter was recently adopted by ASTM as a tentative (grey pages) method, P 190. The British Standards Institution (BSI) has also recently started working on a draft method based on the Cone Calorimeter. This method is being put forth to ISO TC92 SC1 WG5 (the ISO working group on heat release rate) as a basis for developing an international standard in this area. The number of installed instruments has been expanding rapidly, and there are now some 18 units in various laboratories throughout the world. A **User's Guide** for the Calorimeter is in the final stages of preparation. ASTM has also organized a round-robin for the Calorimeter and testing in being started this Fall. The increasing need for an accessible database in this area has been recognized and software development has been started. Work on smoke, soot, and gas production correlations between bench-scale and full-scale tests has also been progressing, jointly in cooperation with the Smoke Dynamics Research Group. During the last few years, some 40 reports and journal articles dealing with the Cone Calorimeter functions or analyzing data from it have been put out by staff from both NBS and from other laboratories. A few of the most recent are:

> Babrauskas, V., The Cone Calorimeter--A Versatile Bench-Scale Tool for the Evaluation of Fire Properties, pp. 78-87 in _New Technology to Reduce Fire Losses & Costs_, S.J. Grayson and D.A. Smith, eds., Elsevier Applied Science Publishers, London (1986).
>
> Babrauskas, V., and Parker, W.J., Ignitability Measurements with the Cone Calorimeter, to appear in _Fire and Materials_. Also issued as Nat. Bur. Stand. Report NBSIR 86-3445 (1986).

2. Prediction of Fire Toxicity from Analysis of the Main Gaseous Components (the "N-gas model")

The toxicity of single and multiple fire gases is being studied to determine whether the toxic effects of a material's combustion products can be explained by the toxicological interactions (as indicated by lethality) of the primary fire gases or if minor, more obscure gases need to be considered. LC_{50} values for Fischer 344 rats have been obtained for CO and HCN (as individual gases in air) for 1 through 60 min exposures plus relevant post-exposure periods using the NBS Toxicity Test Method apparatus. The results show a constant concentration-time product for the various HCN exposures; for CO, however, the concentration-time products decreased for the 1 to 5 min exposures and then increased for the longer times. In exposures ranging from 5 to 60 min, the toxic effects of CO plus HCN were additive and, except for the 5 min exposures, the presence of 5% carbon dioxide (CO_2) decreased the LC_{50} values of CO, indicating synergistic effects. Decreasing the oxygen concentrations in the presence of various mixtures of the other major fire gases increased the toxicity even further. A pharmacokinetic study examined the formation of COHb in rats during 30 min exposures to lethal concentrations of CO with and without 5% CO_2. The results at these high concentrations agreed with earlier results from experiments at less than lethal concentrations (i.e., the COHb formation was faster and the pH was lower in the presence of CO_2). When the observed toxicity for 24 cases of material decomposition was interpreted in terms of the current N-gas model, the majority, but not all, of the cases could be correctly predicted. These results provide necessary information for the computer model currently being developed in the Center for Fire Research to predict the toxic hazard that people will experience under various fire scenarios.

Levin, B.C., Paabo, M., Gurman, J.L., and Harris, S.E., Effects of exposure to single or multiple combinations of the predominant toxic gases and low oxygen atmospheres produced in fires. Fundam. Appl. Toxicol. 9, 236-250 (1987)

Babrauskas, V., Levin, B.C., and Gann, R.G., A new approach to fire toxicity data for hazard evaluation. Fire J. 81, 22-71 (1987).

3. Fire Toxicity Scaling

This project, sponsored by the Consumer Product Safety Commission, involves further studies to determine the degree to which toxicity measurements taken in the bench scale (BS) can be used to predict full scale (FS) toxicity in fires. For this project, the toxicity of the thermal decomposition products from two flexible polyurethane foams (with and without a fire retardant) and a cotton upholstery fabric was evaluated by a series of both BS and FS tests to either the smoldering or flaming decomposition products from upholstered chairs. The BS tests included the NBS protocol toxicity test, along with Cone Calorimeter and Furniture Calorimeter tests. The degree of toxicity observed during and following the FS and BS flaming tests could be explained by the current N-Gas Model. Essentially no animal deaths were noted within the exposures to the non-flaming or smoldering combustion products produced in the BS or FS tests. The concentrations of CO, CO_2, and HCN were also comparable. Post-exposure deaths, however, occurred following the BS non-flaming foam or cotton tests, but not following exposures to the smoldering phase of the FS tests. In the FS room tests, little toxicological difference was noted between decomposition products from the burn room and a second room 12 m away. In a second series of FS fire tests, recently conducted, the toxicity of combustion products from smoldering, flaming or combined smoldering-flaming tests was examined and the results are being analyzed.

Braun, E., Levin, B.C., Paabo, M., Gurman, J.L., Holt, T., and Steel, J.S., Fire toxicity scaling (NBSIR 87-3510). [U.S.] Nat. Bur. Stan. (1987).

4. Standard Reference Material for Small-scale Toxicity Test Methods

Several jurisdictions are presently considering legislation to address the toxicity of smoke from the combustion of building products. As a result of this, combustion toxicity testing has begun in many testing laboratories, giving rise to the need of a standard reference material (SRM) for checking the apparatus and the operating procedures. The first phase of this project involved the selection and screening of a suitable material for combustion toxicity evaluation. A suitable material should burn reproducibly and have a moderate level of toxicity which is not solely due to carbon monoxide. The first material, a black polymethylmethacrylate (PMMA), was unsatisfactory since it was not toxic when decomposed in the non-flaming mode at the highest allowable mass loading. The second material, an acrylonitrile-butadiene-styrene (ABS 1007a), is one that has been certified as an SRM for the NBS smoke density chamber. When tested by the NBS toxicity test method, this material showed repeatable, satisfactory results in both the flaming and non-flaming modes. Four outside laboratories are participating in an interlaboratory evaluation of this material by the NBS test method to determine the reproducibility of results among laboratories. This material, however, proved to be unsuitable for the University of Pittsburgh test method. They are in the process of testing a nylon material, which turns out to be more acceptable.

5. Cigarette Ignition Study

This work was performed under the Cigarette Safety Act of 1984. It was established that the propensity to ignite upholstered furniture and mattresses of 12 typical commercial cigarettes varied only within a narrow range. However, the ignition propensity of 41 experimental cigarettes, produced by the cigarette industry, varied greatly. Some cigarettes which had very low ignition propensity combined the following design parameters: low tobacco packing density, low paper porosity and citrate content (citrate is widely used as an ash modifier and smolder promoter), and low circumference. Several patented concepts (paper modification, fire stops in or additives to the tobacco column) also showed promise, and offer directions for further investigation. Some of the low-ignition-propensity cigarettes had tar, nicotine, and CO yields (measured by the FTC method) within the ranges of the best-selling commercial cigarettes. It was concluded that the manufacture of low-ignition-propensity cigarettes is feasible, with some advances in cigarette design and manufacturing technology. A benefit/cost study by the Center for Applied Mathematics of NBS indicated that the modification needed for low cigarette ignition propensity may result only in small changes of price, employment, health care cost, and the financial status of the affected industries and professions.

A detailed experimental characterization was made of the cigarette as an initiator of smoldering combustion in upholstery materials. Particular emphasis was placed on measuring the spatial distribution of heat flux passing from the cigarette coal to an upholstery substrate. Single measures of this flux distribution were checked for their correlation with ignition propensity of the experimental cigarettes. Peak flux did not vary sufficiently among the cigarettes to reveal any correlation. The total heat input to a typical point on the substrate surface caused by passage of the flux distribution correlated only weakly with ignition propensity. Cigarette coal area (which varies mainly via variations in coal length) showed a moderately good correlation with ignition propensity. A shorter, less ignition-prone coal can be obtained by decreasing cigarette packing density, diameter or paper porosity.

Measurement of cigarette ignition propensity on upholstered furniture mockups was found to be reasonable indicators of the performance on full-scale furniture. However, a standard method to measure cigarette ignition propensity in the laboratory could not be developed in the given time, but several promising concepts have been identified.

Krasny, John F., Cigarette Ignition of Soft Furnishings - a Literature Review with Commentary. NBSIR 87-3509 (1987). Also printed as a report by the Technical Study Group, Cigarette Safety Act of 1984 to the U.S. Congress.

Gann, R,G., Harris Jr., R.H., Krasny, J.F., Levine, R.S., Mitler, H.E., and Ohlemiller, T.J., The Effect of Cigarette Characteristics on the Ignition of Soft Furnishings, NBS Technical Note; also printed as a report to Congress.

Technical Study Group on Cigarette and Little Cigar Fire Safety, Toward a Less Fire-Prone Cigarette, Final Report to Congress.

Associated Grants

1. **Brown University**, Merwin Sibulkin - Study of Effects of Material Properties on Flaming Combustion of Charring Fuels.
2. **Factory Mutual**, Archibald Tewarson - Development of a Model to Provide Comprehensive Fire Property Data.
3. **SRI International**, Charles S. Rebert - Electrophysical Incapacitation and Persistent Behavioral Dysfunction of Rats Associated with Combined Exposure to Carbon Monoxide and Carbon Dioxide.
4. **Southwest Research Institute**, Gordon Hartzell - Analysis of Hazards to Life Safety in Fires.
5. **University of Dayton Research Institute**, Mark Dietenberger - Mathematical Modeling of Furniture Fires.
6. **University of Pittsburgh**, Yves Alarie - Toxicity of Plastic Combustion Products.

FLAMMABILITY AND TOXICITY MEASUREMENT GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Brown University

Grant No.: NBS Grant 60NANB6D0629

Grant Title: Burning of Charring Materials

Principal Investigator: Professor M. Sibulkin
Division of Engineering
Brown University
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Telephone: (401) 863-2867

Other Professional Personnel: Y. Chen, Graduate Research Assistant
A. Frendi, Graduate Fellow

NBS Scientific Officer: Dr. V. Babrauskas

Technical Abstract:

The objective of the present research program is to determine the effects of changes in material properties on the burning rates and extinction limits of solid fuels. In particular, we are currently looking at the effects of solid phase fire retardants on the burning of cellulose. We wish to measure the changes in material properties caused by these retardants, and to use this information to determine how these retardants act to suppress fires. This information will help in the design of materials with improved fire safety characteristics.

In a previous investigation we studied the flaming combustion of pure and fire retarded cellulose, and measured the effects of retardant concentration on burning rates and flammability limits. In the present program we wish to measure the major combustion related material properties for the same series of retarded cellulose samples. Last year we reported on the heat of combustion of the volatiles produced by the pyrolysis of cellulose under burning conditions; this year's report will concentrate on measurements of the heat of gasification of the same materials. These measured properties will then be used as inputs to a mathematical model of flaming combustion. The results of these calculations for burning rates and flammability limits will be compared with the previous measurements in order to determine how the retardants act to suppress fires.

The heat of gasification is defined by

$$h_g \equiv \dot{q}''_{net} \, / \, \dot{m}''_w \qquad (1)$$

where $\dot{q}''_{net}$ is the sum of the heat inputs and losses at the fuel surface and $\dot{m}''_w$ is the mass flux of gaseous products leaving the surface. Two other terms are used in the literature to describe energy changes which occur during pyrolysis of a solid fuel: (i) the heat of pyrolysis h_p defined as the difference in enthalpy between the products (gas plus char) at T_w and the reactant (fuel) at T_∞, and (ii) the heat of reaction h_r defined as the difference in enthalpy between the products and reactants at T_∞. Whereas h_p and h_r are thermodynamics quantities, h_g is not. Previously it has been shown that $h_g=h_p$ *only* for steady burning of a vaporizing fuel; for a charring material (such as cellulose) there is no simple relationship between h_g and h_p.

A schematic side-view of the apparatus developed to measure h_g is shown in Fig. 1. The heat flux from the flame to the fuel surface is simulated by a pair of I.R. lamps. Tungsten filament, quartz envelope lamps giving a blackbody distribution of energy are used. The cellulose sample (in the form of a horizontal 2.5 cm diameter cylinder) is mounted inside an extensively modified glass draft shield of a top-loading electronic balance. A nitrogen supply system is attached to the weighing system to first scavenge air from the chamber and then maintain a reduced flow of nitrogen around the sample during pyrolysis. Oxygen is excluded from the atmosphere to simulate conditions at the surface of a burning material enveloped by a diffusion flame. A combination of a quartz absorption plate, radiation shields and cooling coils is used to prevent breakage of the front window of the chamber. In addition, air cooling (not shown) is used to keep the temperature of the chamber window and quartz plate below 200 °C so that the thermal radiation from these surfaces can be neglected in determining the surface temperature (as described below).

The basic measurements needed to obtain the heat of gasification [see Eq. (1)] are the mass loss rate and the net heat flux. Values of the time-dependent mass m(t) measured by the electronic balance are stored in a computer. A running least squares fit to m(t) is generated, and then differentiated to obtain values of $\dot{m}(t)$. The net heat flux is found from

$$\dot{q}''_{net} = \epsilon \dot{q}''_{ex} - \epsilon \sigma \left[T_w^4 - T_\infty^4 \right] - \dot{q}''_{conv} \tag{2}$$

using the following procedure: (1) The value of the incident heat flux $\dot{q}''_{ex}$ is obtained by calibration of the I.R. lamps against a water-cooled radiation flux gage; (2) the surface temperature T_w is found from a calibration curve of the I.R. pyrometer versus thermocouple measurements of T_w made in a separate set of runs; (3) the convective heat loss from the sample surface is calculated from heat transfer theory; and (4) a value of $\epsilon=0.96$ obtained from a separate set of surface reflectance measurements is used.

Cellulose samples which are homogeneous, free from cracks and of adequate mechanical strength are needed for these experiments. A method for producing such samples has previously been described. Briefly, a slurry of cellulose, distilled water (and fire retardant) is blended in a mixer and pressed into a cylindrical shape. The sample is then oven dried to 105 °C and stored in a dessicator until needed. The fire retardant used was 0 to 3 wt. % of sodium hydroxide. A special technique was developed for determining the retardant mass concentration Y_R *in the sample.*

Measurements were primarily made at an absorbed heat flux $\dot{q}''_{ab}=\epsilon\dot{q}''_{ex}$ of 40 kW/m^2. This heat flux gives mass loss rates which are comparable to those found for cellulose samples burning in air. Additional measurements were made at fluxes of 35, 30 and 25 kW/m^2. Average values of the mass loss rate as a function of time are shown in Fig. 2 at 40 kW/m^2 for pure cellulose ($Y_R=0$) and for fire retarded cellulose ($Y_R=0.03$). Contrary to what might have been expected, the addition of the retardant leads to an increase in the mass loss rate (even through the char fraction remaining after pyrolysis also increases). The qualitative shape of the curves, a rapid rise to a peak mass loss rate followed by a steady decline, is similar to that predicted by theory.

The effect of retardant addition on the surface temperature at t=200 s is shown in Fig. 3. While the increase in T_w from 829 K at $Y_R=0$ to 861 K at $Y_R=0.03$ is not large, it increases the radiative heat loss from the surface enough to have a significant effect on $\dot{q}''_{net}$ (see Eq. [2]) and therefore on h_g. The combination of the increase in $\dot{m}''_w$ and the increase in surface heat loss causes a major reduction in the heat of gasification with retardant addition as shown in Fig. 4.

Our current efforts are directed towards determination of the inert and combustible fractions of the total volatiles. These measurements will be made by passing a sample of the pyrolysate produced by the apparatus in Fig. 1 through a gas chromatograph. Once the inert fraction of the volatiles is known, final results for the heat of combustion and stoichiometric ratio of the "fuel" will be calculated, and the resulting property values will be used in combustion calculations for burning rates and flammability limits.

In order to aid in the dissemination of the results of previously sponsored research, a review paper on the results of diffusion flame studies was presented at the 1987 ASME Heat Transfer Conference.

Publications

"Pyrolysis of Bulk Samples of Cellulose," M. Sibulkin, Int. Conf. on the Physical and Chemical Processes Occurring in a Burning Cigarette (1987).

"Heat of Gasification of Pure and Fire Retarded Cellulose" M. Sibulkin, S. S. Tewari and Y. Chen, Eastern Section: The Combustion Institute (1987).

"Heat of Combusjtion of Pure and Fire Retarded Cellulose", M. Sibulkin and A. Frendi (in process).

"Free Convection Diffusion Flames: A Review of Results", M. Sibulkin, 24th National Heat Transfer Conference, ASME Symposium Volume H392 (1987).

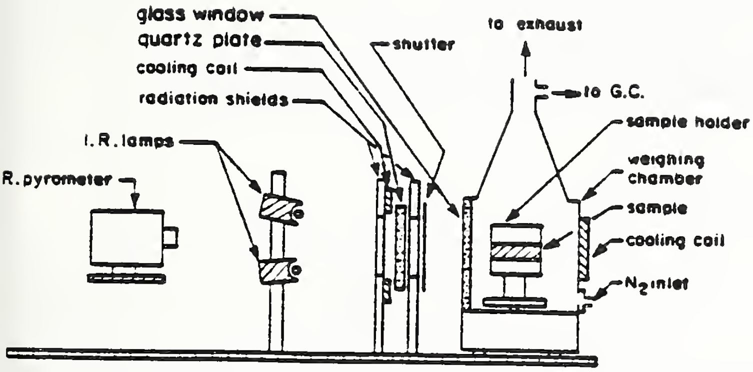

Fig. 1

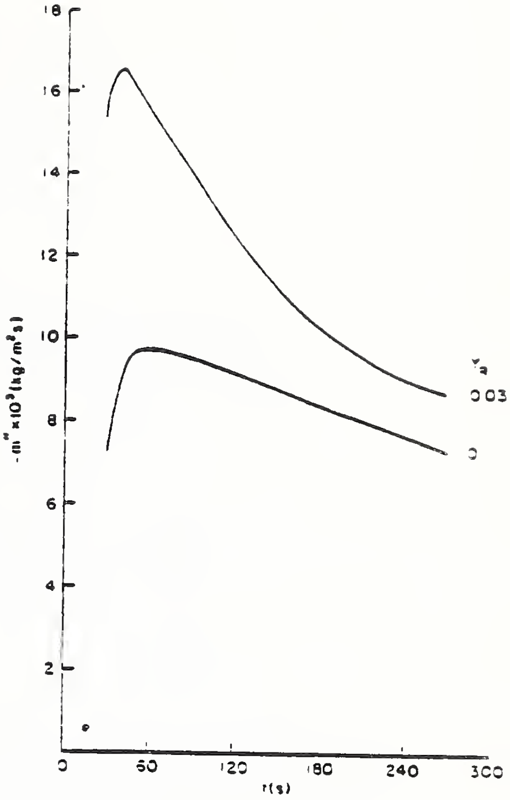

Fig. 2

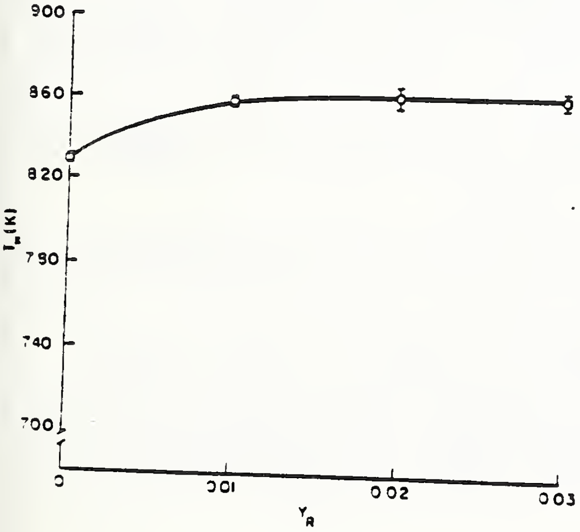

Fig. 3

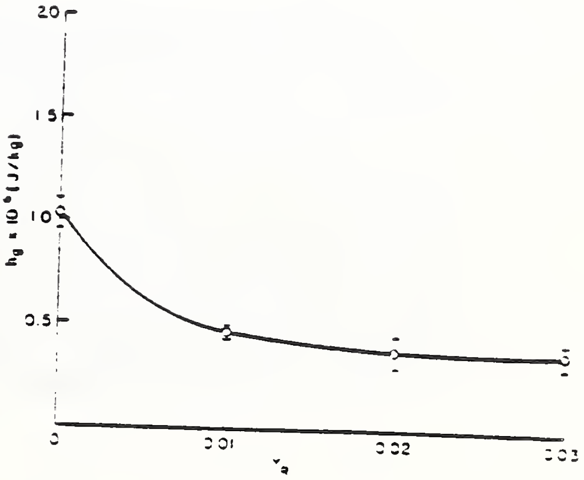

Fig. 4

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Factory Mutual Research Corporation

Grant No: 60NANB4D-0043

Title: Development of a Model to Provide Comprehensive Fire Property Data

Principal Investigator: Dr. Archibald Tewarson
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NBS Scientific Officer: Dr. V. Babrauskas

Technical Abstract:

The objective of the study is to develop generalized relationships, using existing data, for the engineering calculations of combustion properties of materials. The combustion properties are used for the assessment of hazard presented by various environments and protection requirements. The combustion properties being considered are: 1) net heat of complete combustion, ΔH_{Comp}; 2) chemical, convective and radiative heat of combustion, ΔH_{Chem}, ΔH_{Con}, and ΔH_{Rad}, respectively; 3) combustion efficiency, χ_{Chem}, and its convective and radiative components, χ_{Con} and χ_{Rad}, respectively; and 4) yields of chemical compounds generated during combustion, Y_j, especially CO and particulates. ΔH_{Chem} is calculated from the yields of CO and CO_2 and/or O_2 (depletion). χ_i is defined as $\Delta H_i/\Delta H_{Comp}$.

ΔH_i, χ_i and Y_j depend on the chemical structures of fuels and ventilation, but not on the size of turbulent fires; thus, effects of the chemical structures of fuels and fire ventilation on combustion properties are being examined.

Chemical Structures of Fuels. Relationships between ΔH_i, χ_i, Y_j and molecular weight (M) are being sought. Note that the majority of polymeric materials gasify as oligomers rather than as monomers.

In the study, correlations are being sought between smoke point heights reported in the literature and heights measured in our apparatus with corresponding values for ΔH_i and Y_j; ΔH_{Comp} is either taken from the literature or calculated from the standard heats of formation of the chemical bonds. For about 250 fuels, linear relationships are found between ΔH_i and M values and between Y_j and M values, within each group of fuels with similar types of chemical bonds. An example is shown in Figure 1, where ΔH_{Con} is plotted against M for fuels with C-H-N and C-H-S types of structures.

The following relationships are suggested for the engineering calculations of ΔH_{Comp}, ΔH_{Chem}, ΔH_{Con}, ΔH_{Rad}, Y_{CO} and Y_s (where s represents particulates).

$$\Delta H_i = A_i M + B_i, \qquad (1)$$

and, $$Y_j = C_j M + D_j, \qquad (2)$$

where ΔH_i is in kJ/mole; M is in g/mole; Y_j is in g/mole and A_i, B_i, C_j and D_j are constants. A_i is in kJ/g; B_i is in kJ/mole; C_j is in g/g and D_j is in g/mole. The constants derived from the regression analysis of data for about 250 fuels using Eqs. (1) and (2) are listed in Table 1. The values of ΔH_i and Y_j, calculated using the constants in Table 1, show very good agreement with the values calculated from the experimental data measured in large-scale fires.

Some examples of the data calculated from the constants listed in Table 1 are shown in Figures 2, 3 and 4, where it can be noted that $\Delta H_{Chem}/\Delta H_T$ or χ_{Chem} decreases and Y_{CO} and Y_s increase with increase in the degree of unsaturation and aromatic nature of the chemical bonds. χ_i values are strongly dependent on M for smaller molecules. In terms of the dependency on M and chemical structures, χ_{Con} follows χ_{Chem}, whereas χ_{Rad} shows an opposite dependency; for example, χ_{Chem} is lowest for aromatic fuels, whereas χ_{Rad} is highest. Since most of the polymeric materials gasify as oligomers rather than as monomers, the effect of M on combustion properties may be insignificant.

Fire Ventilation.. Relationships between ΔH_i, χ_i, Y_j and fire ventilation are being sought. Fire ventilation is expressed in terms of air-to-fuel stoichiometric fraction, ϕ.

Data are being measured in our apparatus for ΔH_i and Y_j at various ϕ values, where changes are made by varying air flow rate, oxygen concentration and generation rate of fuel vapors. Data for enclosure fires, concentration profiles in flames and downstream region of the flame, data from the toxicity tests, etc., reported in the literature are also being used. In addition, the generalized relationships in combination with the N-Gas Model of the National Bureau of Standards are being used to extend the application of the engineering calculations to the assessment of toxicity of fire environments and extent of dilution required to reduce the hazard.

The data show that χ_{Chem} and χ_{Con} decrease and χ_{Rad}, Y_{CO} and Y_s increase with decrease in ϕ. The extent of variations in χ_i and Y_j due to changes in ϕ is significantly larger than variations due to changes in the chemical structures.

Some examples of the data are shown in Figures 5 and 6. In Figure 5, $\Delta H_{Chem} \approx 18$ kJ/g, for propane and propylene, is very close to the flame extinction limit. The maximum value of Y_{CO} in Figure 6 is in the range of about 0.23 to 0.30 g/g of fuel vapors, which is in the range reported in the literature for the ceiling layers of highly under-ventilated enclosure fires.

It is hoped that the study will continue: 1) to refine the values of the constants reported in Table 1 and demonstrate the applicability of the data to large-scale fires, and for the modification of materials to enhance passive fire protection; 2) to develop relationships for under-ventilated fires; 3) to seek combined relationships for combustion property and N-Gas Model of NBS; and 4) to understand the fire behavior of materials in terms of their chemical structures and fire ventilations.

Reports and Papers

1. Tewarson, A., "Generation of Heat and Chemical Compounds in Fires," Society of Fire Protection Engineers (SFPE) Handbook (in Press).
2. Tewarson, A., "Correlation for the Generation of Carbon Monoxide in Small- and Large-Scale Fires," 9th Meeting of the United States/Japan Panel of Fire Research and Safety, May 1987 (to be Submitted to the J. Fire Science).
3. Tewarson, A., "A Study of Diffusion Flames of Hydrocarbons to Understand Fire Behavior of Materials," (Submitted to the Fall Technical Meeting of the Eastern Section of the Combustion Institute, November 1987).
4. Newman, J.S., and Tewarson, A., "Ventilation Effects on Particulate Generation," (Submitted to the Fall Technical Meeting of the Eastern Section of the Combustion Institute, November 1987).
5. Tewarson, A., "Prediction of Fire Properties of Materials," Technical Report Grant 60NANB4D-0043, National Bureau of Standards (to be issued).

CONSTANTS FOR THE CALCULATION OF HEAT OF COMBUSTION AND YIELDS OF CO AND PARTICULATES FOR WELL-VENTILATED TURBULENT DIFFUSION FLAMES

Fuels	Heat of Combustion (kJ/mole)								Yield (g/mole)			
	Complete (Net)		Chemical		Convective		Radiative		CO		Particulates	
	A_{Comp}	B_{Comp}	A_{Chem}	B_{Chem}	A_{Conv}	B_{Conv}	A_{Rad}	B_{Rad}	C_{CO}	D_{CO}	C_S	D_S
C-H Structure												
Normal Alkanes (C-H)	43.6	104	39.3	192	24.8	280	14.5	- 88	0.0135	-0.362	0.0469	-1.02
Branched Alkanes (b-C-H)	43.6	101	37.2	268	22.1	364	15.9	-177	0.0226	-0.760	0.0675	-1.81
Cyclic Alkanes (c-C-H)	41.3	209	33.1	430	17.6	457	15.6	- 28	0.0276	-0.700	0.0917	-2.55
Alkenes (C = C-H)	43.3	131	38.4	88	22.2	143	16.3	-100	0.0245	-0.714	0.0577	0.517
Alkynes (C ≡ C-H)	43.7	107	35.7	27	18.9	- 5	18.9	- 5	0.0339	0.204	0.0934	0.0659
Arenes (ϕ-C-H)[a]	41.0	21	28.5	- 74	11.8	- 59	16.8	- 15	0.0612	0.433	0.165	1.22
C-H-O Structures												
Esters (Aliphatic)	43.8	-1750	42.3	-1660	25.2	- 863	13.6	-677	0.0186	1.19	0.0608	-3.67
Esters (Aliphatic-Others)[b]	44.0	-1558	42.1	-1471	30.8	- 974	11.4	-501	0.0159	-1.72	0.0526	-5.01
Normal Alcohols (Aliphatic)	45.4	- 883	40.4	- 682	25.7	- 307	14.7	-378	0.0095	-0.400	0.0371	-1.34
Alcohols (Aliphatic-Others)[c]	44.0	-1558	42.1	-1471	30.8	- 974	11.4	-501	0.0136	-0.186	0.0445	-0.541
Ketones (Aliphatic)	45.0	- 928	42.1	- 825	29.5	- 534	12.6	-290	-	-	-	-
Others (Aromatic)	39.4	- 732	36.5	-1529	22.0	-1379	14.5	-150	-	-	-	-
C-H-N Structures												
Aliphatic	44.0	- 441	38.9	- 360	23.9	- 188	15.0	-173	0.0176	-0.405	0.0560	-1.22
Aromatic	42.3	- 795	30.8	- 535	13.1	- 127	17.3	-362	0.0763	-3.08	0.204	-7.91
C-H-S Structures												
Aliphatic	39.0	- 706	33.3	- 381	19.5	1.1	13.6	-353	0.0248	-2.16	0.0741	-5.81
Aromatic	41.3	- 793	28.3	- 410	11.5	- 59	16.9	-370	0.0897	-4.95	0.237	-12.7

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a: ϕ - benzene rings; b: oxalates, malonates, lactates, etc.; c: unsaturated and cyclic; -: not calculated.

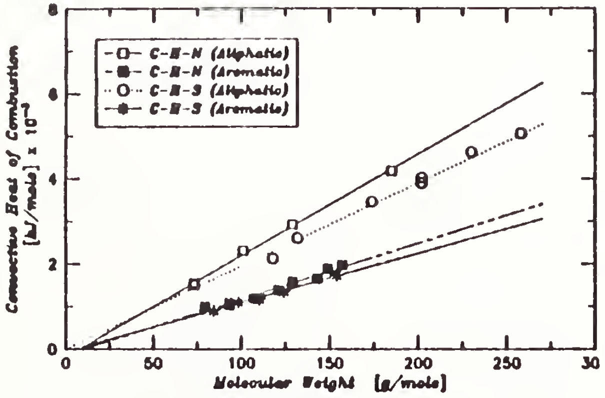

Figure 1. Convective Heat of Combustion as a Function of the Molecular Weight of Fuels with C,H,N and S Atoms in the Chemical Structure.

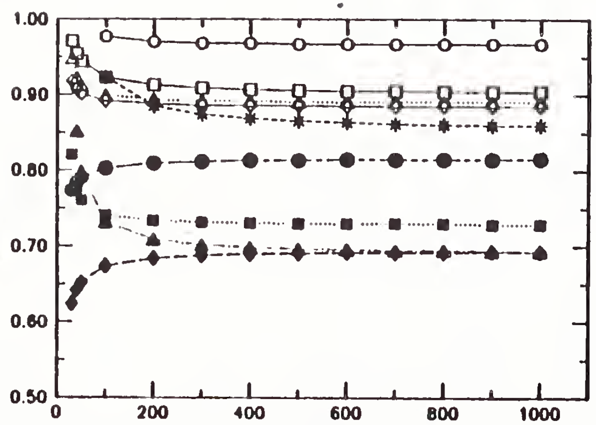

Figure 2. Combustion Efficiency as a Function of the Molecular Weight of Fuels with the Following Chemical Structures: 1) C–H: C–C–H (☐); C=C–H (●); ⧫–C–H (◆); 2) C–H–O: Aliphatic Esters; (○); Aliphatic Alcohols (△); 3) C–H–N: Aliphatic (◇); Aromatic (■); 4) C–H–S: Aliphatic (✱); Aromatic (▲). ⧫: Benzene Rings.

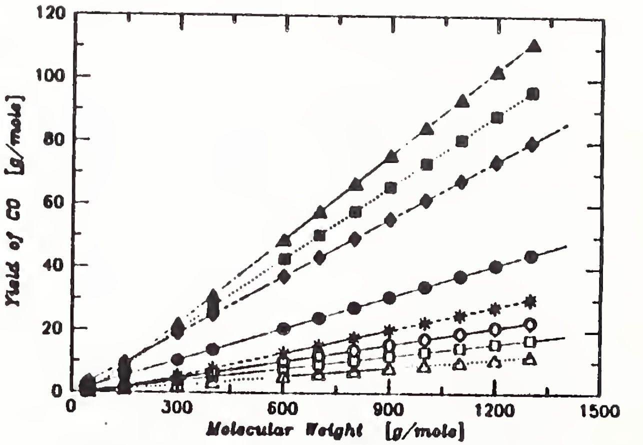

Figure 3. Yield of Carbon Monoxide as a Function of the Molecular Weight of Fuels with the Following Chemical Structures: 1) C–H: C–C–H (☐); C=C–H (●); ⧫–C–H (◆); 2) C–H–O: Aliphatic Esters; (○); Aliphatic Alcohols (△); 3) C–H–N: Aliphatic (◇); Aromatic (■); 4) C–H–S: Aliphatic (✱); Aromatic (▲). ⧫: Benzene Rings.

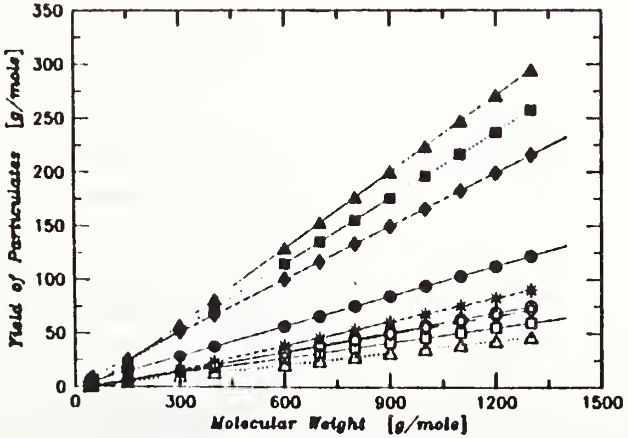

Figure 4. Yield of Particulates as a Function of the Molecular Weight of Fuels with the Following Chemical Structures: 1) C–H: C–C–H (☐); C=C–H (●); ⧫–C–H (◆); 2) C–H–O: Aliphatic Esters; (○); Aliphatic Alcohols (△); 3) C–H–N: Aliphatic (◇); Aromatic (■); 4) C–H–S: Aliphatic (✱); Aromatic (▲). ⧫: Benzene Rings.

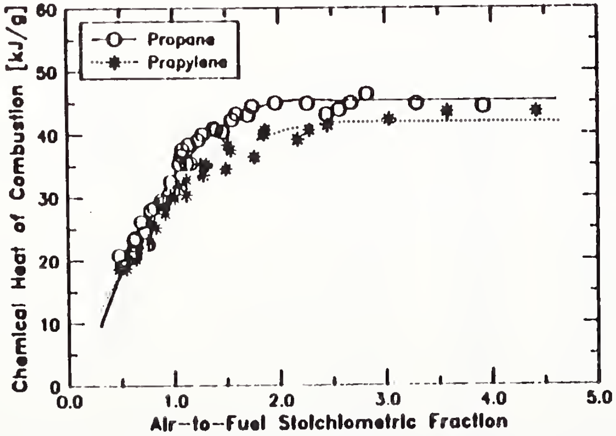

Figure 5. Chemical Heat of Combustion as a Function of Air-to-Fuel Stoichiometric Fraction. Data Measured in Our Apparatus.

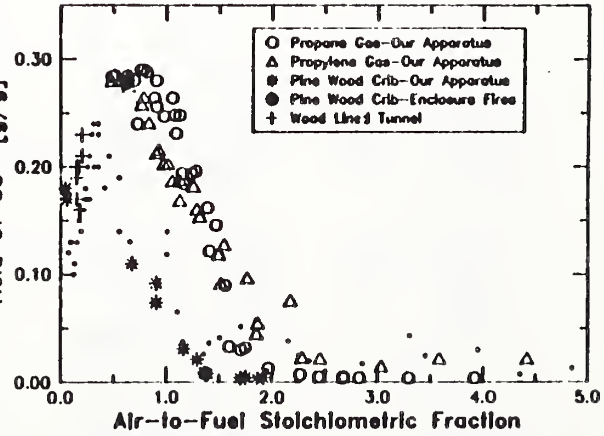

Figure 6. Yield of CO as a Function of Air-to-Fuel Stoichiometric Fraction.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution:	Southwest Research Institute
Grant No.:	60NANB6D0635
Grant Title:	Analysis of Hazards to Life Safety In Fires: A Comprehensive Multi-Dimensional Research Program--Second Year
Principal Investigator:	Dr. Gordon E. Hartzell Director, Department of Fire Technology Southwest Research Institute 6220 Culebra Road San Antonio, Texas 78238 Telephone: 512/522-3038
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NBS Scientific Officer:	Dr. Barbara C. Levin

Technical Abstract:

The overall objective of this research program has been to develop data and methodology to assess toxicological hazards from the time course of analytical data on fire gases. A previous project resulted in the development of methodology for the Fractional Effective Dose model, a method by which the time to a toxicological effect could be estimated for asphyxiant gases from analytical data. That project also yielded considerable LC_{50} data on exposure of rats to hydrogen chloride. The major focus of this current project has been to conduct further studies on the toxicity of smoke containing HCl, particularly in combination with CO.

The mechanism of action of HCl is so very different physiologically from that of CO, that it would be anticipated that these two toxicants should be considered separately in predicting hazardous exposure conditions through the use of the Fractional Effective Dose model. Fractional doses would not be expected to be additive, as in the case of CO and HCN. However, the LC_{50} data on mixtures of CO and HCl tempt one to consider additivity on an empirical basis. In Table 1 are shown data for some limited mixtures of CO and HCl in which the summation of fractional lethal doses approximates unity for 50-percent lethality with 30-minute exposures (14-day observation). In Table 2 is shown a comparable treatment of data using PVC as the source of HCl. It would appear that the increased lethal toxicity of HCl as contained in smoke from the flaming combustion of PVC may be attributed only in part to

the contribution of CO produced. The full explanation may be quite complex since the gas/aerosol/particulate nature of real smoke may result in a different pattern of respiratory penetration. For example, particulate deposition in the upper respiratory tract may obstruct breathing of rodents and further stress an already compromised oxygen transport system.

TABLE 1

SUMMATION OF FRACTIONAL EFFECTIVE (LETHAL) DOSES FOR 30-MINUTE EXPOSURE OF RATS TO MIXTURES OF CO AND HCl

CO		HCl		
ppm	Fractional Lethal Dose	ppm	Fractional Lethal Dose	$\sum$ FED (50% Lethality)
6400	1.0	—	—	1.0
5700	0.89	600	0.16	1.05
5300	0.83	1000	0.26	1.09
4150	0.65	1900	0.50	1.15
3000	0.49	2100	0.55	1.04
—	—	3800	1.0	1.0

TABLE 2

SUMMATION OF FRACTIONAL EFFECTIVE (LETHAL) DOSES FOR 30-MINUTE EXPOSURE OF RATS TO MIXTURES OF CO AND HCl AS PRODUCED FROM PVC

CO		HCl		
ppm	Fractional Lethal Dose	ppm	Fractional Lethal Dose	$\sum$ FED (50% Lethality)
ca. 700	ca. 0.11	2100 (flaming)	0.55	ca. 0.66
7100	1.11	1000 (nonflaming)	0.26	1.37
—	—	2900 (nonflaming)	0.76	0.76

Smoke from the nonflaming decomposition of PVC would appear to be more irritating that expected from the HCl content. Thus, in the case of CO being the major toxicant, the summation of FED's was found to be considerably greater than unity when HCl from nonflaming PVC smoke was present at the sensory irritation level. Although smoke from the nonflaming combustion of PVC would appear, based on summation of HCl FED's, to be more toxic (as a pulmonary irritant) than expected, the significance of the difference is questionable.

Particularly striking, both in the case of the flaming combustion of PVC (with which up to 1680 ppm CO was produced) and in the case of HCl in the presence of 3000 ppm CO supplied from a cylinder source, was the incidence of postexposure deaths the same day as the exposure, usually within an hour. This is rare, except at high concentrations, for HCl, alone. Data showing the incidence of these early postexposure deaths are shown in Table 3.

TABLE 3
COMPOSITE LETHALITY OF RATS EXPOSED TO ATMOSPHERES
CONTAINING HYDROGEN CHLORIDE*

Atmosphere	Animals Exposed	Number of Deaths				LC_{50} HCl in ppm
		Exposure	Day 0	Days 1-4	Days 5-14	
HCl	60	0	0	21	9	3800
PVC Smoke-Nonflaming	36	0	0	10	8	2900
PVC Smoke-Flaming	30	1	4	5	19	2100
HCl + 3000 ppm CO	30	1	2	8	17	2100

* At nominal approximate HCl concentrations of 1800, 2600, 3500, 4300, 5500 and 6500 ppm.

Attempts to elucidate the effect of CO on the postexposure lethality of HCl were inconclusive, but did suggest somewhat impaired ability of rats to return to homeostasis following exposure. Exposure of rats to a mixture of 5300 ppm HCl and 3000 ppm CO was characterized by a relatively rapid initial drop in blood pH and slower than normal postexposure unloading of COHb. Even with these data (compared with those for CO alone), it is difficult to speculate as to the cause of the incidence of same day postexposure lethality. The observations reported with rodents may pose some significance in the case of immediate postexposure complications following human exposures to mixtures of CO and HCl (e.g., prolonged hypoxemic conditions after rescue or escape).

In summary, it would seem that the lethal toxicity of combinations of CO and HCl can be predicted from an FED model. However, only limited success was obtained when applied to real smoke from PVC. This may be due to complications in respiratory penetration patterns involved with the complex gas/aerosol/particulate mixtures found in smoke.

Reports and Papers

1. "Analysis of Hazards to Life Safety in Fires: A Comprehensive Multi-Dimensional Research Program," Final Report, NBS Grant No. 60NANB6D0635, Southwest Research Institute, San Antonio, Texas, March 1987.

2. Hartzell, G. E., A. F. Grand and W. G. Switzer, "Modeling of Toxicological Effects of Fire Gases: VI. Further Studies on the Toxicity of Smoke Containing Hydrogen Chloride," J. Fire Sciences (In Press).

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY87

Institution: SRI International

Grant No.: 60NANMB6D0644

Grant Title: Electrophysiological Incapacitation and Persistent Behavioral Dysfunction of Rats Associated with Combined Exposure to Carbon Monoxide and Carbon Dioxide

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NBS Scientific Officer: Dr. Barbara C. Levin

Technical Abstract:

The primary objective of this project is to characterize the effects of carbon monoxide (CO) alone or CO in combination with 5% carbon dioxide (CO_2) on sensory-evoked potentials of Fischer 344 rats. Interactive effects of these gases are of interest because, as shown by other investigators, CO intoxication alone cannot account for all smoke-related deaths, typical levels of hydrogen cyanide are also insufficient to account for deaths, but the presence of 5% CO_2 exacerbates the lethality of CO at about 2500 ppm when Fischer 344 rats are exposed in a nose-only exposure apparatus.[1] However, using a multiple-animal exposure chamber without restraining the rats, we found the presence of 5% CO_2 to decrease CO lethality. This could be mediated by an increased PaO_2 due to CO_2-induced hyperventilation and greater O_2 release to tissues because of the CO_2-induced rightward shift of the oxyhemoglobin dissociation curve. Potential differences in the interactive effects of CO and CO_2 in restrained and unrestrained rats requires additional study.

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[1] Levin et al., Fund. Appl. Toxicol., 1987, in press.

We have begun studying the effects of CO and CO + CO_2 on visual, auditory, and somatosensory evoked potentials of male Fischer 344 rats prepared with chronic recording electrodes implanted in the skull. The rats are restrained in a head-only exposure apparatus which is placed inside a chamber containing a strobe lamp, speaker, and device for electrically stimulating the tail. Potentials evoked by the visual and somatosensory stimuli reflect activity in cerebral cortex, whereas the response to auditory stimulation reflects neuronal activity in the brainstem auditory pathway. In previous independent studies of hypoxia and hypercapnea the EPs were affected when PaO_2 was less than 30 mm Hg, and by an $FiCO_2$ of 8% (the lowest level studied).

In this current study we first determined that exposure (30 min) to about 1500 ppm CO was required to affect the EPs and exposure to about 2500 ppm CO almost abolished the cortical responses, without much effect on the brainstem auditory evoked response (BAER). A formal study of 11 rats involved exposure first to 5% CO_2 and then to 2000 ppm CO alone or 2000 ppm CO + 5% CO_2, followed by exposure to the opposite CO condition in a third test. The tests were separated by several days, and no deleterious consequences were observed due to the multiple exposures. No rats died.

The waveforms have not yet been quantitatively analyzed, but judging from the group average waveforms (Fig. 1), there was a slight effect of 5% CO_2, involving increased interwave time in the BAER (suggesting slowed conduction velocity in the brainstem auditory pathways) and slight decreases in amplitudes of the somatosensory and flash evoked potentials (SEP and FEP, respectively). The effects of 2000 ppm CO alone on the BAER was about the same as the 5% CO_2 alone. Amplitude decreases for the SEP and FEP were much more pronounced with the 2000 ppm CO alone than for 5% CO_2 alone, and certain components of the waveforms also increased in latency. The combined gases had about the same effect as CO alone, except for a possible slightly larger effect on FEP amplitude.

Colonic temperature declined from baseline by 0.6 and 0.3°C in exposure and recovery conditions, respectively, in the 5% CO_2 condition, and by 0.9 and 1.7°C (exposure and recovery) in the CO and CO + 5% CO_2 conditions.

Recovery of the EPs was complete for the SEP in all conditions, but was slightly less complete for the FEP when combined gases were used compared to the CO-alone condition--the waveform for combined gases was flatter than when CO alone was administered. This may not be a statistically significant effect, however. The general recovery noted for the SEP and FEP indicates that the effects in exposure were not due to the decline in colonic temperature, as temperature declined even further in the recovery phase. In contrast, increases in the latency of BAER components were more pronounced during recovery than during exposure, indicating the temperature dependence of these changes.

In this study we roughly estimated the threshold of effect for CO on EPs and determined a level (about 2500 ppm) that caused a large effect on them. This might be related to the finding noted above that the CO-CO_2 interaction on lethality is maximal at 2500 ppm. Using a CO level causing a moderate effect on EPs, we also determined that the combination of 2000 ppm CO and 5% CO_2 had only slightly more effect on EPs than did CO alone, and the enhanced effect was confined to the FEP. It would be interesting to determine if combinatory effects would be greater when a higher level of CO is used, and, given the apparent special sensitivity of the visual system to the combined gases, if a more sophisticated test such as the pattern-reversal EP would be more affected than the FEP.

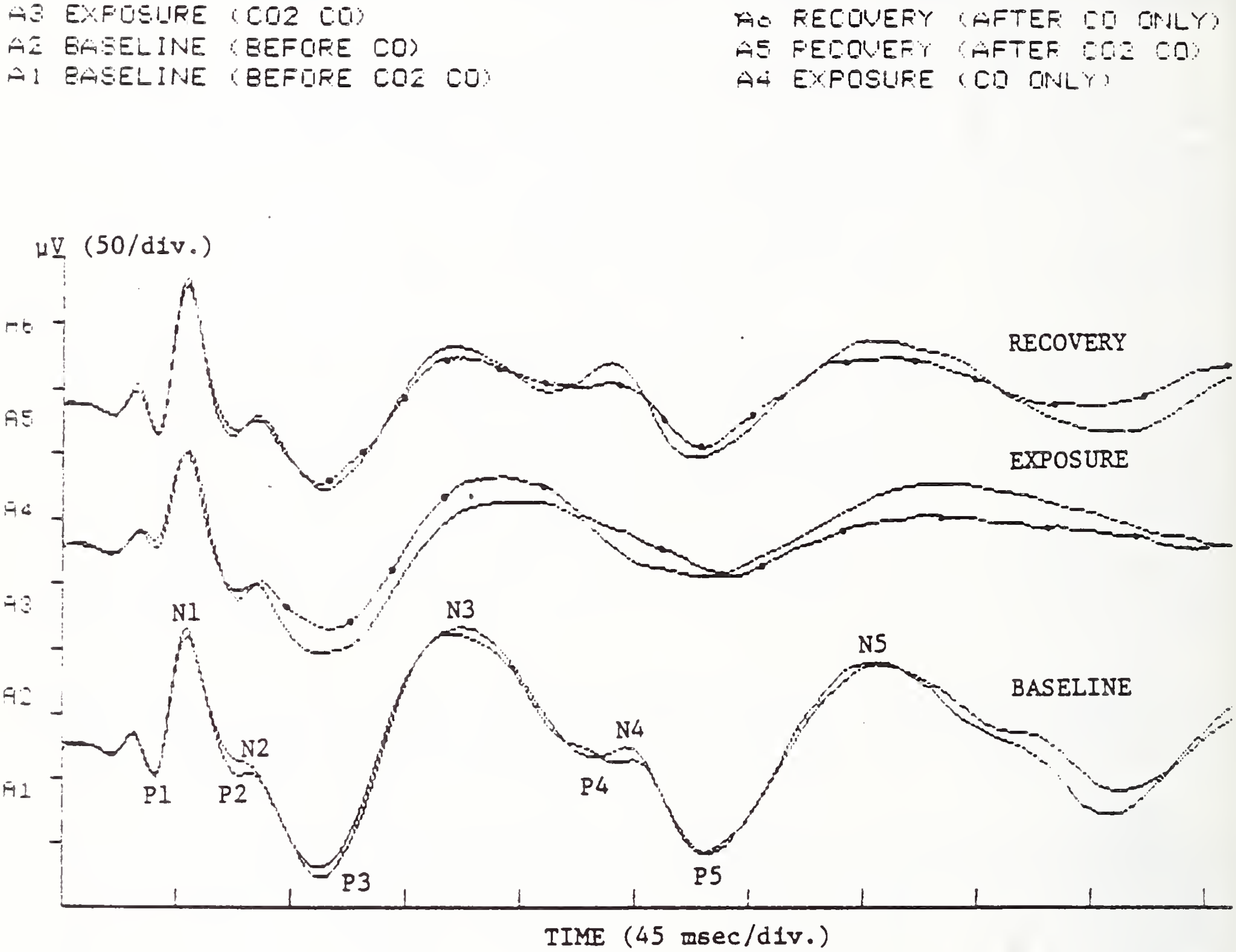

FIGURE 1 CHANGES IN THE GROUP AVERAGE FLASH-EVOKED POTENTIAL INDUCED BY 30-MIN EXPOSURES TO 2000 PPM CO or 2000 PPM CO + 5% CO_2 (DOTTED LINES)

Early components (P1-N2) of the response were not affected, but CO produced a decrease in amplitude of middle and late components (P3-N5). The effect during exposure and recovery was only slightly greater with the combined gases than with CO alone.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of Dayton Research Institute

Grant No.: 60NANB5D0556

Grant Title: Mathematical Modeling of Furniture Fires

Principal Investigator: Mark A. Dietenberger
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NBS Scientific Officer: Dr. Vytenis Babrauskas

Technical Abstract:

Introduction. The objective of this work is to improve a working computer model of a furniture fire in a room environment which only uses the cone calorimeter and the flame spreading apparatus database for description of the material properties. Although the primary prediction of the model is the furniture burning rate as a function of time, the combustion products such as carbon monoxide, water vapor, soot, etc. that can be measured in the cone calorimeter can also be predicted as a function of time. Since the furniture fire model has been merged with a room fire model, FAST, resulting in a program now called HEMFAST, the focus during this contract period was to improve the HEMFAST model. The first version of HEMFAST has been implemented on the Center of Fire Research computers and now provides qualitative predictions of a particular furniture fire.

The current research has concentrated on two areas of improvement in the HEMFAST code with the goal towards quantitative predictions: (1) Revise the bench scale data processing routines to take advantage of the recent upgrades in the cone calorimeter apparatus and of the consequentual new scaling relationships for the material burning rates and combustion products. (2) Improve the predictability of the furniture fire modules by restructuring the code to improve the time integrations of virgin surface temperature, of the flame front positions, and of the local burn history. Other improvements include a model of convective heat transfer on burning areas and a new soot formation model.

New Scaling Relationships. Past work has demonstrated the cone calorimeter database could not be used directly by the furniture fire model unless the data was processed into a useable form. The reason is that the material is burned at constant conditions and at much smaller scale in a cone calorimeter than in a furniture fire. However, the cone calorimeter can be made to simulate varying scales by adjusting the cone irradiances. Under these conditions the measurements of burning rate, mass loss rate,

combustion products rate, and the soot formation rate as a function of time are made in the cone calorimeter. To be used in a furniture fire model these data are rescaled into intrinsic variables of the material. For a very simple material an intrinsic variable would be the heat of pyrolysis, for example, and is the mass loss rate divided by the net surface heat flux. Thus instead of burning rate, mass loss rate, combustion product rate, and soot formation rate we could have the corresponding variables of heat of combustion, the heat of pyrolysis, the combustion product mass fraction, and the soot mass fraction of the fuel. Instead of the time variable we could have the total mass loss of the material as the intrinsic variable. For a complicated material such as that of the furniture, the conversion of the measured variables to the intrinsic (or scaled) variables was not obvious and has been a subject of research by other investigators.

Our attempt at the conversions of the measured variables was found to be successful for several furniture materials and it turns out to be a simple scheme as follows. The cone calorimeter measurements of carbon monoxide and of soot are used to directly convert the burning rate measurements to the stiochimetric heat release rate. The numerical time integration of the stiochimetric heat release rate with a small time stretching parameter is used to define the burning history of the material instead of the actual time. Next a net surface heat flux is calculated taking into account the convective heat flux, the flame radiative heat flux, the cone irradiated heat flux as attenuated by the flame, the burning surface radiance, and a constant heat flux, attributed to glowing combustion, fitted for different cone irradiances. These surface heat fluxes are computed in the same way as it is done in the furniture fire model. The scaled heat release flux is computed as the stiochometric heat release flux divided by the calculated net surface heat flux. This scaled variable can be thought of as the complete heat of combustion divided by the effective heat of pyrolysis. By choosing a proper value for the constant surface heat flux, it was found the data points of the scaled heat release flux at different cone irradiances coalesce into a single well-behaved curve as a function of the burn history for many materials. Now that both the vertical and the horizontal scales for the burn rate data are in intrinsic dimensions we can interpolate and extrapolate from the scaled database for direct use in the furniture fire model.

Similarly, the scaled fuel loss flux curve is computed as the fuel mass loss flux divided by the same net surface heat flux as above as a function of the burn history, also as defined as above. The scaled fuel loss can be thought of as the inverse of the effective heat of pyrolysis. Again, we observed a single well-behaved curve at different cone irradiances for many materials. The combustion products mass rate likewise can be divided by the net surface heat flux as a function of the burn history to also obtain the combustion products in intrinsic dimensions for scaling up to the furniture fire dimensions. The scaling of soot production rates is not as straight forward because the formation of soot is known to be affected by the structure of the fire plume and by the thermal radiation intensity in the flame.

Since the cone calorimeter can now measure the time resolved values of the exiting soot extinction coefficient and of the soot mass formation, and also measure the time to ignition of the materials at different cone irradiances, means that the database for input to the furniture fire model from the cone calorimeter and the flame spread apparatus should be sufficient. Eventually no reliance will be made on any other material database except for deriving and/or validating the model equations in the furniture fire model.

The successful scaling of the cone calorimeter database and its completeness and comprehensiveness had a significant effect on the modification of the bench scale data processors and of the furniture fire modules in the HEMFAST code. For one thing the scaled database with their intrinsic dimensions has allow us to closely coupled the solution of the thermal radiation field with the solution of the fuel mass loss rates, which directly controlls the size of the fire plume. Meanwhile it allows the explicit time integration of the burn history to be done separately from the coupled solutions of the radiative heat fluxes, the convective heat fluxes, and the fuel heat release and mass loss rates.

Code Restructuring. The HEMFAST code was restructured to improve the numerical time integrations of virgin surface temperature, flame front positions, and local burn history, to accomodate coupled solutions of radiative and convective heat fluxes and the fuel heat release and mass loss rates, and to simplify the interfaces between the furniture fire model and FAST. These changes were sufficient to described the restructured code as the second version of HEMFAST. This version of HEMFAST would be appropriate for validation with full scale furniture and room fire experiments, but it would hardly accomodate the novice user. Current and future efforts with the second version is debugging and validating.

The time integration of the flame front positions and of the local burn history by the Euler method so far has not show any appearance of instability in their solutions. Meanwhile, instability in the virgin surface temperature predictions were noted. Since the furniture material was deduced to behave like a thermally thin material at least during the time it takes to ignite, the temperature solution is the integration of a first order nonlinear differential equation with irradiant heat flux as the only input from the other furniture fire modules. By considering the irradiant heat flux to be a constant during a time step and linearizing the ODE, an analytic solution was derived for a stabilized surface temperature prediction over a time step. In fact for a very large time step the predicted surface temperature approaches the equilibrium value, which is a basis for predictors designed for stiff ODE's. Since the FAST code has a general first order ODE solver which should be accurate and stable, it may be worth while to incorporate it into the furniture fire model to avoid any future problems with time integration of furniture fire variables.

A vitally needed model equation is the functional relationship between the exiting soot extinction coefficient and the flaming soot absorption coefficient, which is critical in calculating the thermal radiation field. Such a relationship has been developed for application to the furniture fire model and comparison with the data shows it has good prospects. Because Bard and Pagni reported a nearly constant soot volume fraction within the solid flame and a flame temperature of 1200 °K for several fuels for pool fires; our analysis of the fire plume model from McCaffrey shows that the soot mass formation rate within the solid flame is a constant. Thus the amount of soot mass increases with vertical height in the solid flame but the air entrainment is just enough to result in a fairly constant soot volume fraction.

This result seem to imply that a good approximation to the chemical kinetics is that rapid soot formation occurs near 1200 °K and that the net mass rate of soot formation is controlled by the thermal radiation from the soot as a mechanism of thermal sink (rather than the heat of chemical reaction as a thermal sink). It is also suggested the thermal radiation field has a catalytic role in reducing the soot activation energy by photo absorption in the fuel, thus insuring rapid soot reactions. The radiation cooling of a newly formed soot particle would tend to prevent the soot particle from disintegrating unless the particle has passed through the combustion zones. However, it seems just as likely that the soot particle migrates from the soot reaction zones to the center of a burning fuel parcel. A mechanism proposed for quenching the soot formation would be the bursting of the burning fuel parcel by vigorous turbulent action or by partial fuel burnout. This occurs at the top of the solid flame region, which according to McCaffrey's correlations correspond to the plume mass flow rate divided by the pool fire heat release rate ratio of 0.00266 g/J. This assumption leads to the exiting soot extinction area as proportional to the product of the heat of combustion and the flaming soot absorption coefficient for constant flame and ambient air temperatures. Using Bard and Pagni correlation for the flaming soot absorption coefficient and no fitting parameters, we obtained good comparisons with the exiting soot extinction areas obtained from the cone calorimeter database of a few furniture materials. Complete details will be in the next yearly report and in a article submitted to a journal.

The above results on soot formation modeling were incorporated into the second version of HEMFAST and it also had an impact on restructuring the code. Direct calculation of the local surface convective heat transfer for both horizontal and inclined burning surfaces were incorporated into the second version to improve the code predictability in the early phase of the furniture fire. All the essential physics of a furniture fire growth are now incorporated in the model. Each physical phenomena, such as the flame spread rate, the flame height, the soot production, the burning rate, etc are all described with an analytical equation of approximately equal complexity. The most complex part of the model are in the geometrics of the furniture and the fire and in the thermal radiation analysis associated with it.

Report

1. M.A. Dietenberger, "Description and Results of Furniture Fire Modules Within FAST (HEMFAST)", Interim Technical Report on NBS Grant No. 60NANBSD0557, University of Dayton Research Institute, UDR-TR-87-29, Jan. 1987.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Graduate School of Public Health, University of Pittsburgh

Grant No.: 60NANB4D001

Grant Title: Toxicity of Plastic Combustion Products

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D. Malek (Ph.D. Student)
F. Esposito (Ph.D. Student)

NBS Scientific Officer: B. C. Levin, Ph.D.

Technical Abstract:

One of the current objectives of this project is to establish animal models of escape performance which can be used to provide a data base suitable for inclusion in toxic hazard analysis in fire situations. A guinea pig ergometer has been developed for this purpose. Using this apparatus, guinea pigs were trained to run at a constant speed. The running speed selected is such that it resulted in an increase in oxygen uptake of three times above baseline resting conditions. This running speed can be considered "moderate" exercise since this level of increase in oxygen uptake is approximately one third of the maximum oxygen uptake that guinea pigs can achieve. Each animal is trained for several days to run at this speed for a period of at least 35 to 40 minutes prior to exposure to toxicants commonly found in smoke from burning polymeric materials. This guinea pig ergometer is so constructed that room air can flow through it on a continous basis. Therefore, known concentrations of toxicants can also be added to study their incapacitating effects on running animals.

So far, the effects of two toxicants have been studied. With carbon monoxide, incapacitation occurred at one-half the concentration and twice as fast in running animals as in sedentary animals. With this toxicant, incapacitation occurs in sedentary animals due to narcosis, and animals fall on their side unconscious. The effect in running animals is quite different. Here, incapacitation is their inability to continue to run. Although the animals are no longer capable of running, they are still conscious and even alert since the concentration of CO is too low to induce narcosis. Thus, they can remain alert but are incapable of muscular movement. With HCl, incapacitation is much more dramatic than with CO. At concentrations between 550 and 600 ppm, HCl produces incapacitation of running guinea pigs within 45 sec which is followed by death within 3 min. The animals cough, choke and they die of suffocation. This is in contrast to the effect of this toxicant in sedentary guinea pigs where incapacitation or death did not occur during 30 min. of exposure at concentrations up to 1,300 ppm. Thus the guinea pig ergometer

model can be used to study the effects of two types of toxicants found in smoke, namely the asphyxiants and the irritants. The data available from this model will include the distances traveled prior to incapacitation and the time-concentration relationships for incapacitation with each toxicant and thus provide the necessary data for toxic hazard analysis in fire situations.

Reports and Papers

1. Kennah, H.E., Stock, M.F. and Alarie, Y. Toxicity of thermal decomposition products from composites. J. Fire Sciences 5, 3-16.
2. Malek, D.E., Stock, M.F. and Alarie, Y. Performance under intoxicating atmospheres. Fund. Appl. Toxicol. 8, 335-345.
3. Malek, D.E. and Alarie, Y. A model for physiologic and behavioral evaluation of animal performance during toxic inhalation exposures. Toxicologist 7, 31 (1987).
4. Esposito, F.M. and Alarie, Y. Lethal blood concentrations of cyanide and carbon monoxide in mice following inhlation of these gases or thermal decomposition products of polymers containing these toxicants. Toxicologist 7, 12 (1987).

POLYMER COMBUSTION RESEARCH
CENTER FOR FIRE RESEARCH
FY 87

Professional Personnel

Thomas J. Ohlemiller, Head
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Elizabeth Finlayson, Guest Worker
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Program Objectives

(1) Improve the understanding of the chemical and physical processes which underlie macroscopic fire phenomena. The research embraces broad areas covering both solid and gas phase processes, with particular attention to phenomena in the solid phase such as degradation chemistry as well as heat and mass transport processes.

(2) Devise new techniques and methods for studying these phenomena.

(3) Furnish fundamental scientific information to support the other activities within the Center for Fire Research.

Scope

Chemical and physical processes associated with ignition, flame spread and smoldering of polymeric materials are being studied. The approach of this group is basic and aims to understand the mechanisms of polymer degradation (natural and synthetic polymers), heat and mass transport processes in the solid phase and to obtain appropriate thermal properties of the material.

Projects

Carbon Monoxide Generation from Smoldering Combustion

Smoldering combustion is responsible for a large fraction of residential fire deaths and it appears that CO poisoning is a major underlying cause. We have thus undertaken a program to characterize the emissions from this mode of combustion. The initial work has focused on the smoldering of solid wood since this dovetails with prior work for DOE. A first set of experiments has been completed in which samples of red oak and white pine were made to undergo self-sustained smolder under conditions of controlled air supply. Achievement of self-sustained smolder over solid wood requires a configuration which limits the heat loss rate from the oxidizing char surface; propagation along the interior surface of a U-shaped channel was used here. The first results are all for the case in which the smolder zone propagates in the same direction as the air flow along the channel. The range of air flow rates for which stable propagation is possible in the current configuration is rather narrow -- about 8 to 22 cm/sec referred to the initial channel cross section. Transition to flaming occurs with higher flow rates and extinction occurs with lower flow rates. In the range of stable smolder, CO comprises 3 to 4 mole % of the exhaust gases evolved from the combustion chamber and 10 to 20 weight % of the evolved mass from the wood. Other products are also being characterized and compared with those evolved from the same woods in other modes of gasification. Future work includes expanding the range of configurations for solid wood and examination of CO from the smoldering of other residential fuels, particularly upholstery materials. Plans also include the development of a model for the rate of evolution of CO from char forming materials.

Related Publications:

"Wood Gasification at Fire Level Heat Fluxes" by T. Ohlemiller, T. Kashiwagi and K. Werner, **Combust. Flame 69**: 155-170 (1987)

"Effects of External Radiant Flux and Ambient Oxygen Concentration on Nonflaming Gasification Rates and Evolved Products Of White Pine" by T. Kashiwagi, T. Ohlemiller and K. Werner, **Combust. Flame 69**: 331-345 (1987)

Related Grants:

"Kinetics of Oxygen Chemisorption and Desorption of Combustion Products in the Smoldering Combustion of Cellulosic Material", G. Richards, U. of Montana

"A Study of the Effects of Oxygen Transport, and Temperature History on the Chemistry of PMMA and Cellulose Pyrolysis", E. Suuberg, Brown Univ.

Mass Burning Rate and Gasification

The objective of this new project is to understand and characterize fire plumes, the heat feedback mechanism from the plume to a burning fuel surface and the gasification processes of burning polymeric materials. Ultimately the aim is to develop a predictive model for the mass burning rate of polymeric materials in a pool burning configuration by combining the above results.

This project consists of the following subsets; (1) characterization of fire plumes and the development of theoretical models for plume properties (this is done by Fire Growth and Extinction Group.), (2) characterization of energy feedback rate from the plume to the fuel surface, and (3) experimental and theoretical analysis of the gasification process of synthetic and natural polymeric materials. The last two subsets are being addressed by the Polymer Combustion Research Group under the following headings.

(a) Characterization of the Energy Feedback Rate from a Fire Plume

A new experimental setup to measure energy feedback rates from a flame to the fuel surface in a pool burning configuration is being constructed. Also, detailed radiation absorption-emission measurements and distribution measurements of key chemical species concentrations and temperature throughout the plume are planned. Aliphatic and aromatic liquid fuels (some of which are the monomer of vinyl polymers) will be used. The design and most of the construction of the pool burning facility are completed. The installation of measurement devices is in progress.

Related Grant

"Flame Radiation", Chang-Lin Tien, University of California, Berkeley.

(b) Gasification of Synthetic Polymers

The rate of gasification(burning rate) is determined by the rate of energy feedback from a flame to a fuel surface, by the degradation chemistry, and by the heat and mass transport processes in the material. Therefore, the objective of this subset of the project is to understand the degradation chemistry, coupled with the heat and mass transport processes and to develop theoretical models to be able to predict the gasification rate at the specified rate of energy input to the material.

Theoretically calculated molecular weight and sample weight during the isothermal degradation of anionically polymerized PMMA having three different initial molecular weights were rigorously compared with experimentally determined results. In this calculation, the degradation scheme consists of random initiation, depropagation and termination reactions without any transport processes. The comparison raises a question about the validity of the commonly-used approximation of equal reactivity between primary polymer radicals and tertiary polymer radicals. A new model based on rearrangement of the primary polymer radicals was developed and solved numerically. The results indicate that molecular weights and sample weights calculated from the new model agree with the experimental results better than those calculated from the previous model and furthermore they provide consistent values for degradation kinetic constants.

In another phase of this subset, temperature distributions inside a PMMA sample near a traveling flame front were measured using holographic interferometry at various sample orientations, from vertical downward to vertical upward. Streamwise and normal to streamwise heat flux distributions and heat flow vectors in the sample were calculated from the temperature distributions. It was found that the contribution of streamwise heat conduction through the sample to flame spreading decreases with increase in inclination angle from vertically downward through horizontal angle to vertical upward angle. The same technique was applied to measure timewise temperature distributions inside a fused silica sample (first step toward a polymer sample) at four different external radiant fluxes. Two theoretical models were developed to calculate temperature distribution of a diathermic material. The first model is a rigorous model based on an integral-differential equation for radiative and conductive heat transfer (including internal reradiation) and the second model approximately calculates reradiation in the sample. The results of the first model agree with the experimental data within 4°C through the sample, except near the backside of the sample. The results of the second model tend to overestimate at most 4°C over that of the first model.

Related Publications:

"Effects of Weak Linkages on Thermal and Oxidative Degradation of Poly(methyl methacrylate)" by Kashiwagi, T., Inaba, A., Brown, J.E., Hatada, K., Kitayama, T., and Masuda, E., **Macromolecules, 19**, 2160 (1986).

"A Calculation of Thermal Degradation Initiated by Random Scission. 1 Steady State Radical Concentration", by Inaba, A., and Kashiwagi, T., **Macromolecules, 19**, 2412 (1986).

"A Calculation of Thermal Degradation Initiated by Random Scission. Unsteady Radical Concentration" by Inaba, A., and Kashiwagi, T., **European Polymer Journal** (in press).

"Effects of Initial Molecular Weight on Thermal Degradation of Poly(methyl methacrylate) - Model 1" by Inaba, A., Kashiwagi, T., and Brown, J.E., **Journal of Polymer degradation and Stability** (submitted).

"A Measurement Technique for Determining the Temperature Distribution in a Transparent Solid Using Holographic Interferometry" by Ito, A., and Kashiwagi, T., Applied Optics, 26, 954 (1987).

"Characterization of Flame Spread over PMMA Using Holographic Interferometry - Sample Orientation Effects" by Ito, A., and Kashiwagi, T. **Combustion and Flame** (in press).

Related Grants:

1. "Thermal Stabilization of Polymers by Cross-Link Formation", C. Wilkie, Marquette University.

2. "Mechanisms of Action of Metallic Smoke Suppressants and Fire Retardants for Poly(vinyl chlorid", W. Stones, Polytechnic University.

3. "Interaction of Radiation and Conduction in Polymeric Materials", W. Aung, Howard University.

(c) Rate of Heat Release from Wood

In order to understand and predict the heat release rate, flame spread rate and charring rate of char forming materials, it is necessary to be able to predict their mass burning rate. A model has been under development for the prediction of the mass burning rate and heat release rate of wood as function of the incident radiant flux, thickness, moisture content, rear surface boundary conditions and the thermophysical and thermochemical properties. The thermophysical properties include the density, thermal conductivity and specific heat. The thermochemical properties include the heat of combustion of the volatiles, the heat of pyrolysis and the kinetic parameters which describe the rate of mass loss. These properties are taken to be a function of the temperature and the residual mass fraction. The thermochemical properties must be determined separately for all of the major chemical components of the wood. A critical element in the model development is the determination of the required material properties so that the predictions can be compared with measurements in the Cone calorimeter.

During this past year the concentration has been on the determination of the thermophysical properties up to 550°C and their incorporation into the model along with the thermochemical properties that were measured earlier on this project. In particular a method for measuring the thermal diffusivity of wood char has been devised. The thermal diffusivity of Douglas fir and its char was found to have a relatively constant value of about 2.1 $m^2/s \times 10^{-7}$ up to a temperature of 550°C for mass retention fractions above 0.30. The comparison of the predictions of the model with measurements on instrumented specimens in the Cone calorimeter have been encouraging. At 25 kW/m^2 the overall agreement with the heat release rate is within 20 percent over most of the burning time. For the higher incident heat fluxes the time scale of the calculated heat release rate curves become progressively longer than the measured ones. The reason for these differences may be due to the lack of property data above 600°C. Some measurements are presently being made to overcome this deficiency.

The measurement of the required property data for every type of wood would be a tedious process. However, all woods are, to a reasonable degree of approximation, made up of some combination of a small number of chemical components in different proportions and the thermal conductivity of wood, at least near room temperature, is a well known function of the density. Therefore, the possibility exists for predicting the required properties of the wood and their temperature and residual mass fraction dependence from a small set of more easily determined parameters such as the density and the chemical composition. Thus future research on this project will include the development of models for the properties themselves. Since wood is a very complex material, this can only be done in an approximate way, but it may be adequate for fire modeling purposes.

Due to a project on the heat release rate of aircraft cabin materials soon to be initiated for the FAA the present work on wood will be extended to composites including honeycomb materials.

Related Publications:

Parker, W.J., "Prediction of the Heat Release Rate of Wood", Proceedings of the First International Symposium on Fire Safety Science, Hemisphere Publishing Corporation, 1986, pp 207-216.

Parker, W.J., "Determination of the Input Data on a Model of the Heat Release Rate of Wood," International Symposium on Mathematical Modeling of Fires and Related Test Methods, Sponsored by ASTM, New Orleans, Dec 1986.

Parker, W.J., "Determination of the Kinetic Parameters and the Heat of Combustion of the Volatiles for Wood," (presented at the UJNR Panel on Fire Research and Safety, May 1987).

Parker, W.J., "Prediction of the Heat Release Rate of Douglas Fir," (submitted for presentation at the Second International Symposium on Fire Safety Science in 1988).

Parker, W.J. and LeVan, S.L., "Kinetic Properties of the Components of Douglas Fir and the Heat of Combustion of their Volatile Combustion Products," (to be submitted to Wood Fiber Science).

POLYMER COMBUSTION RESEARCH GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Brown University

Grant No.: 60NANB4D0036

Grant Title: A Study of the Effects of Oxygen Transport and Temperature History On the Chemistry of PMMA and Cellulose Pyrolysis

Principal Investigator: Professor Eric M. Suuberg
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Other Professional Personnel: Viraf Dalal, Postdoctoral Assistant
William Lilly, Research Engineer

NBS Scientific Officer: Dr. Takashi Kashiwagi

Technical Abstract:

Introduction: The goal of this project is an elucidation of the effect of several key variables on the chemistry of pyrolysis of polymethyl methacrylate (PMMA) and cellulose. These variables include the heating rate of the sample, the partial pressure of oxygen at the surface of the sample, and sample characteristics as affect the transport of pyrolysis products out of the sample. Detailed product analysis of both vapor and condensed phase products of pyrolysis are used to infer under what conditions already established or suggested chemical mechanisms may or may not be applied to fire modeling situations. In the case of PMMA, vapor products mainly consist of monomer. The condensed phase products are characterized by gel permentation chromatography (GPC), providing information concerning the degree of polymerization as a function of cited variables. The analysis of vapor and liquid products of cellulose pyrolysis is somewhat more complex. Particular attention will be given to characterization of what are commonly called "tar" products, since these are the products that represent the most combustible vapor products. GPC is being used to characterize these materials, providing information about molecular weight distributions and hence, vapor pressures of the products.

This project is presently at the midpoint of its third year. The initial focus was the pyrolysis of PMMA and the effects of heating rate and oxygen partial pressure on observed kinetics.

These results were reported on last year and the following conclusions drawn:

1. Heating rate was not important in determining the kinetics of PMMA degradation in the range 5K/min to 1000 K/min.

2. Oxygen affects the kinetics of PMMA degradation only at low heating rates (5 K/min). At 100 K/min heating rates, the relevant kinetics are the same as in inert gas.

The remainder of this report will focus on similar issues in cellulose pyrolysis.

Experimental

Pyrolysis Experiments

All pyrolysis experiments were carried out in a heated wire mesh reactor. Samples are heated in a wire gauze which is stretched between two electrodes. The reactor shell was designed for near atmospheric pressure and vacuum work. It consisted of a stainless steel cone with a narrow neck (a modified funnel). The base of the funnel was about 20 cm in diameter and was sealed with a flange containing various feedthrough for the electrodes and for gases. The cone was about 15 cm high and had a neck of 2.54 cm in diameter. The conical shape facilitates collection of condensible products of pyrolysis, not discussed in this paper. The large volume of the reactor ensures that gaseous products of pyrolysis are dilute and can quickly escape the hot region in the reactor, and thus are quenched.

Cellulose from two different sources was examined and showed no difference in behavior. The first was Whatman cellulose powder CF11, medium length fibers (ash content 0.015 wt %). The diameter of the fibers was typically 10 to 30μm. As an alternative to the powder, cellulose samples were also cut from an acid washed filter paper (Munktell's OK/S2-80-200) which had an average ash content of 0.007%. These papers had a thickness of 168 ± 8μm, and thus were an order of magnitude thicker than the powder, in smallest sample dimension. Nevertheless, there was little significant difference between the behaviors of the powder and paper during pyrolysis, so the majority of results reported here are for the paper samples. For most experiments, paper samples were cut into a rectangular shape (approximately 2 cm x 1 cm, and mass less than 20 mg). They were placed in a folded strip of 400 mesh stainless steel screen positioned between two relatively massive aluminum electrodes. In the experiments performed thus far, the pyrolysis was carried out under (1) a pure helium atmosphere, (2) air, or (3) a mixture of 1% oxygen in helium. It has been verified by chromatographic analysis, that in the experiments in "pure" helium, the oxygen level in the vessel is about 10 ppm.

The temperature history of the samples (actually, the mesh) was controlled through a thermocouple sensor signal which was fed into a control computer. Calibration of the thermocouples assured a temperature measurement uncertainty of not more than about 5K.

The total mass loss during pyrolysis was determined as the difference between the mass of the mesh plus sample before and after heating. Thus, one experiment could lead to only one single mass loss datum, compared to TGA-type analysis which yields a continuous record of mass vs temperature (or time). This makes the experimental procedure for determining reaction kinetics rather tedious compared to other methods. However, the advantage of the present method is almost unlimited control of heating rate, not available in thermogravimetric analysis techniques.

Results and Discussion

The data for mass loss in inert gas are shown in Figure 1, for three different heating rates--5 K/min, 100 K/min, and 1000 K/min. Again, each datum represents the mass loss from one experiment in which the sample was heated at the indicated rate to the indicated temperature, and then immediately permitted to cool at a rate of between 200 and 300 K/s. Also shown on Figure 1 are calculated kinetic curves.

The assumed model is based on a single, simple first order process:

$$dM_p/dt = k_o\exp(-E/RT)M_p$$

Where M_p is the mass of pyrolyzable material left at any time t, k_o is the Arrhenius pre-exponential, E is the activation energy, R the universal gas constant, and T is temperature. If the initial mass of the pyrolyzable fraction is (fM_o), then the above may be integrated using well known approximations for linear heating and cooling rates, to give

$$M/M_o = f\left[\exp\left\{-(k_o\ RT^2E)(1/m_h + 1/m_c)\ \exp(-E/RT)\right\}\right] + (1-f)$$

where M is the remaining mass of cellulose, $M = M_c + M_p$, where M_c is the char forming fraction = $[1-f]M_o$, m_H is the heating rate and m_c is the cooling rate of the sample.

While obviously the approximation of the very complex mechanism of cellulose pyrolysis by a single first order rate law is quite crude, the excellent fit achieved with quite a narrow range of k_o and E values over a range of heating rates of 5 to 1000 K/min is surprising. Figure 1 shows a comparison of the calculated and measured mass losses using $k_o = 6.79 \times 10^9$ and E = 33.4 kcal/mol, as suggested earlier by Lewellen et al. at M.I.T., based on experiments performed at heating rates of 400 K/s. The fact that constant kinetic parameters apply reasonably well irrespective of variations of the heating rate over many orders of magnitude suggests that despite the crudeness of the model, it may indeed be reflecting a basic, fundamental, rate controlling step. The poorest fit is seen at 5 K/min heating rate, at which the pseudo constant kinetic parameters underpredict rate. This is, on the surface, not particularly surprising in light of the generally accepted view that the decomposition can proceed along two competitive pathways--a low temperature mechanism dominated by dehydration reactions and a high temperature mechanism dominated by depolymerization. However, the fact that the char yield is about the same regardless of heating rate is inconsistent with that sort of mechanistic explanation, since the dehydration route should lead to higher char yields; f seems to be about 0.9 in all cases.

Certainly for any fire modeling it appears that the use of kinetics of mass loss that are independent of heating rate seems reasonable (at least when oxygen is excluded from the surface, and mass transfer of products from the pyrolyzing zone is fast). There remains a question of what value to use for f, the fraction of char formed. It has been shown previously that f is somewhat sensitive to heating rate. Here, we have observed no such heating rate dependence, and f is taken as constant. It would, of course, be expected that the composition of the starting cellulose, particularly with respect to catalytic inorganic matter, will affect f. As has earlier been pointed out, the ease of mass transfer of decomposition products from the surface will also affect char yields.

Figure 2 shows similar data to those shown in Figure 1, but obtained in air. Comparison of these data with the curves from Figure 1 shows that (1) at 5 K/min, air does significantly accelerate the rate of decomposition, over that in inert gas; (2) at 100 K/min, air accelerates the rate only at higher extents of conversion; and (3) at 1000 K/min, the rates in inert gas and helium are virtually identical.

Figure 3 shows that small amounts of oxygen in inert gas (1%) have an effect which is comparable to that of air. Thus, the oxygen partial pressure dependence of rate of decomposition (at low heating rates) is quite significant.

Conclusions

- Variations in heating rates from 5 K/min to 400 K/sec have a negligible effect on the global kinetics of weight loss during cellulose pyrolysis in inert gas.

- Oxygen catalyzes decomposition (or more precisely, weight loss) at heating rates of 100 K/min and below, but not at 1000 K/min.

Reports and Papers

1. "A Study on the Effects of Heating Rate and Ambient Oxygen on the Global Rates of Cellulose Pyrolysis," submitted to the Eastern Section of The Combustion Institute. E. M. Suuberg and V. F. Dalal.

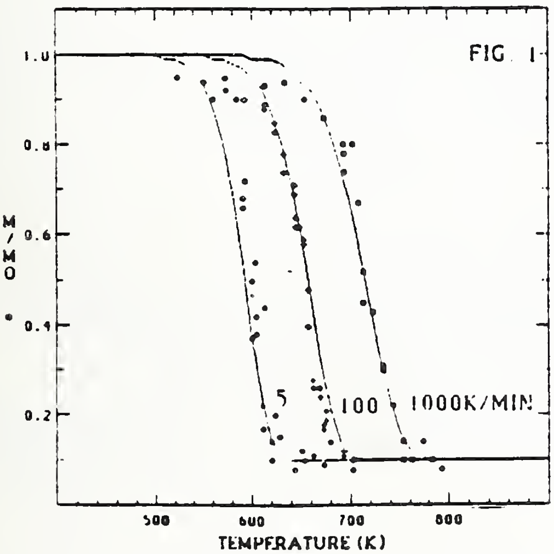
FIG. 1

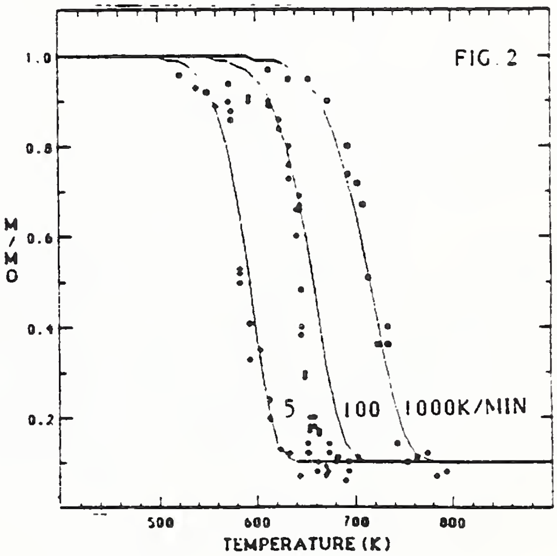
FIG. 2

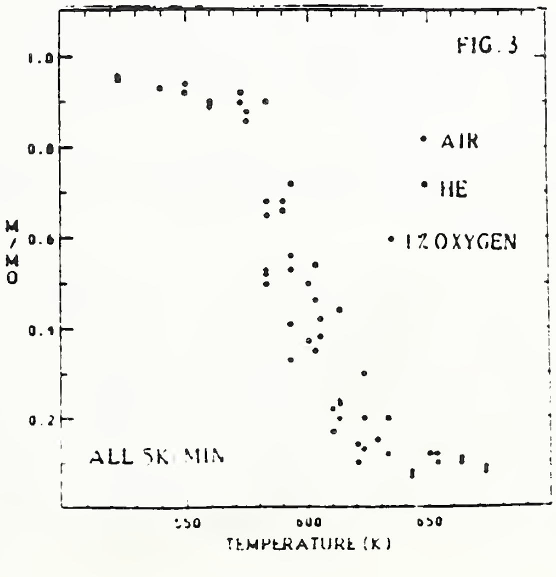
FIG. 3

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY87

Institution:	Howard University
Grant No.:	70NANB5H0529
Grant Title:	Interaction of Radiation and Conduction in Polymeric Materials
Principal Investigator:	Dr. Win Aung (Adjunct Professor) Mechanical Engineering Department Howard University Washington, DC 20059
Other Professional Personnel:	Elizabeth Upson Finlayson (Guest Worker) Hamid Moghadam (Guest Worker)
NBS Scientific Officer:	Dr. Takashi Kashiwagi

Technical Abstract:

The objective of this combined theoretical and experimental study is to obtain a fundamental understanding of the transient heating process for polymeric materials. Such an undersatnding is necessary in order to describe the pre-ignition heating mechanisms of semitransparent solids. In the course of the present study, a numerical model has become available that is capable of predicting the temperature profiles in a solid heated by a high temperature radiation source. The model accounts for combined radiation and conduction, and is formulated in non-dimensional terms [1, 2].

During the past year, efforts were concentrated on the verification of the numerical scheme through comparison with experimental measurements, and on documentation of a user's guide for the computer code. The latter is described in [3]. Experimental verification was carried out by measurements on fused silica samples by means of holographic interferometry. The experimental data were compared with those obtained theoretically by specializing the model to the physical situation.

The solid considered is a plane, one-dimensional solid. Thermal radiation from a graphite plate, modelling the thermal energy emitted by a fire, strikes one face of the plane solid at normal incidence. The flux from the external source has a spectral distribution consistent with Planck's law. Convection heat transfer from the faces of the solid is computed using the usual correlation for laminar free convection heat transfer from a vertical plate. The solid is homogeneous, and hence scattering of radiation is negligible. The reflection of radiation at the

air-solid interfaces is assumed to be purely specular. A portion is the incoming radiation is at wavelength bands over which the solid is opaque; this flux is absorbed at the surface. Radiative energy in the wavelength range in which the solid is semitransparent is in part absorbed within the solid and the rest is transmitted through the solid with no interaction.

In the theoretical model, a numerical method is employed to solve the unsteady form of the energy equation using an implicit finite difference scheme. The solution to the equation of radiative transfer is divided into two contributions. The contribution from the external source is calculated once and is a constant function of the spatial variable. The contribution from the internally emitted flux must be recalculated for each temperature profile. Thus, there is a nonlinear coupling between the energy equation and the equation of transfer. In the solution procedure, an iterative method is employed in which the temperature distribution at any time step is used to solve the equation of transfer. The resultant flux distribution is substituted into the energy equation to obtain a new temperature profile. The new temperature profile is again used to obtain an updated expression for the radiative transfer, with which a new temperature field can again be ascertained. The process continues until the temperature distributions from successive iterations meet a predetermined convergence criterion. Convergence is aided by the Newton-Raphson method.

Solutions for the above model, called the "hot model" since it incorporates internal re-radiation, are obtained using the Cyber 205. When re-radiation is ignored, the model is known as the "cold model", and here the problem becomes a decoupled, linear problem. Results for the latter model can be readily obtained using a small computer.

Consideration has been given to several factors that can influence the response of fused silica to heating. The first factor is the temperature dependence of the material physical properties. A linear variation with temperature of the thermal conductivity and specific heat is considered. This representation is in agreement with the behavior of fused silica over the temperature range of interest.

The second governing factor is the spectral dependence of the physical properties. Data for the spectral variation of the absorption coefficient of fused silica are obtained by infrared spectroscopy. The spectral dependence of the index of refraction is obtained from manufacturers' data which are supplemented by additional data obtained during a previous NBS study. The material is assumed specularly reflecting, and spectral values of the reflectivity are calculated from the refractive index using the Fresnel equations. Owing to the lack of information, the thermal dependence of these properties is not considered.

In many theoretical studies conducted date on combined radiation and conduction, the authors have posed the problem in terms of frequency. This simplifies the analysis because the frequency of thermal radiation, an electromagnetic phenomenon, remains unchanged when passing through materials of different indices of refraction. We have chosen to formulate our problem in terms of the wavelength. Care has been taken to match the spectral variation of optical properties measured corresponding to radiation emitted into air with the internal radiation emitted into a solid whose index of refraction is typically not equal to unity.

Traditionally, the spectral variation of the optical properties is treated using a rectangular band model. This method divides the spectrum of thermal radiation into regions over which the optical properties are considered constant. The result is therefore a summation of gray solutions. It was desired to develop a method that would more accurately account for the spectral dependence of the optical properties. This variation was considered to be especially important in regard to the external flux. Originating at 1300 K, the magnitude of this flux varies greatly over the spectral range. Thus, the solution to the equation of transfer for the external contribution was integrated using 800 intervals in the wavelength range 2-10 microns. The internally radiated flux is emitted by a lower temperature body (at roughly 400 K). The magnitude of this flux is a much flatter function of the wavelength. A rectangular band model is used to model this flux.

Typical dimensionless temperature distributions as a function of the dimensionless distance have been obtained. The effect of optical length has been investigated, as are the effects of the temperature dependence of the thermal conductivity and specific heat. Discussion of these results may be found in [2].

Typical results showing comparisons between the theoretical results and the measurements for fused silica are given in Fig. 1. The agreement between prediction and experiments is encouraging, with the re-radiating model showing better agreement with the measurement. The better agreement, however, is obtained at the expense of a significant increase in computer time. The use of numerical integration for the external flux leads to an improvement of the results by a maximum of 2 K. The experimental uncertainty is one fringe line, equal to approximately 3 K.

Papers and Reports:

1. Win Aung, E.U. Finlayson, T. Kashiwagi, "Interaction of Radiation and Conduction in Polymeric Materials," Summaries of Center for Fire Research Grants and In-House Programs-1986, U.S. Department of Commerce, National Bureau of Standards, Gaithersburg, MD, September, 1986, pp. 124-127.

2. E.U. Finlayson, W. Aung, and T. Kashiwagi, "Theoretical

Models for Combined Radiation-Conduction in Polymeric Solids Heated by External Radiative Flux," Proceedings of 1987 ASME-JSME Thermal Engineering Joint Conference, ASME, New York, N.Y., ed. P.J. Marto and I. Tanasawa, Vol. 1, pp. 427-432.

3. H. Moghadam, E. Finlayson, and W. Aung, "User's Guide to CONRAD Program," Technical Report ME/TR-87-1, Howard University, Department of Mechanical Engineering, Washington, DC, August 15, 1987.

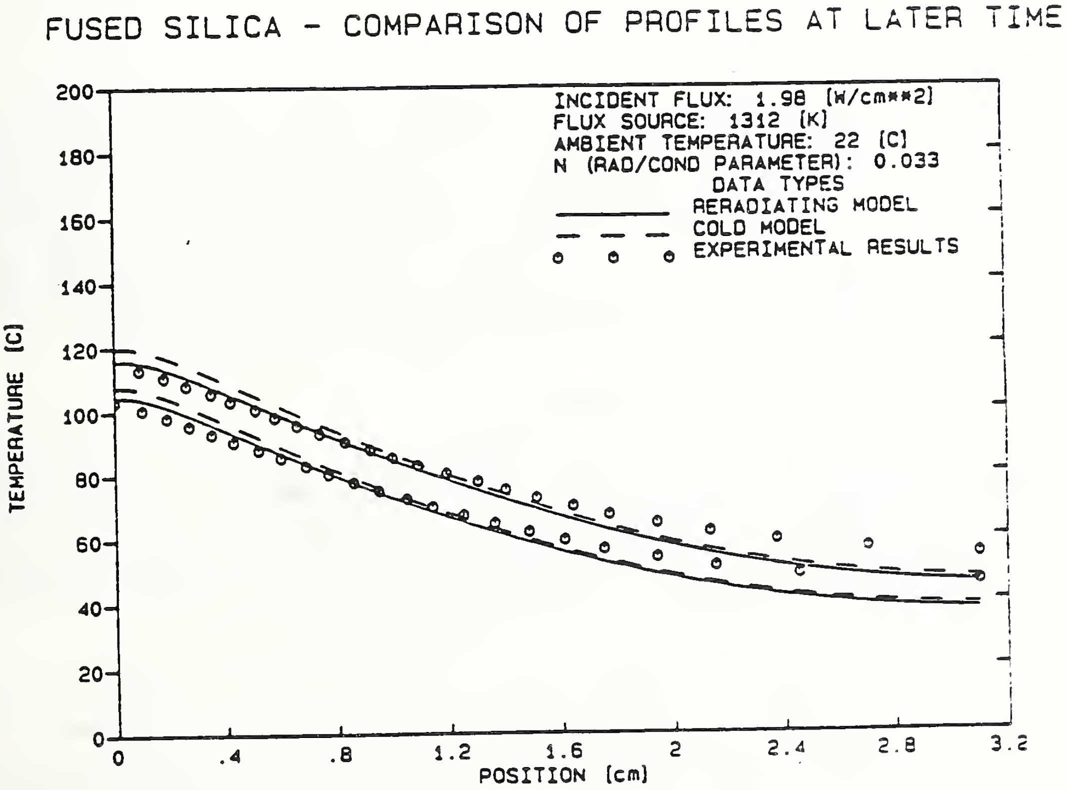

FIGURE 1

CENTER FOR FIRE RESEARCH
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FY 87

Institution:	Marquette University
Grant No.:	60NANB6D0602
Title:	Stabilization of Polymers by Cross-Link Formation
Principal Investigator:	Charles A. Wilkie Department of Chemistry Marquette University Milwaukee, WI 53233 Telephone (414) 224-7239
Other Professional Personnel:	S. J. Sirdesai, Postdoctoral Fellow T. Suebsaeng, Graduate Assistant B. Chang, Graduate Assistant
NBS Scientific Officer:	James Brown

Technical Abstract:

Introduction. The objective of this research program is to understand the chemical basis of pyrolysis reactions of polymers and to use this information to develop suitable schemes for cross-linking of polymers to produce intractable chars. The production of char does not proceed spontaneously, rather additives are required in order to promote these reactions. Each polymer has a unique set of requirements for the cross-linking reactions, these must be elucidated for the polymers in question. The polymers that are addressed in this research are poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET).

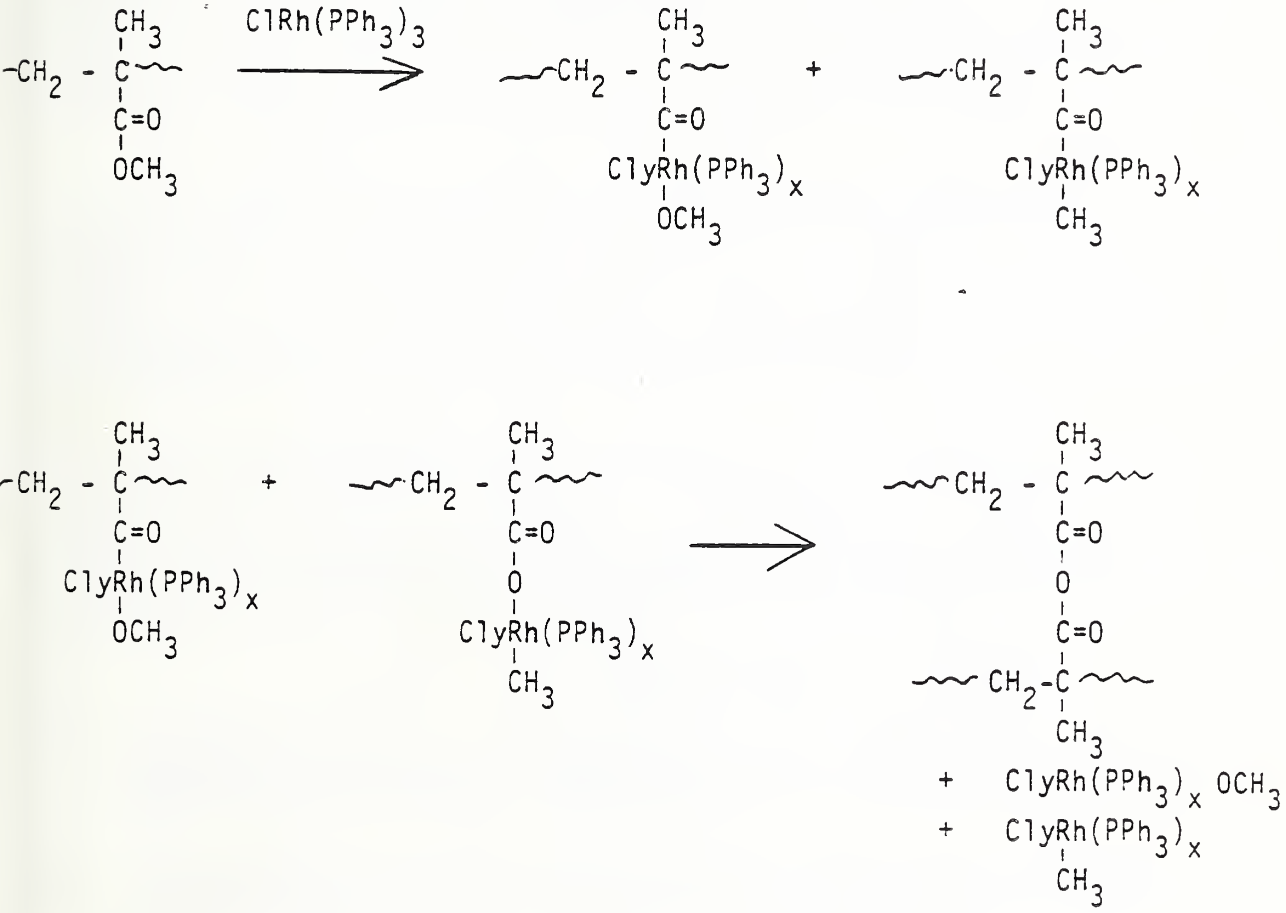
Progress to Date

PMMA. The pendant groups on the PMMA chain provide a convenient site for cross-linking reactions. If these esters can be converted to a more reactive functionality then they may undergo reaction with each other and lead to cross-linking. Two approaches may be identified for this reaction: 1) Conversion of the ester to an anhydride linkage and 2) oxidative addition of a metallic compound to the ester and subsequent coupling of this metal compound.

We have found that it is possible to convert the ester to an anhydride by reaction with a strong acid. The reaction is presumed to proceed by the intermediate formation of a carboxylic acid followed by dehydration of a pair of acid moieties to produce anhydrides. This anhydride forming reaction could occur between adjacent pairs of esters, between pairs within the same polymer strand or between pairs in different chains. Only the last reaction leads to true cross-linking, however the other reactions do provide some increase in thermal stability since a second bond must be broken in order to produce monomer. It is well-known that the formation of anhydride increases the glass transition temperature of PMMA.

Since it is established that Wilkinson's salt, $Rh(PPh_3)_3Cl$, reacts with the carbonyl moiety in acyl halides, we have chosen to examine the reaction of this compound with PMMA. This reaction proceeds by an oxidative addition of the rhodium species to a C-O bond of the ester to give a transitory rhodium species. Coupling of this rhodium species results in the elimination of various organorhodium compounds with the concomitant formation of anhydrides. As above, we observe anhydride formation within the same polymer chain and between polymer chains.

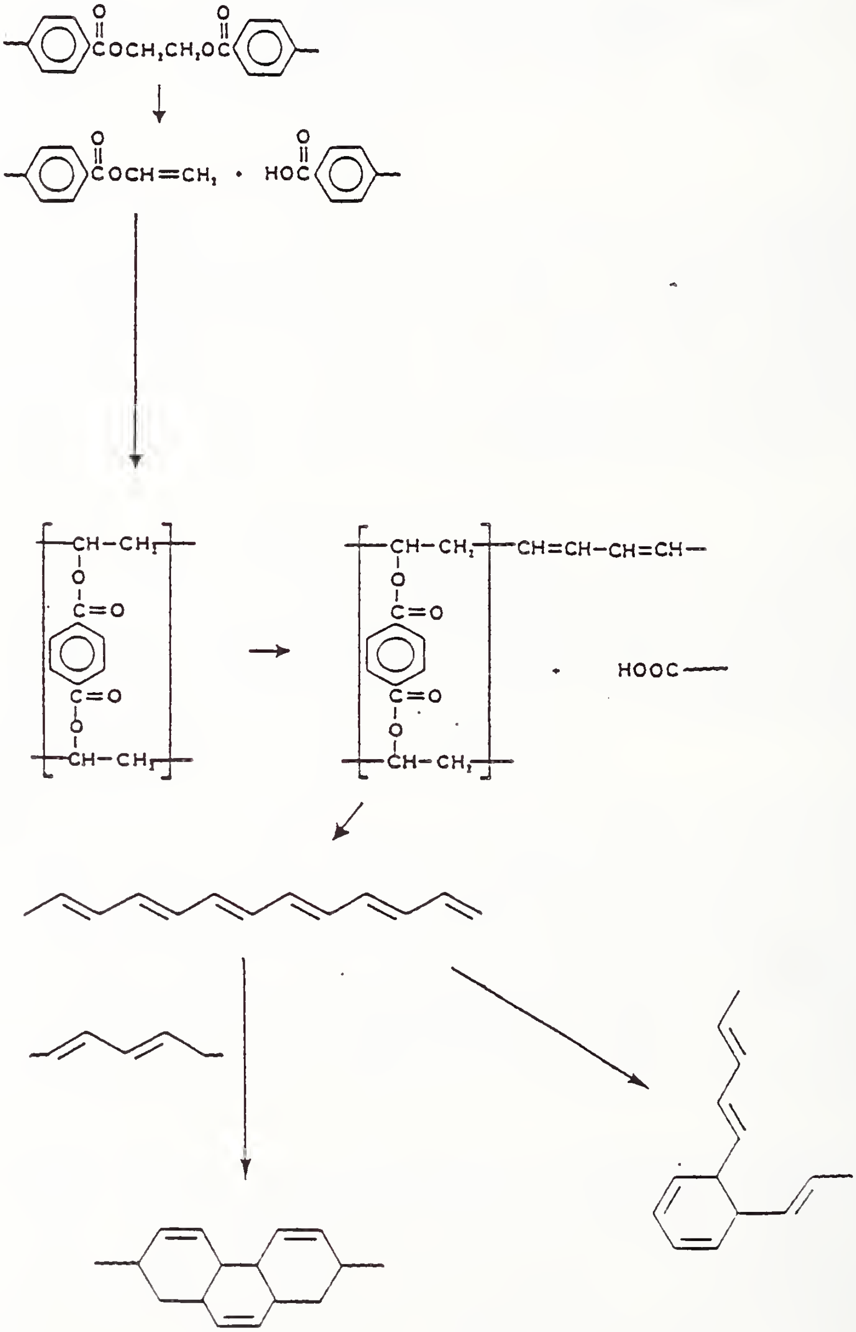
The reaction is presented in Scheme 1. The oxygen index is measured at 20, for PMMA the oxygen index is near 14 (bottom ignition). The glass transition temperature has increased by 14°C and approximately 25% of the material is non-volatile at 600°C. It is unlikely that this compound will ever be used as a flame retardant due to cost, color and toxicity. The value of the investigation lies in the ability to identify other materials that may undergo similar reactions and that do not have the same liabilities.



SCHEME 1

PET. Unlike PMMA, PET offers no pendant groups as sites for cross-linking reactions. It is necessary either to use an additive to participate in this reaction or to make use of the initial decomposition reaction. We have chosen to utilize the vinyl ester that is produced in the initial step of PET decomposition as a reactive intermediate to promote cross-linking of the polymer. Scheme 2 presents a series of reactions that we believe are operative in the cross-linking and flame retardation of PET. There are four steps in this reaction scheme. In the first step the vinyl ester is produced, this undergoes vinyl polymerization in the second step. The third step is chain-stripping of this polymer and, in the last step, this polyene cyclizes to produce the final cross-linked char.

SCHEME 2



We have investigated the formation of the vinyl ester, its polymerization and the subsequent chain-stripping reaction. The decomposition of PET is promoted both by red phosphorus and zinc chloride. This vinyl ester immediately participates in the subsequent reactions and it is impossible to study this reaction in isolation from the other steps. The use of vinyl methyl terephthalate as a model of PET allows the study of the second and third reactions. At 250°C vinyl methyl terephthalate produces only polymer, at higher temperature the chain-stripping reaction also occurs. We have polymerized this vinyl species using conventional techniques at modest temperatures and have studied the chain-stripping reaction by the use of this polymer. It appears that the production of the vinyl ester and its subsequent polymerization are the most critical steps in the process, the last two reactions likely will proceed under thermal conditions from the vinyl polymer. There are rigid temperature requirements on the production of the vinyl ester. Suitable additives must be identified that will allow this reaction to proceed at a temperature only a little above the normal processing temperature of PET. Work continues on all aspects of the reaction scheme.

In a separate investigation we have examined the reaction of PET with triphenylphosphine. This reaction proceeds by the formation of a zwitterionic intermediate which produces a phosphonium ylid. This ylid then attacks another molecule with the production of triphenylphosphine oxide and ethylene. All flame retardant activity of triphenylphosphine may be attributed to the formation of triphenylphosphine oxide, the co-production of ethylene renders triphenylphosphine a less-effective retardant than is triphenylphosphine oxide.

This investigation will lead to additives that will significantly increase the thermal decomposition temperature of the target polymers. It is not possible to render polymers totally non-flammable but it is feasible to change the nature of the polymer, in the presence of a suitable additive and by the application of heat, to require much greater thermal input to cause burning. This would remove the fuel for the flame and eliminate the possibility of combustion.

Reports and Papers

1. S. Sirdesai and C. A. Wilkie, "$RhCl(PPh_3)_3$: A Flame Retardant for Poly(Methyl Methacrylate)", presented at the American Chemical Society Meeting, Denver, CO, April, 1987, POLY 097.

2. T. Suebsaeng, C. A. Wilkie, and C. E. Brown, "Flame Retardant Chemistry. The Reaction of Triphenylphosphine with Poly(Ethylene Terephthalate", submitted for publication.

3. S. Sirdesai and C. A. Wilkie, "Wilkinson's Salt: A Flame Retardant for Poly(Methyl Methacrylate)", submitted for publication.

4. S. Sirdesai and C. A. Wilkie, "A Mechanistic Study of the Reaction of $RhCl(PPh_3)_3$ and Poly(Methyl Methacrylate)", manuscript in preparation.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution:	Polytechnic University
Grant No.:	60NANB6D0647
Grant Title:	Mechanisms of Action of Metallic Smoke Suppressants and Fire Retardants for Poly(vinyl chloride)
Principal Investigator:	Professor W. H. Starnes, Jr. Head, Department of Chemistry and Life Sciences Polytechnic University 333 Jay Street Brooklyn, NY 11201
Other Professional Personnel:	C.-H. Oliver Huang, Predoctoral Scholar
NBS Scientific Officer:	Dr. Thomas Ohlemiller

Technical Abstract:

Introduction. This research is directed toward the elucidation of the mechanisms of action, at the molecular level, of certain metal-containing smoke suppressants and/or fire retardants for poly(vinyl chloride) (PVC). Our initial studies, summarized here, have been concerned with substances containing copper. Such materials are of particular interest because copper compounds, as a group, probably are the most effective metal-based PVC smoke suppressants that have been discovered to date.[1] Our investigative procedure involves detailed studies of the products (and, subsequently, the rates) of reactions between copper species and simple organic compounds that are models for structural segments of virgin PVC or PVC that has been degraded thermally. Similar investigations carried out earlier with the additive, MoO_3,[2,3] have shown that this approach is capable of providing remarkable amounts of information about the mechanistic chemistry that operates in PVC itself. The present work will provide basic facts that should facilitate the design of improved smoke suppressants and/or fire retardants for this very useful polymer.

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[1] W. J. Kroenke, J. Appl. Polym. Sci. 26, 1167 (1981).

[2] W. H. Starnes, Jr., L. D. Wescott, Jr., W. D. Reents, Jr., R. E. Cais, G. M. Villacorta, I. M. Plitz, and L. J. Anthony, in "Polymer Additives"; J. E. Kresta, Ed.; Plenum: New York, 1984; p. 237.

[3] L. D. Wescott, Jr., W. H. Starnes, Jr., A. M. Mujsce, and P. A. Lickwiler, J. Anal. Appl. Pyrol. 8, 163 (1985).

Results and Discussion. Reactions with model compounds were carried out in sealed tubes under anaerobic conditions using 10±2% (w/v) of metallic additive. Product mixtures were analyzed by gas chromatography and IR spectroscopy.

(a) Cis-trans Isomerization. In partially dehydrochlorinated PVC, conversion of cis alkenes into trans alkenes would prevent the formation of benzene, which is a major source of smoke and flame under low-enthalpy-input conditions.[2] We find that $CuCl_2$, CuCl, CuO, and Cu_2O do not catalyze the isomerization of cis-5-decene into trans-5-decene during 60 min of heating at 350 °C. However, the isomerization is catalyzed by MoO_3 under these conditions (though not at 250 °C)[2] and by MoO_2Cl_2 at a temperature of only 100 °C.

(b) Dehydrochlorination. In the case of PVC, this process produces polyene sequences that can lead to crosslinking via alkylation reactions and intermolecular Diels-Alder cyclizations. Crosslinking prevents the formation of volatile species that are sources of flame and smoke. Therefore, dehydrochlorination catalysis might lead indirectly to fire retardance and smoke suppression. We have examined the effects of various copper species on the dehydrochlorination of 3-chloropentane and 7-chlorotridecane, and we have compared these effects with those produced by MoO_3 and MoO_2Cl_2. Conditions for the gc analyses were optimized very carefully in order to prevent dehydrochlorination of the substrates while these analyses were being performed.

In reactions carried out with 3-chloropentane at 200 °C for 10 min, the following dehydrochlorination percentages were determined from several replicate runs: no additive, ca. 0; CuCl, ca. 0; Cu, 1.3-1.8; Cu_2O, 1.6-2.1; $CuCl_2$, 4.4-6.3; CuO, 6.2-9.2; MoO_3, (ca. 0)-8.7; MoO_2Cl_2, ca. 40. In similar experiments performed with 7-chlorotridecane at 200 °C for 60 min, the extents of dehydrochlorination were much greater, qualitatively (ranging up to ca. 50%), when the copper additives (including CuCl) were used, as compared to ca. 4% of dehydrochlorination when no additive was present. However, the quantitative reproducibilities of the 7-chlorotridecane data were not satisfactory, apparently owing to the heterogeneity of the reaction mixtures. By way of contrast, in parallel experiments with 7-chlorotridecane at 200 °C for 60 min, MoO_3 and MoO_2Cl_2 gave very complex mixtures containing both light (cracking) and heavy (condensation/oligomerization) products, as expected.[2]

(c) Alkylation. In thermally degrading PVC, polyene alkylation by alkyl chloride or allyl chloride moieties would lead to crosslink formation. In order to investigate the catalysis of alkylation in a more tractable system, we have examined the effects of metal species on the Friedel-Crafts alkylation of benzene by 3-chloropentane or 7-chlorotridecane.

In a representative series of runs carried out with 3:1 (v/v) benzene:7-chlorotridecane mixtures at 255 °C for 30 min, dehydrochlorination of the alkyl chloride was the only reaction observed in the presence of $CuCl_2$, CuCl, CuO, Cu_2O, or Cu. On the other hand, under identical conditions, MoO_3 and MoO_2Cl_2 produced a mixture of tridecylbenzenes (at least four isomers) in total yields of about 60-65%, based upon the starting amounts of 7-chlorotridecane. Analogous results were obtained in experiments performed with 3:1 (v/v) benzene:3-chloropentane mixtures at 200 °C for 60 min; i. e., only dehydrochlorination was observed with $CuCl_2$, CuCl, CuO, Cu_2O, or Cu, while good yields of pentylbenzenes were produced when MoO_3 or MoO_2Cl_2 was used.

(d) Reductive Coupling. Crosslinking via reductive coupling (equation 1) has been suggested to be a possible means of

$$2RCl + 2M^{+n} \longrightarrow R\text{-}R + 2M^{+n+1}Cl \qquad (1)$$

$$(RCl = PVC;\ M = \text{a metal ion})$$

smoke suppression in PVC formulations containing certain metal species.[4] However, in keeping with earlier findings for MoO_3 and MoO_2Cl_2,[2] we have observed no reductive coupling products in any of our experiments (see above) with alkyl chlorides and copper additives.

(e) Cracking. Model-compound experiments (see part b, above, and reference 2) have strongly suggested that metal-catalyzed cationic cracking of the char into volatile products is responsible, at least in part, for the accelerated flame spread observed at very high temperatures with PVC formulations containing MoO_3. In similar high-temperature experiments with $CuCl_2$, CuCl, CuO, Cu_2O, and Cu, we now have found that all of these substances are much less effective as cracking catalysts than the MoO_2Cl_2 which is formed in situ from MoO_3 and alkyl chlorides. Even after 60 min at 350 °C, only minor amounts of cracking have been observed with the copper species and cis-5-decene, for example. Interestingly, Cu_2O did cause some cracking of 7-chlorotridecane at 250 °C, but the total yield of cracking products was much less than those obtained in parallel experiments with MoO_3 or MoO_2Cl_2.

Conclusions. Our findings lead us to conclude that the copper additives we have studied are relatively weak Lewis acids. Under the conditions of our experiments, they did not catalyze cis-trans isomerization, alkylation, or reductive coupling, and only one of them (Cu_2O) had any significant activity as a cracking catalyst. However, they did accelerate the dehydrochlorination of simple sec-alkyl chlorides. Such acceleration would increase the rate of crosslinking in the case of PVC itself. Thus the dehydrochlorination catalysis could lead to smoke suppression with the polymer, and the absence of cracking products also would be beneficial in this regard. What remains to be decided is

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[4] R. P. Lattimer and W. J. Kroenke, J. Appl. Polym. Sci. 26, 1191 (1981).

whether these effects are sufficient to account for the smoke-suppression activity of typical copper additives. Our investigations of this problem are continuing.

<u>Report</u>:

W. H. Starnes, Jr., "Mechanisms of Action of Metallic Smoke Suppressants and Fire Retardants for PVC: Current Status," Gordon Conference on Analytical Pyrolysis, Plymouth, NH (1987).

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution:	University of California - Berkeley
Grant No.:	60NANB4D0018
Grant Title:	Flame Radiation
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NBS Scientific Officer:	Dr. Takashi Kashiwagi

Technical Abstract:

Introduction. The objective of this research is to develop a simplified methodology of calculating radiation heat transfer in moderate to large-scale fires, while retaining the fundamental physical framework of the problem. From the careful experimental investigation and theoretical analysis, convenient and useful calculational methods are established for applications. During the past year, three primary topics were studied: (1) experimental and theoretical determination of the infrared absorption properties of several hydrocarbon gases which are major pyrolysis products of PMMA; (2) development of a simple method to calculate thermal radiation in pool fires and plumes; and (3) theoretical investigation into the radiative properties of agglomerated soot particulate.

Radiation Properties of Hydrocarbon Gases. The infrared absorption properties of hydrocarbon gases evolved from the degradation of burning condensed fuels are important in determining the characteristics of large fires (L>0.7m), which are primarily controlled by radiant feedback from the flames. The radiation properties of methyl methacrylate $C_5H_8O_2$ (MMA) and ethylene C_2H_4 have been under investigation in the past year [1,2].

The experimental measurements and property correlations have been completed for the eight significant infrared absorption bands of MMA vapor [1]. The spectra obtained were relatively insensitive to both pressure broadening effects and temperature variations, which are due in turn to the high spectral line density of the many superimposed bands within each major band structure and the large number of atoms in the MMA molecule which tends to constrain the bond freedom of interior atoms. The properties are reported in terms of correlated parameters for the Goody statistical narrow-band model for spectral calculations, the Edwards exponential wide-band model for band-averaged calculations, and the super-band model for total property applications. Figure 1 shows the total emissivity of gaseous MMA in the standard chart format of emissivity versus temperature with various pressure pathlengths. The monomer vapor of PMMA is highly absorbing in the infrared and should be always considered in the study of radiation transfer in PMMA fires.

Modeling of Large Pool Fires and Fire Plumes. Pyrolysis rates and radiative heat fluxes of moderately sized PMMA pool fires have been successfully predicted using a simple zone model with two discrete homogeneous conical volumes for the core and flaming regions [3]. The core properties were assumed to be constant and estimated from the available experimental data in the original published model, but an improved version for PMMA fires is now possible since the infrared absorption properties of MMA are available. The new analysis adds several simple features which improve the correspondence of the model to the physics of an actual fire. The radiative flux to the fuel bed is calculated using the Chan-Tien scaling method to accommodate the differing properties of the two zones. Figure 2 shows the excellent agreement between the prediction of the average radiant heat flux to the fuel bed by the two-zone model and experimental measurements [4].

Simple models for radiative heat transfer in the lower regions of the plume for large pool fires are currently under development. An integral formulation for the plume, including the effects of radiation heat transfer within the flow and to the environment, is linked to the two-zone model to provide initial conditions for the simulation. Preliminary investigation reveals that the radiant flux in the plume can be accurately estimated from simple homogeneous cylinder calculations.

Radiative Properties of Agglomerated Soot Particulate. The phenomenon of agglomeration by small spherical particles into large clusters is encountered in flames and in combustion systems that contain ash and soot particulates. The study of the effect of conglomeration on the radiative characteristics is important from the standpoint of computing heat transfer in such systems, as well as from the aspect of experimental determination of radiation properties. To obtain simple analytical models for this study, the concept of an effective diameter is suggested [5], which can be defined as the diameter of a sphere that has the same specified characteristics as the agglomerated cluster, where this equivalent sphere is made up of the same material as the primary particles. Figure 3 presents the effective diameter based on the extinction and scattering cross-sections for two common soot morphologies, straight chains and random clusters. The scattered radiation from all other particles that is incident on each particle increases the net energy incident on the individual particles. Thus the net energy absorbed and extinguished by the system of particles increases. This increase is more pronounced in large dense systems [6] but is negligible when the particles are few. This trend is theoretically predicted for large systems [6] and confirmed by experimental observation [7].

Absorption of radiation is the dominant mechanism of radiation extinction by small absorbing particles in the Rayleigh regime. A method to model the dependent absorption characteristics of dense particulate systems as well as a complete model for evaluating the dependent scattering has been established [6]. Statistical averages based on the random character of particulate medium are introduced to obtain simple expressions for the model. The evaluation of radiative transfer in such systems is shown to be more sensitive to the variations in the absorption characteristics than those in the scattering.

Reports and Papers

1. Park, S.H., Stretton, A.J., and Tien, C.L., "Infrared Radiation Properties of Methyl Methacrylate Vapor," Comb. Sci. Tech., submitted.
2. Tuntomo, A., Park, S.H., Stretton, A.J., and Tien, C.L., "Infrared Radiation Properties of Ethylene," in preparation.
3. Brosmer, M.A. and Tien, C.L., "Radiation Blockage in Large Pool Fires," Comb. Sci. Tech. **51**, pp. 21-37 (1986).
4. Park, S.H., Stretton, A.J., and Tien, C.L., "Radiative Heat Transfer in Plastic Fires," Twentieth Fall Technical Meeting, Eastern Section of the Combustion Institute, Gaithersburg, MD, submitted.
5. Kumar, S. and Tien, C.L., "Effective Diameter of Agglomerates for Radiative Extinction and Scattering," Twentieth Fall Technical Meeting, Eastern Section of the Combustion Institute, Gaithersburg, MD, submitted.
6. Kumar, S. and Tien, C.L., "Dependent Scattering and Absorption of Radiation by Small Particles," Fundamentals and Applications of Radiation Heat Transfer, HTD-Vol. 72, pp. 1-7 (1987).
7. Drolen, B.L., Kumar, S., and Tien, C.L., "Experiments on Dependent Scattering of Radiation," AIAA 22nd Thermophy. Conf. (Honolulu), Paper 87-1485, June 8-10 (1987).

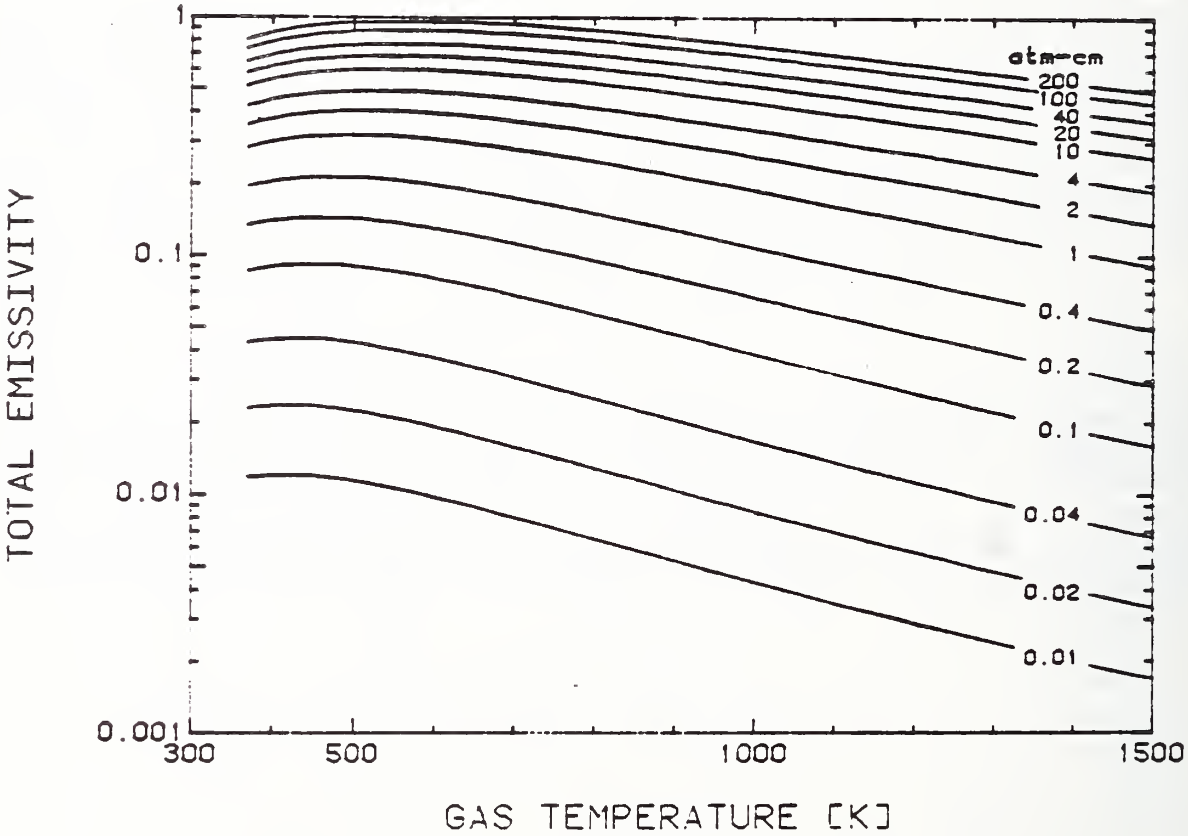

Fig. 1 Total emissivity of MMA vapor for an effective pressure of unity.

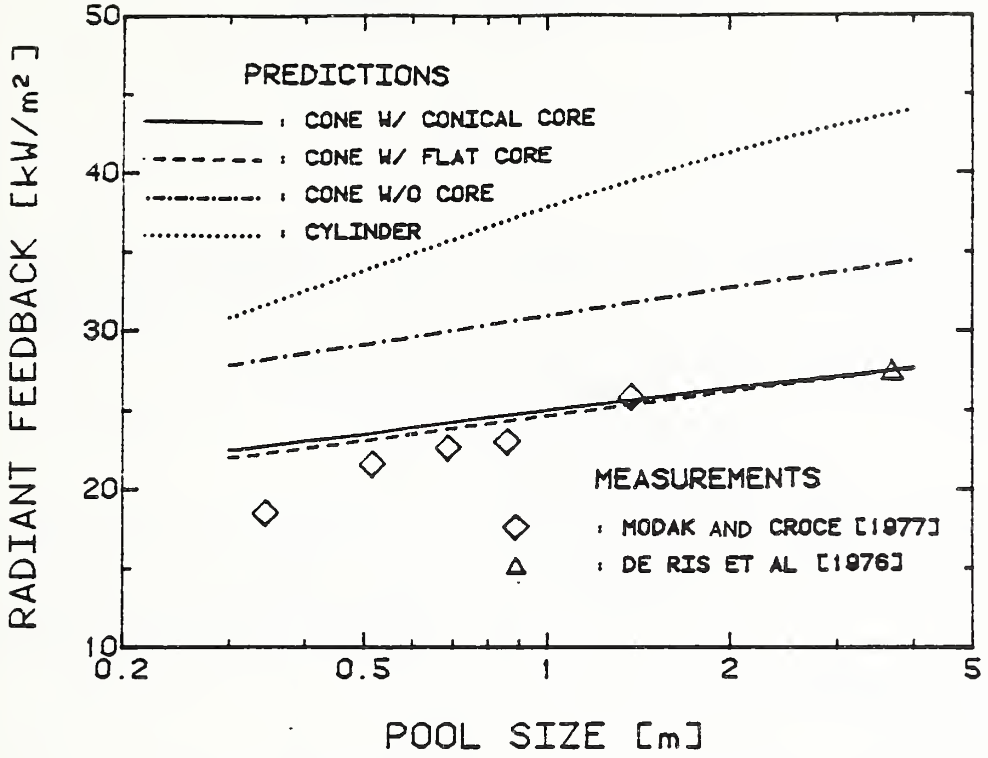

Fig. 2 Average radiant feedback to the fuel bed for PMMA fires.

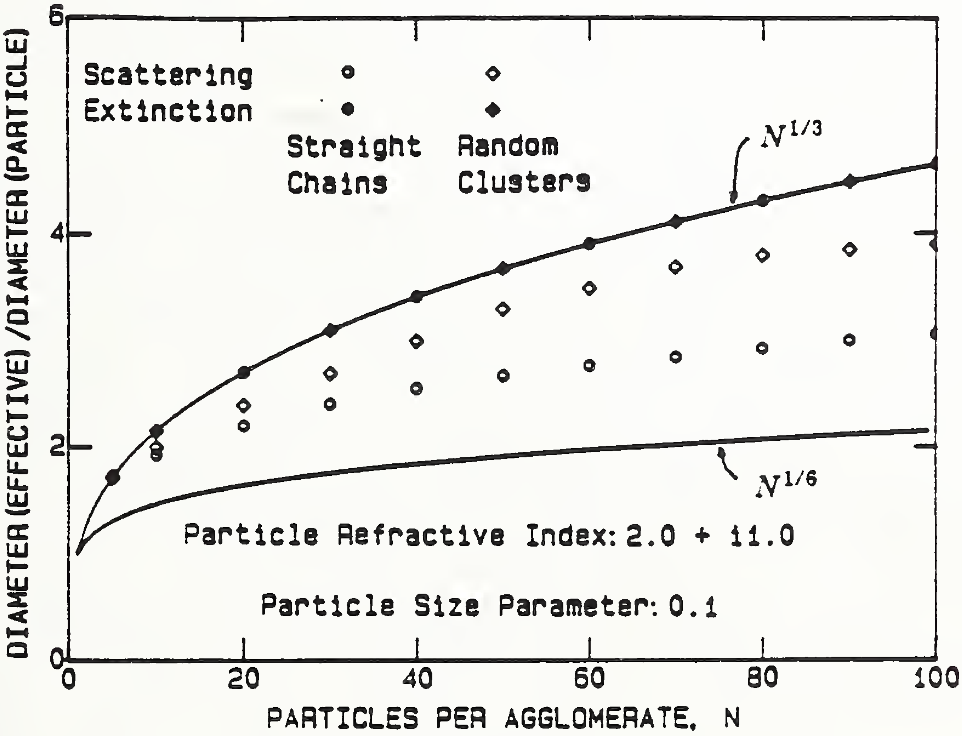

Fig. 3 The effective diameter of agglomerates.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of Montana

Grant Number: 60NANB5D0554

Grant Title: Kinetics of Oxygen Chemisorption and Desorption of Combustion Products in the Smoldering Combustion of Cellulosic Material

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Technical Abstract:

Introduction. The tendency of a material to support smoldering combustion has previously been correlated with the kinetics of oxygen chemisorption at low temperatures on stable chars formed under pyrolytic conditions. This investigation commenced in January, 1986 and aims to extend the analysis of chemisorption kinetics to chars formed at lower temperatures and includes kinetic analysis of gasification reactions which occur simultaneously with or subsequent to oxygen chemisorption. In the preceding year, methods were developed to study the volatile pyrolysis and combustion products evolved by wood and wood chars over temperatures from 250-550°C by the combined techniques of thermogravimetry and Fourier transform infra-red (TG/FTIR). The same techniques were also used to study the effect of "natural" and of ion-exchanged cations on thermal behaviour. Wood was selected as raw material because many substances whose thermal decomposition and smoldering combustion are of importance are, like wood, lignocellulosics. Commonly used cellulosic insulation prepared from newsprint is in this class and its combustion behavior, and that of its chars, is likely to be significantly different from pure celluloses. Preliminary results, described briefly in the previous report, indicated that the low-temperature oxidative pyrolysis of wood, which is likely to be a major factor in smoldering combustion, involves first the degradation of hemicelluloses and lignin, while the cellulose survives to higher temperatures. The nature of the trace amounts of cations in the wood has major effects on these processes. These preliminary indications have now been confirmed and are detailed below.

First chemical events in pyrolysis of wood. Wood has been heated at 250°C on a thermal balance and the evolved gases analyzed by FTIR. The heated wood has been analyzed for glycoses, uronic acids and by nitrobenzene oxidation to vanillin and syringaldehyde. About 60% of the weight loss is

accounted for by five compounds, which are the only products detected in the gases by FTIR. These products are water, carbon dioxide, methanol, acetic acid and formic acid. By relating the rates of formation of these compounds to weight loss, the following major conclusions are reached regarding the first chemical events in pyrolysis of wood. Uronic acids in the hemicelluloses and pectic substances decompose very readily to yield carbon dioxide, water, char (or char precursors) and perhaps some methanol. This decomposition may lead to further pyrolysis of the xylose units to which the uronic acids are attached in the hemicelluloses. Acetyl ester groups in the hemicelluloses are much more resistant to pyrolysis, but are released slowly as acetic acid. A small proportion of the potential methanol product is released very readily and at least part of this product is derived from lignin. Formic acid is released at a slow and continuing rate at 250°C by unknown mechanisms and is probably derived from degradation of hemicelluloses.

Influence of cations on oxidative pyrolysis of wood. The indigenous cations of wood are predominantly potassium and calcium. These have been removed by mild acid-washing and replaced by single cation species by ion exchange without any other change in the chemistry or morphology of the wood. The results from TG/FTIR studies of the resulting woods show that potassium catalyzed pyrolysis of all three major components of wood (viz. cellulose, hemicelluloses and lignin), while calcium retards the same processes. The same generalizations apply to oxidative pyrolysis, with especial emphasis of low temperature (e.g., 280°C) catalytic effects of potassium. The influence of the trace amounts of cations on oxidation of the char in air is dramatic. Above 430°C the char oxidation is highly catalyzed by potassium but strongly suppressed in char from acid-washed wood, with the char from calcium-exchanged wood being intermediate. These effects confirm earlier results and indicate promising leads for future work on smolder control in lignocellulosics. The CO_2:CO ratio formed from char oxidation changes from 2:1 for original wood to 1:1 for acid-washed wood. This effect should be of considerable importance in heat balance in oxidizing chars and hence probably in smolder behavior, because of the greater heat of formation of CO_2 compared with CO.

Oxygen chemisorption on chars. The chars used have been prepared in the thermal balance from wood discs under nitrogen and all subsequent measurements of chemisorption activity (CSA) made without removal from the balance, in order to avoid intermediate exposure of the char to air or mechanical effects. After some difficulties, procedures have been designed to give reproducible CSA measurements. These have shown that the char, as it forms from slowly heated wood, begins to develop significant CSA at about 370°, peaks at 500° and by 600°C the CSA has fallen to about a quarter of the maximum. This type of maximum in char reactivity had been indicated in previous studies with chars from pure celluloses. The effect may be of considerable importance in smoldering combustion and also in the phenomenon of spontaneous ignition of lignocellulosics. The mechanism is not known and will be further studied.

The influence of cations on CSA has been measured using chars from ion-exchanged wood and shown to be small but significant. The CSA appears to be catalyzed by potassium and to a smaller extent by calcium and is lowest in acid-washed wood.

Influence of cations on ignition. The study of ignition has been commenced by heating chars from ion-exchanged wood after chemisorption of oxygen in the thermal balance. The preliminary results show increase in ignition temperature from 377° for potassium-exchanged wood, through 384° for untreated wood to 393°C for calcium-exchanged wood, but most dramatically, the char from acid-washed wood oxidized without ignition in these experiments.

In general, the detailed results for the current period have demonstrated quite separate and different influences of cations in wood respectively upon pyrolysis, oxygen chemisorption, combustion, and ignition.

Reports and Papers

1. G.N. Richards, "Kinetics of Oxygen Chemisorption and Desorption of Combustion Products in the Smoldering Combustion of Cellulosic Material," Annual Report, NBS Grant No. 60NANB5D0554, Wood Chemistry Laboratory, University of Montana, Missoula, MT, February 1987.

2. G.N. Richards, "Volatile Products of Low-temperature Oxidative Pyrolysis of Wood - Influence of Cations," Annual Conference on Fire Research, NBS Center for Fire Research, 1986.

3. W.F. DeGroot, W.-P. Pan, M.D. Rahman and G.N. Richards, "Early Products of Pyrolysis of Wood," Prepr. Pap., 193rd National ACS Meeting, Division of Fuel Chemistry, Denver, 32(2), (1987) 36-43.

4. W.F. DeGroot and G.N. Richards, "The Influence of Pyrolysis Conditions and Ion-Exchanged Catalysts on the Gasification of Cottonwood Chars by Carbon Dioxide," *Fuel*, in press.

5. W.F. DeGroot and G.N. Richards, "The Effects of Ion-Exchanged Cobalt Catalysts on the Gasification of Wood Chars in Carbon Dioxide," *Fuel*, in press.

6. F.-Y. Hshieh and G.N. Richards, "Factors Influencing Chemisorption of Oxygen and Ignition of Wood Chars," Prepr. Pap., Combined Meetings, Eastern Section: The Combustion Institute 12th Fall Technical Meeting, Chemical and Physical Processes in Combustion and the National Bureau of Standards Annual Conference on Fire Research, Washington, D.C., in press.

7. W.F. DeGroot, W.-P. Pan, M.D. Rahman and G.N. Richards, "First Chemical Events in Pyrolysis of Wood," *J. Anal. and Appl. Pyrol.*, in press.

8. M.G. Essig and G.N. Richards, "1,5-Anhydro-β-L-arabinofuranose from Pyrolysis of Plant Cell Wall Materials (Biomass)," submitted to *Carbohydr. Res.*

9. M.D. Rahman and G.N. Richards, "Interference by Flavonoids in Phenol-Sulfuric Acid Analysis of Carbohydrates," *Carbohydr. Res.*, in press.

10. M.D. Rahman and G.N. Richards, "Interactions of Starch and Other Polysaccharides with Condensed Tannins in Hot Water Extracts of Ponderosa Pine Bark," *J. Wood Chem. and Tech.*, in press.

11. W.F. DeGroot and G.N. Richards, "The Effects of Ion-exchanged Cobalt Catalysts on the Gasification of Wood Chars in Carbon Dioxide," Prepr. Pap. 194th National ACS Meeting, Division of Fuel Chemistry, New Orleans, 32(4), (1987) 193-202.

12. G.N. Richards, "Synthetic Applications of Thermal Degradation of Sucrose," 3rd New Orleans Carbohydrate Symposium, 1987.

13. G.N. Richards, "Interactions between Condensed Tannins (Polymeric Proanthocyanidin Glucosides) and Polysaccharides,"194th National ACS Meeting, Cellulose, Paper and Textile Division, New Orleans, 1987.

14. G.N. Richards, "Studies of Thermal Degradation of Sucrose and Influences of Impurities at Processing Temperatures," 194th National ACS Meeting, Agricultural and Food Division, New Orleans, 1987.

Smoke Dynamics Research Group
Center for Fire Research
FY 87

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Program Objectives

Develop scientifically sound principles, metrology, data, and predictive methods for the formation/evolution of smoke components in flames for use in understanding and modeling general fire phenomena.

Scope

This work embraces broad areas underpinning CFR programs with focussed study in the areas of hot gas physics and chemistry. Effects are directed toward improved understanding of the chemical and physical processes which underlie macroscopic fire phenomena and include development of new techniques and methods for studying these processes.

1. Soot Formation Chemistry and Physics

Flame radiation from incandescent soot dominates flame spread and heat transfer in large fires. Escaping particulates hinder vision and impair breathing, as well as being a sensitive signature for fire detection. It has been predicted that smoke from mass fires ignited by a major nuclear exchange would absorb enough solar radiation to reduce the ambient temperature by 10°C or more on a global scale. Despite the importance of soot, there is little understanding at the molecular level of the soot formation process; i.e., how small molecules grow rapidly to become soot particles. There is also little information on the amount of soot emitted from fires and on the properties of the soot particles. We are engaged in a broad program to provide information and understanding regarding soot formation and properties.

This is the eighth year of a long-term study of the fundamental chemistry of soot formation, carried out jointly with the NBS Thermal Processes Division and also in collaboration with the Chemical Kinetics Division. A series of optical and mass spectrometric profile measurements have been completed for methane/air diffusion flames on a Wolfhard-Parker slot burner. We have used fluorescence to monitor OH, C_2, and polycyclic hydrocarbons (three ways), multiphoton ionization to detect methyl radicals and small soot particles and

Rayleigh-Mie scattering to observe the emergence of large soot particles. In addition, mass spectrometric profiles of CO_2, H_2O, methane, acetylene, butadiene, benzene, toluene, diacetylene, triacetylene, vinyl acetylene, methylacetylene, and allene have been taken. These results clearly delineate the region of soot nucleation: soot particles first appear on the high temperature, radical-rich side of a zone containing numerous pyrolysis products. Velocity measurements using laser Doppler velocimetry and thermocouple temperature profiles have also been obtained. The combined data provide the most detailed description of the chemical structure in a hydrocarbon diffusion flame obtained to date.

The species profiles have been analyzed to determine production and destruction rates of intermediate hydrocarbons in our methane/air diffusion flame. These results show that acetylene plays the major role in surface growth on particles (as found in premixed flame studies). Furthermore, direct tests of proposed models of chemical growth can now be made which strongly suggest that a pathway involving vinyl radical addition to acetylene is the fastest route to form benzene. Recent experiments have investigated fuel structure effects on chemical growth pathways by the addition of small amounts of ethylene, butadiene, and toluene to the base methane flame. In addition, measurements have been obtained in an ethylene/air diffusion flame which further clarify the key role of acetylene in molecular growth reactions.

In addition to species characterization studies, physical properties of soot are being investigated. The kinetics of cluster agglomeration and structure of the resulting clusters have been studied using a "Brownian dynamics" computer simulation of conditions appropriate for soot growth. The average cluster size is found to be proportional to the square of the time while previous models of soot growth predicted a much slower growth based on particle coagulation and coalescence. We have shown that using a kinetic rate kernel based on the fractal geometry of soot leads to a size distribution in good agreement with the self-preserving distribution obtained with the computer simulation. An experimental study of the size distribution of soot leaving the flame is now in progress.

Parallel instrumentation for measuring fire smoke aerosols has been developed in bench scale, as part of the Cone Calorimeter, and in large scale, in a specially built measuring rig. Since the principles of design were similar, data could be directly compared. For solid and liquid combustibles, it was found that large-scale smoke emission rates could be well represented from Cone Calorimeter data if the specimen mass loss rates, per unit area, were matched for the two cases. The matching of the mass loss rates was accomplished in bench scale by exposing the specimen to a suitable level of external irradiance. For gaseous fuels, a similar clear conclusion could not be drawn, and further studies are seen to be necessary. The specific extinction area, when computed on a smoke particulate mass basis, was seen to be independent of fuel type and of the conditions of test.

"Chemical Production Rates of Intermediate Hydrocarbons in a Methane/Air Diffusion Flame" by Miller, J.H., Mallard, W.G., and Smyth, K.C., Twenty-First Symposium (International) on Combustion (in press).

"Methyl Radical Concentrations and Production Rates in a Laminar Methane/Air Diffusion Flame" by Miller, J.H. and Taylor, P.H., Combustion Science and Technology, 52, 139 (1987).

"Measurement and Rate Law Analysis of D_2 Q-Branch Line Broadening Coefficients for Collisions with D_2, He, Ar, H_2, and CH_4" by Smyth, K.C., Roscasco, G.J. and Hurst, W.S., J. Chem. Phys., 87, 1001, (1987).

"Chemistry of Molecular Growth Processes in Flames" by Smyth, K.C. and Miller, J.H., Science, 236, 1540 (1987).

"Soot Formation in Hydrocarbon Diffusion Flames" by Miller, J.H., Hamins, A., Kohout, T.A., Smyth, K.C. and Mallard, W.G., Energy and Fuels (in press).

"Soot Particle Formation in Laminar Diffusion Flames" by Santoro, R.S. and Miller, J.H., Langmuir, 3, 244 (1987).

"Simulation of Aerosol Agglomeration in the Free Molecular and Continuum Flow Regimes" by Mountain, R.D., Mulholland, G.W., and Baum H., J. Colloid and Interface Science, 114, 67 (1986).

"Smoke Production and Properties" by Mulholland, G.W., Society of Fire Protection Engineers Handbook (in press).

"Fractal Analysis of Soot Agglomerates" by Samson, R.J., Mulholland, G.W., and Gentry, J.W., Langmuir, 3, 272 (1987).

"Cluster Size Distribution for Free Molecular Agglomeration" by Mulholland, G.W., Samson, R.J., Mountain, R.D., and Ernst, M.H., Energy and Fuels (in press).

"The Effect of Scale on Smoke Emission" by Mulholland, G.W., Henzel, V., and Babrauskas, V., submitted to 2nd International Fire Safety Science Symposium.

1. Prediction of CO

This multi-discipline, long-range program is designed to provide the basic understanding necessary to allow the prediction of CO in both pre- and post-flashover room fires. Flame chemistry, fluid mechanics, and their interactions must all be considered. Experiments here at NBS and in other laboratories supported by the grants program are being coordinated to address this fundamental problem.

Work at NBS has focused on the area of chemically-reacting turbulent flow. The goal is to provide the experimental foundation for theories designed to calculate the behaviors of these complex flow fields. Such theories are necessary if the formation of incomplete products of combustion, such as CO and soot, are to be predicted.

During the past year a new experimental diagnostic has been developed in cooperation with workers from the University of Maryland for the study of variable density turbulent flows. This technique combines Rayleigh light scattering (concentration measurement) with an array of hot-wires (velocity measurements) to allow simultaneous, real-time, spatially-resolved measurements of velocity and concentration along a line in the flow field. Preliminary measurements have demonstrated the role of large scale turbulent structures in the entrainment behavior of an axisymmetric jet of propane flowing into air. A new flow facility is under development which will allow this powerful diagnostic to be employed for the investigation of buoyancy-driven turbulent plumes.

Experimental findings of variable density flows have been utilized to predict the lift-off and blow out behaviors of turbulent jet diffusion flames. These flame extinction processes, which are relatively easy to experimentally characterize, serve as tests of various chemically reacting flow theories. Our work has shown that the large scale entrainment behaviors of isothermal jets of the fuel are sufficient to predict lift-off and blow out behaviors for the corresponding turbulent jet diffusion flames. This finding suggests that models based on mixing in large scale turbulent structures may provide a means for the prediction of chemically reacting turbulent flow.

> "Development of a Line Camera for Real-Time Measurements of Concentration in Turbulent Flow Fields," Pitts, W.M., Proceedings of the Fifth International Congress on Applications of Lasers and Electroptics, Volume 58, The Laser Institute of America, 1987, pp. 7-14.
>
> "The Effects of Global Density and Reynolds Number Variations on Mixing in Turbulent, Axisymmetric Jets--Implications for Turbulent Jet Diffusion Flames," Pitts, W.M., Proceedings of the 1987 ASME/JSME Thermal Engineering Joint Conference, Vol. 1, Eds. P.J. Marto and I. Tanasawa, The American Society of Mechanical Engineers, 1987, pp. 123-135.
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> "Mixing in Variable Density, Isothermal Turbulent Flows and Implications for Chemically Reacting Turbulent Flows," Pitts, W.M. and Kashiwagi, T., National Bureau of Standards Internal Report, NBSIR 87-3550, May, 1987.
>
> "Importance of Isothermal Mixing Processes to the Understanding of Lift-Off and Blow Out of Turbulent Jet Diffusion Flames," Pitts, W.M., submitted to Combustion and Flame.

Associated Grants

1. "Soot Dynamics in Flames", R.A. Dobbins, Brown University.
2. "Chemical Pathways to Soot Formation in Diffusion Flames", J.H. Miller, George Washington University.
3. "Soot Particle Formation and Destruction in Diffusion Flames", R.J. Santoro, Pennsylvania State University.
4. "Soot Formation, Smoke and Corrosion Hazards in Fires", B. Zinn and J. Jagoda, Georgia Institute of Technology.
5. "Characterization of Large Scale Turbulent Structures in Variable Density Flows", J. Wallace, University of Maryland.
6. "Kinetics of Agglomerate Formation", J.W. Gentry, University of Maryland.

SMOKE DYNAMICS RESEARCH GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 1987

Institution: Brown University

Grant No.: 60NANB6D0643

Grant Title: Soot Dynamics in Flames

Principal Investigator: Professor R. A. Dobbins
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Other Professional Personnel: Dr. Constantine Megaridis,
Postdoctoral Research Associate

NBS Scientific Officer: Dr. George Mulholland

Technical Abstract:

This research has resulted in the development of a thermophoretic sampling technique for the extraction of soot particles from flames. The technique has been described in detail in a recent journal article. Electron microscope analysis of soot particles sampled from the ethene diffusion flame shows them to be highly aggregated chains of essentially monodisperse spheres. This result implies that the particles grow predominantly by surface growth. Modeling of the process by the aerosol dynamic equation has led to an understanding of the relative contributions of the various phenomena involved. The variation of primary particle size with height and the velocity measurements of others allow the determination of the specific surface growth rate of the soot particles. These important results are reported in detail below. The availability of information on actual soot morphology in the ethene flame allows an attack on the calculation of soot extinction and scattering properties with particle shape properly considered. This aspect of the work will be reported at a later date.

I. EXPERIMENTAL: The combustion system studied in the current work is a coannular laminar ethylene/air diffusion flame under atmospheric pressure. The burner consists of two concentric brass tubes of 11.1 mm and 101.6 mm i.d. The fuel flows through the inner tube while the ventilating air flow passes through the annulus between the two tubes. The flow rates adopted for ethylene and air are 3.85 and 713.3 cm^3/s respectively. These flow rates result in a nonsmoking laminar flame with definite shape and height (~88 mm) which displays the yellow incandescence characteristic of soot. The structure of the soot field of the above flame has been previously investigated using laser light-scattering and extinction measurements[1-4], as well as a thermophoretic sampling technique[5] with remarkably short sampling times. The current study is a continuation of the latter work on soot particle morphological characteristics using the same technique. A detailed description of the thermophoretic sampling method is given in ref. 6.

II. RESULTS AND DISCUSSION: The thermophoretic sampling technique, combined with electron microscopy for high quality observations, was used to study the morphology of soot aggregates collected from the coannular ethylene diffusion flame. These aggregates consist of individual particles, called primary particles, of approximately spherical shape and rather uniform size. A vertical survey of primary particle size has been performed for particles corresponding to radial positions of maximum soot volume fraction (annular region). A variety of probes was used to collect the particles thermophoretically from the flame environment and a high consistency of the measured primary particle size was observed.

The current results refer to the intermediate region of the flame, i.e. heights (z) from 10 mm to 50 mm. These regions are characterized by intense particle growth, which occurs by both mechanisms (agglomeration and surface growth) simultaneously as depicted in Figure 1. Examining a series of electron micrographs, we produced quantitative data on the primary particle diameter D_p of soot particles corresponding to the annular region ($r=r_c$). These values of D_p vs the axial coordinate z for a variety of thermophoretic probes are plotted in Figure 2. The maximum size shown occurs at z=40 mm which marks the lower boundary of the oxidation region. The evolution of the primary particle size distribution with height, for particles transported on the annular region can be characterized by the ratio σ/D_p, where σ is the standard deviation of the primary particle diameter. From our measurements we obtained that σ/D_p = 0.22, 0.18, 0.15 and 0.13 corresponding to heights z=10, 20, 30 and 40 mm respectively. These values show that the distribution of the primary particle size narrows considerably with height above the burner mouth. This behavior clearly illustrates the dominant effect of surface growth reactions on soot particle morphology at low and intermediate heights of the flame.

Figure 2 provides additional information on the specific surface growth rate f of soot particles corresponding to the annular region. This rate is defined as the mass deposition rate per unit of particulate surface area and it is generally a function of the axial location z. The dependence on z translates into a dependence on the residence time t of the particles[7], through a series of particle trajectory measurements reported by Santoro et al.[4] for the identical flame. The specific surface growth rate is related with the material density ρ_p, the axial velocity component v_z and the z-gradient of the primary particle diameter through

$$f = \frac{\rho_p v_z}{2} \frac{d D_p}{dz} \qquad (1)$$

The axial velocity values are taken from ref. 4. A soot density of 1.86 gr/cm^3 was used in Eq. (1). Thus we retrieve the values of f given in the following table

TABLE 1 Selected Data for the Ethene Diffusion Flame

t^a (m s)	25	31	36	44	47
z (mm)	10	15	20	30	35
$f\times10^5$ (gr/cm^{2}s)	9.4	10.5	10.1	6.2	3.1

[a] From ref. 7.

In the above calculations no assumptions were adopted on the size distribution of the soot aggregates or the regime these particles belong to. These calculations resulted in a maximum value of $f=10.5\times10^{-5}$ gr/cm^{2}s corresponding to z=15 mm above the burner mouth (t=31ms). Harris and Weiner[8] reported a maximum value of $f=6\times10^{-5}$ gr/cm^{2}s for a series of rich premixed ethylene/air flat flames. This value was calculated by them using purely optical obervations, adopting Rayleigh scattering theory and assuming a self-preserving size distribution of smooth spheres.

Some recent studies[9] suggest that acetylene may be the soot growth species in a diffusion flame environment. Under this assumption the surface growth rate can be expressed as

$$f = K\left[C_2H_2\right] \tag{2}$$

where K is the rate constant for the surface reactions that convert C_2H_2 into soot and $[C_2H_2]$ the mole fraction of acetylene. In Eq. (2) we have already assumed first order surface growth reaction kinetics. Using the mass spectrometric measurements by Miller[10] for our diffusion flame system we have $[C_2H_2]\approx0.022$ corresponding to the annular region at a height z≈9 mm. The corresponding value for f at z=10 mm from our measurements derives through Eq. (2) the surface growth reaction constant $K\approx4\times10^{-3}$ gr/cm^{2}s atm corresponding to the annular region at a height of z=9mm above the burner mouth where the temperature[4] is T≈1700K.

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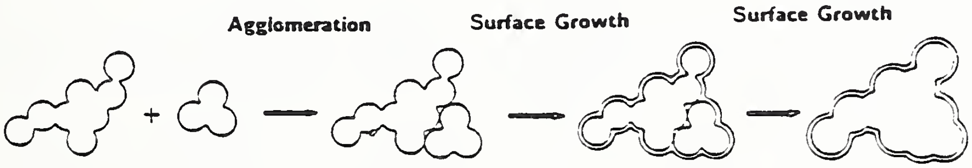

Figure 1 Mechanisms of soot particle growth.

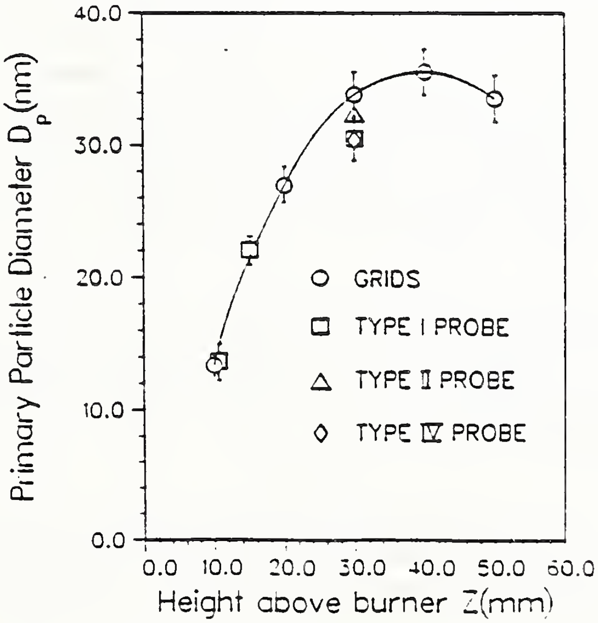

Figure 2 Primary particle size as function of height, near $r=r_c$, for the ethylene diffusion flame. Each size measurement is an average over about 100 primary particles. Various thermophoretic probes were used to obtain the above data points.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS

Institution: The George Washington University
Grant Number: 60NANB6D0625
Grant Title: Chemical Pathways to Soot Formation in Diffusion Flames
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Technical Abstract

The chemistry of the combustion of simple hydrocarbons to form carbon dioxide and water has been extensively studied and is generally well established. Our level of understanding of the chemistry which leads to the formation of polynuclear aromatic hydrocarbons (PAH) and soot particles is less fully developed. Because of the importance of radiation from soot particles in flame spread, a predictive capability for particle generation rates in fires is an essential component of any useful fire model. However, simple schemes which attempt to correlate soot production with global flame properties (such as stoichiometry) are unlikely to be able to account for new and puzzling data which is being collected in laminar diffusion flames. For example, Hura and Glassman have observed an increase of more than an order of magnitude in the soot volume fraction with addition of 10% oxygen to the fuel stream of a counterflow ethylene/air diffusion flame [1]. Addition of oxygen to other fuels did not show nearly as dramatic an effect. Clearly, effects such as these will only be understood from a knowledge of the dominant chemical pathways which lead from fuel pyrolysis to particle inception. The goal of our work is to develop a data base of flame structure information for laminar diffusion flames. This data is then used to calculate the rates of chemical processes which lead to the formation and growth of aromatic ring structures.

During the past year, we have performed experiments on two flame geometries: an axial burner supporting ethylene/air diffusion flames and methane/air diffusion flames on a Wolfhard-Parker slot burner. The results of these studies are summarized below.

Ethylene/Air Flames:

Over the past few years, work in this laboratory has been concerned with detailed flame structure measurements in laminar methane/air diffusion flames. There are many important questions which remain unanswered from our previous investigations. These include:

1) Are the conclusions which have been derived concerning the early chemical steps leading to aromatic formation

unique to the methane/air flame or are they generally applicable to hydrocarbon diffusion flames?

2) Can correlations be made between the chemical structure of a flame (species concentrations and production rates) and the evolution of the soot particle field?

To address these questions we performed a study of an ethylene/air diffusion flame supported on an axially symmetric burner. This particular flame system was chosen because of the wealth of information which is available on the evolution of the soot particle field in this flame, and the availability of temperature and velocity field data for this system [2]. The experimental details and results of this study have been reported previously [3]. Although microprobe sampling in highly sooting environments such as the ethylene/air diffusion flame leads to relatively high uncertainty in species concentrations, these studies have led to a characterization of flame conditions for soot particle growth. In work published during the past few years this region has been characterized through laser light scattering measurements [4,5]. By comparing molecular concentrations with contours of soot volume fraction the area of fastest soot particle growth in the ethylene/air flame is characterized as follows:

- 1500 - 1700 K
- Relatively high concentrations of acetylene (> 1 %)
- Near flame region where acetylene is produced with maximum rate.

These results suggest that acetylene, or a reactive species that may be equilibrated rapidly with acetylene (vinyl or ethynyl radicals), participate in the rapid growth of young particles.

Methane/Air Diffusion Flame:

Although comparisons of concentration data with measurements of the soot particle field are a tremendous advantage for the ethylene flame system, experimental sampling difficulties have precluded the collection of as complete a data base as that available for the methane/air flame supported on the Wolfhard-Parker burner. We have therefore concentrated most of our efforts during the past year on collection of a more refined data set for the methane/air flame. In the past few years in our laboratory, production rates for stable flame species have been determined from measurements of the concentration of chemical species, velocity and temperature [6,7]. The production rate for benzene has been compared to estimated forward rates for the formation of small (two-carbon) free radicals from hydrogen atom attack on acetylene and ethylene. For these calculations, the hydrogen atom concentration was estimated from the equilibrium of methane with methyl radicals [8]. The results of this study indicate that the vinyl radical ($C_2H_3\cdot$) plays the dominant role in benzene formation processes. However, if hydrogen atom abstraction from acetylene by hydroxyl radicals is included as an initiation pathway, both vinyl and ethynyl ($C_2H\cdot$) reactions are fast enough to account for the observed rate of benzene formation [9]. Therefore, the bottleneck in the formation of benzene in diffusion flames probably occurs at larger molecular sizes than ethynyl or vinyl radical.

To investigate these subsequent steps in the formation mechanism of benzene it is necessary to have estimates for concentrations of the radicals which are involved in these elementary steps. To this end, radical concentrations can be calculated from elementary reaction equilibria if the reactions are sufficiently fast in both the forward and reverse directions relative to the rates of transport processes. Concentrations calculated in this way can be used to evaluate the relative importance of specific reactions in the overall benzene formation mechanism. The calculated chemical rates for specific species can be compared with those found experimentally. Further, the set of estimates of radical concentrations can be iterated to improve the agreement between experimental and calculated rates.

This approach is likely to be subject to inaccuracies: radical concentrations calculated from equilibria may be off by an order of magnitude in even the most favorable cases. It is therefore necessary to have a gauge for the impact of specific concentration estimates on the calculated rates. To this end, sensitivity analysis can be used to determine the impact of radical concentrations on calculated rates. Moreover, this analysis can be used to rank the importance of specific reaction pathways toward a common product.

For these calculations it is important that the magnitude and position of features in the species production rate profiles be as accurate as possible. During the past year we replaced our mass spectrometer electronics so that it is now possible to collect concentration data with a dynamic range spanning four orders of magnitude. With the new data chemical rates can be calculated with much greater accuracy particularly for flame regions where oxidation processes are important and species concentrations fall rapidly.

We have also recently initiated a study of methane/air diffusion flames with small additions of other hydrocarbons to the fuel flow. Addition of one to three percent ethylene had very little effect on the concentrations of acetylene and benzene. However, addition of one percent toluene to the fuel flow led to dramatic increases in the concentrations of both one and two ring aromatics. The results of the toluene addition experiments have been summarized as an Eastern States extended abstract for this meeting.

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Publications during the Past Year:

1) "Soot Inception in Hydrocarbon Diffusion Flames."
K.C. Smyth and J.H. MIller, Chemical and Physical Processes During Combustion, Fall 1986 Meeting of the Eastern States Section. Paper C.

2) "The Chemical Structure of an Atmospheric Pressure Ethylene/Air Diffusion Flame."
J.H. MIller, Chemical and Physical Processes During Combustion, Fall 1986 Meeting of the Eastern States Section. Paper C.

3) "Chemistry of Molecular Growth Processes in Flames."
K.C. Smyth and J.H. Miller, Science 236, 1540 (1987).

4) "Soot Formation in Hydrocarbon Diffusion Flames."
J. H. Miller, A. Hamins, T.A. Kohout, K.C. Smyth, and W.G. Mallard, Fuel Division Preprints: Advances in Soot Chemistry, American Chemical Society, August 1987.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Georgia Institute of Technology

Grant No.: 60NANB6D0650

Grant Title: Soot Formation, Smoke and Corrosion in Fires

Co-Principal Investigators:
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Technical Abstract:

Introduction. The objective of the proposed study is to determine the importance of ions in the soot formation process and to obtain information on the sooting and corrosive behavior of various commonly used materials in fire situations. This study is divided into three major tasks to be carried out simultaneously.

In Task I the effect of flame ions on the nucleation and growth processes in diffusion flames will be determined. These tests will be carried out on an opposed flow diffusion flame at sub-atmospheric pressure. The reduced pressure will spread out the reaction zone resulting in better spatial resolution of the optical measurements. The ion concentration in the flame will be varied using a charged probe. This technique has the advantage of permitting a change in local ion concentration without inducing a significant electric field in the flame. Such a field has in the past been found to manipulate the charged soot particles causing a significant change in the soot formation process which would interfere with the measurements. Combined laser light scattering and absorption measurements will be used to characterize the soot particles, in situ, in the flame. Soot particle diameters and number densities as well as soot volume loadings will be measured. The effect of ion concentrations on these parameters and, thus, on the nucleation and agglomeration processes will be determined.

In Task II the Combustion Products Test Chamber (CPTC) at Georgia Tech (Fig. 1) will be used to obtain data on the physical and chemical characteristics of smoke particulates emitted by various polymeric materials. Physical data obtained from laser light scattering and attenuation measurements will be the diameters, effective refractive index, and volume fractions of smoke particles obtained under both smoldering and flaming conditions. Also, the effect of ventilation gas temperature on the smoke physical characteristics will be determined. These data will allow one to estimate the loss of visibility caused by the materials when involved in

accidental fires. The chemical composition of the smoke particles will be obtained by GC/MS analysis of extracted samples. Emphasis will be on the identification of toxic and corrosive compounds in the smoke particles.

In Task III the short and long term corrosive effects of the exhaust gases and particulates generated under Task II on various structural and electrical conductor materials will be investigated. The target materials will be exposed to the combustion products in a corrosion test section (CTS) installed above the CPTC sampling section (Fig. 2). Corrosion rates, changes in tensile strength or electrical conductivity, and type of corrosion will be determined for the target materials. These corrosion measurements will be carried out immediately after the fire exposure period as well as during a post-fire period lasting up to several months during which the samples will be stored in a controlled environment.

In the remainder of this report a brief summary of the accomplishments during the first nine months of this project will be given.

Ions in Soot Formation (Task I) An opposed flow diffusion flame burner inside an enclosure has been designed. Construction has almost been completed. The enclosure, which is fitted with windows for optical access, will permit the flame to be established under conditions of reduced pressure. The burner will be rotatable about its central axis to permit absorption measurements to be carried out at various angles. This is necessary to allow deconvolution of the absorption signal using a tomographic technique. A device has been designed and is currently being built which will allow the ionization probe to be positioned remotely from outside the enclosure.

Preliminary tests have been carried out on an existing counter flow diffusion flame burner at atmospheric pressure. The applicability of the theory to be used to determine the change in ion concentration induced by the probe as a function of applied voltage and ion mobility has been confirmed. Temperature measurements have been carried out using fine, coated thermocouples and preliminary absorption measurements have been made in the atmospheric pressure flame. The effect of introducing the probe into the flame upon the soot formation process has been quantified. This effect was found to be due mostly to a catalytic effect of the probe material.

Smoke Characterization (Task II). The combustion products test chamber and measurement systems had been inactive for approximately two years prior to the initiation of this work. Therefore, these facilities were refurbished and improved during the first six months of this project. Additional modifications of the upper stack section were also accomplished during this period. These were necessary in order to accommodate the corrosion test section of Task III and another test section required by another concurrent project. These modifications required considerable new design and shop work. A system of pulleys and counterweights was also installed in order to support the heavy upper stack section when the two test sections are being interchanged.

During the third quarter of the project two specimens of a composite material were received from the sponsoring agency. This material is a woven carbon fiber composite with a bismaleimide binder. A sample of this material was tested in the CPTC to obtain pyrolysis products for chemical analysis. A thin slab of the material (7.6 x 7.6 x 0.32 cm) was exposed to a radiant flux of 5 W/cm without a pilot flame in room temperature ventilation air (425 liters/min flow rate). The horizontal sample orientation was used in this test. Sampling was accomplished using two glass fiber filters in series with a sampling rate of 28 liters/min. The test required sixty minutes with a four minute heating period before any smoke was visible. Peak light scattering and optical density occurred at 10 minutes with a slow decline in smoke production thereafter. The smoke appeared white like cigarette smoke and seemed to be issuing from cracks in the surface. Nearly 15% of the original sample mass was evolved as gases and particulates during this test. About 18.9 mg of a yellow-brown tarry liquid was collected on the first filter, while only 0.4 mg was collected on the second filter. Approximately 7% of the mass lost during this test appeared as particulates.

The collected samples were subjected to analysis by gas chromatography and mass spectroscopy (GC/MS). At this time a preliminary report on the analysis has been received from the Georgia Tech Research Institute (GTRI) personnel who performed the analysis. About 20 high molecular weight compounds have been identified, and about 20 more remain to be identified by manual interpretation. Most of these compounds are polycyclic aromatic hydrocarbons (PAH) with molecular weights ranging from 280 to 360. Many of the remaining compounds are nitrogen containing substances, both heterocyclic and acyclic. Most of these compounds possess varying degrees of toxicity or carcinogenicity.

The four most abundant compounds thus far identified are:

N-Prop-1-ene-3-(methylphenyl) acetamide (59,400 ppm)
5-Methoxy-6-methyl--2-phenyl-7H-1-benzopyran-7-one (18,800 ppm)
6-Hydroxy-1,2-naphtalenedione (18,200 ppm)
2-Methyl-N-phenylbenzamide (14,800 ppm)

The presence of large quantities of methylphenyl-acetamide suggests that the binder actually consists of a methylphenyl-maleimide. It should also be noted that the benzopyran is a particularly toxic material.

Future plans call for additional tests of this material. The above test will be repeated with cascade impactor sampling and laser scattering and attenuation measurements to determine the particle size distribution and mean particle diameter. Tests at higher radiant fluxes, tests under flaming conditions, and tests with heated ventilation air will also be conducted.

Smoke Corrosivity (Task III). A corrosion test section (CTS) was designated and the shop drawings prepared during the first quarter of the project. This section consists of a 28 cm section of 21 cm diameter stainless steel pipe fitted with access ports and a view port. A revolving specimen rack within the CTS gives uniform exposure of the target materials to the combustion products during a fire test in the CPTC. At the time of this report the CTS was still in the shop, but it is expected to be completed shortly.

Reports and Papers:

Three quarterly reports were submitted to the sponsor.

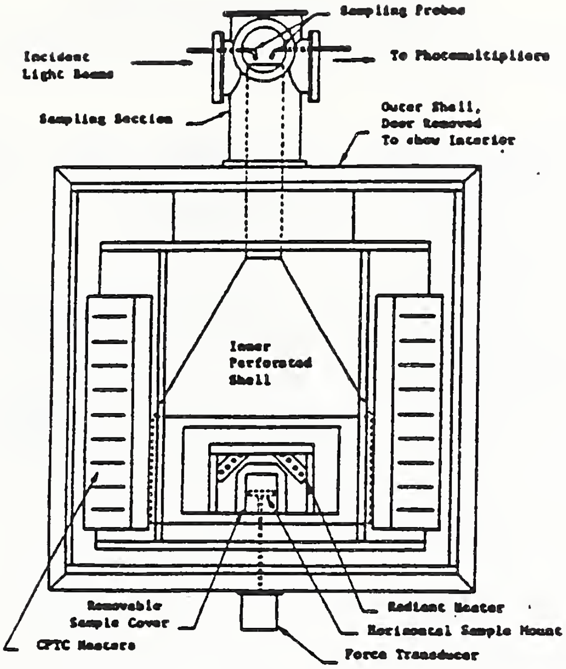


Figure 1. Combustion Products Test Chamber

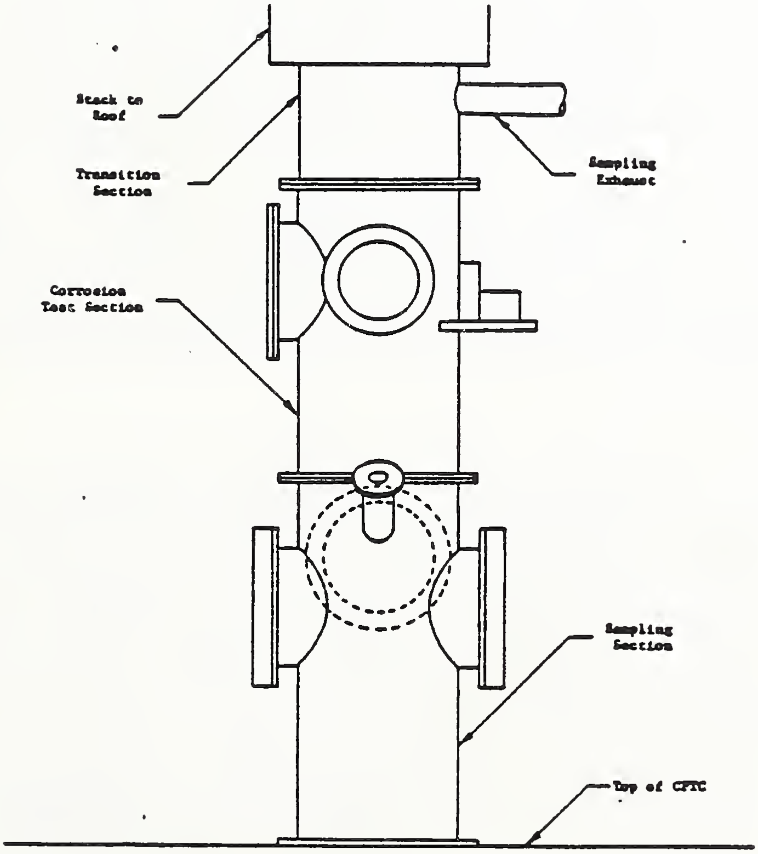


Figure 2. Location of Corrosion Test Section

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution:	The Pennsylvania State University
Grant No.:	60NANB7D0706
Grant Title:	Soot Particle Formation and Destruction in Diffusion Flames
Principal Investigator:	Dr. Robert J. Santoro Department of Mechanical Engineering 313A Mechanical Engineering Building University Park, PA 16802
Other Professional Personnel:	T. F. Richardson, Pre-Doctoral Student
NBS Scientific Officer:	Dr. Kermit C. Smyth

Technical Abstract:

Introduction. The present study focuses on soot particle formation and destruction processes in laminar diffusion flames. The objective of this study is to provide an understanding of the effects of soot particle formation which impact fire growth, spread and combustion product emissions. The approach adopted emphasizes two elements of the problem. The first element concentrates on the processes responsible for the conversion of fuel carbon to soot and particularly stresses the importance of fuel molecular structure. The second element examines the destruction stage of the process which reduces the soot concentration in the later parts of the flame. In particular, specific information on the relationship between soot and CO production is sought. A basic thrust of the work is to identify the overall mechanism relating the emissions of CO and soot particles from flames if one does exist. In addition, fundamental information on soot oxidation processes as well as the role of soot particles in the competition for oxidizing species such as O_2 and OH may be forthcoming.

The results of this study are of direct relevance to the problems of fire research. Soot particle formation and destruction along with other basic phenomena such as ignition, hydrocarbon chemistry, turbulence, radiative transfer and plume dynamics, constitute the fundamental elements of the fire problem. Soot particles, once formed, are not passive species in the evolution of the fire situation. Through their radiative properties, soot particles can strongly enhance flame spread rates or the conditions necessary for "flash over" to occur. Soot particles present other complications through their role in visual obscuration and potential effects on carbon monoxide formation. These effects represent serious problems in terms of victim escape from fire situations and significantly contribute to fire mortality rates. However, with a proper understanding of the fundamental controlling mechanisms significant improvements in the

predictive capabilities of fire science modeling can dramatically improve the present situation.

Present Status. During the first year of the present grant, efforts have concentrated on the assembly and testing of the experimental apparatus. In order to accomplish the objectives of this study, a number of experimental capabilities are required. These include a laser light scattering capability for particle sizing, laser velocimetry for velocity measurements and intrusive probing for temperature and species concentration measurements. Since particle size measurements are critical to understanding the evolution of the soot particle field in flames, emphasis has been given to the laser light scattering apparatus. Figure 1 shows a schematic representation of the laser scattering/extinction system. In addition to the single scattered light detector shown in this figure, light scattering measurements can also be obtained at 45° and 135°. Signal detection from the photodiode (extinction) and photomultiplier (scattered light) systems is accomplished using separate computer controlled lock-in amplifiers. Positioning of the coannular diffusion flame facility is also controlled by the IBM PC/XT laboratory computer using motorized translation stages. This approach allows for a high degree of user independent data acquisition and significantly eases the experimental procedures.

A similar arrangement for the laser velocimetry measurements is now being completed which will also utilize a computer based data acquisition approach. A probe system to obtain CO, CO_2 and O_2 concentration measurements is presently under design. Instrumentation for continuous measurement of these species is presently available using standard on-line techniques (e.g. NDIR for CO and CO_2 measurements). In addition, gas chromatography and mass spectrometry instrumentation is available for more detailed measurements.

The initial flame measurements have concentrated on a series of laminar diffusion flames. These include a study of an ethene/air diffusion flame which has served to validate the laser light scattering measurement system. This particular flame has been well characterized in past studies and provides an excellent comparative data base. Very good agreement has been obtained between these past studies and the present measurements.

In addition to these validation studies, two methane/air diffusion flames have been studied. These methane flames are to serve as baseline reference flames for the fuel molecular structure studies. In these experiments, the various fuel species under study are added to the baseline flame (methane), such that the additional carbon flow rate is held constant. Under this condition, the flame size and shape remain similar for all the flames, thus minimizing changes in burner heat loss or particle transport in the flame. This approach allows fuels of widely varying soot propensity to be studied under similar conditions. The fuels to be studied using this approach include acetylene, butane, butene, butadiene and toluene. These fuels represent a systematic variation in molecular structure while also providing a comparison between aliphatic and aromatic structures. Specific attention will be given to fuel structure effects on particle inception and surface growth processes.

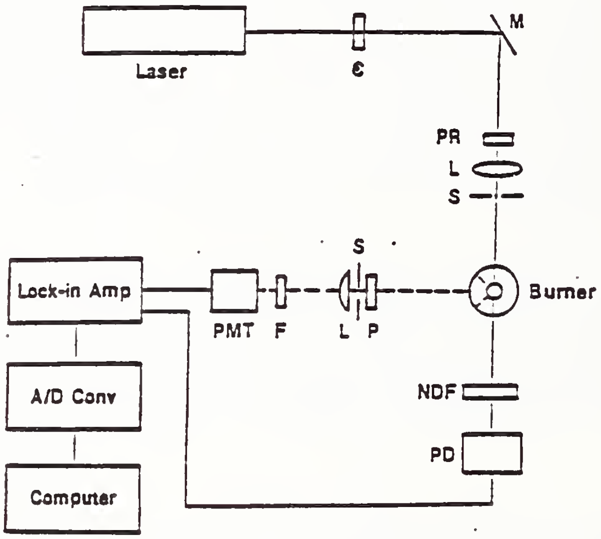
Complementary velocity and temperature field measurements will also be obtained to further characterize the particle growth and oxidation processes. These measurements are being coordinated with related diffusion flame measurements underway in the Center for Fire Research. With the completion of the gas sampling system gas phase species measurements will also be obtained to characterize CO production in these flames. In this phase of the study emphasis will be given to the oxidation processes which significantly reduce soot particle concentration.

As describe above the objective of this study is to provide a detailed understanding of soot particle formation and destruction processes. By undertaking these studies in a well defined and tractable flame environment, fundamental insights into the processes controlling soot particle phenomena and their relationship to other flame emission products can be obtained.

Reports and Papers

1. R. J. Santoro and J. H. Miller, "Soot Particle Formation in Laminar Diffusion Flames", Langmuir, March/April, 244-254, (1987).

Laser Scattering/Extinction System



C - chopper, M - mirror, PR - polarization rotator, L - lens, S - spatial filter
NDF - neutral density filter, PD - photodiode, P - polarizer, F - narrow band filter,
PMT - photomultiplier,

Figure 1

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of Maryland

Grant No.: 60NANB6D0633

Grant Title: Characterization of Large Scale
Turbulent Structures
in Variable Density Flows

Principal Investigator: Professor James M. Wallace
Department of Mechanical Engineering
University of Maryland
College Park, MD 20742

Other Professional Personnel: Dr. Kin C. Muck
Engineering Consultant
University of Maryland
College Park, MD 20742

NBS Scientific Officer: Dr. William M. Pitts

Technical Abstract:

Introduction. The objective of this program is to develop a state-of-the-art diagnostic tool which permits simultaneous, multi-point measurements of concentration and velocity in binary gas mixtures. This complex experimental technique combines laser-induced Rayleigh light scattering measurement of concentration along a line in the flow field and a multi-probe linear array of hot-wires designed to provide velocity measurements. The technique will be used to generate detailed quantitative information concerning the role of large scale structures in turbulent entrainment. The experimental data generated is expected to provide much needed information on the effects of density variations on the turbulent mixing process. Such results will be useful to workers who are attempting to develop numerical models to predict turbulent mixing between two gases in either momentum-driven or buoyancy-driven flows.

Experimental Technique. Previous work at NBS has demonstrated that laser-induced Rayleigh light scattering and hot-wire anemometry techniques can be utilized to make simultaneous, real-time point measurements of concentration and velocity in variable density flows [1]. The present program is designed to extend these techniques to multi-probe capability so that the velocity and concentration fields can be mapped out simultaneously at many spatial locations along a line within the flow field.

The present integrated system is composed of two synchronized subsystems. They are the laser-induced Rayleigh scattering line-scan camera system for concentration measurement (which has been developed at NBS by Dr. Pitts [2]), and a linear array of seven hot-wire probes for velocity measurement. Figure 1 shows a schematic of the overall system.

The line-scan camera system consists of a f/1.9 lens designed for 1:1 focusing, an image intensifier, a 4:1 reduction fiber optic taper, and a Reticon RL128SF line scanner equipped with RC1024S-1 evaluation circuitry. The system scans a 12.8 mm length of the focused laser beam (diameter > 50μm). The Reticon video detector has 128 pixels. TTL pulses are generated by the line scanner circuitry, which indicate both the start of a line read-out and pixel advance. An interface constructed in-house synchronizes the Nicolet 1180 data acquisition system and the line camera so that the sampled and held video signal can be digitized and stored in dynamic memory. The digitizer has twelve bit resolution, millivolt sensitivity and a maximum data rate of 333 kHz. Memory limitations of the Nicolet computer currently restrict the number of lines which can be scanned to 256 during a single run.

The hot-wire system is composed of seven hot-wire probes in a linear array, seven TSI constant temperature anemometers, and a data acquisition system made up of a Metrabyte DASH16 expansion board and an IBM PC XT computer. The hot-wire array was fabricated utilizing the techniques and facilities developed at the University of Maryland. It is designed such that simultaneous measurements of concentration and velocity are obtained at seven locations along a focused laser beam observed by the line camera (see Photograph 1). These probes are produced by spot-welding short lengths ($\approx$0.8mm) of tungsten wires (5μm diameter) to sharpened tungsten needles which are electro-plated with nickel. The tungsten needles are held in place by ceramic tubes and secured using epoxy resin. Initial phase of the program was confined to using (normal) hot-wires to record the axial velocity component only. The DASH16 board utilizes a 12 bit successive approximation A/D converter with 12 microsecond conversion time. A maximum throughput of 50 kHz is possible via the DMA mode of the IBM XT. The present set-up uses seven differential channels with a bipolar range of +/- 5 Volt. The maximum sampling rate possible with the current set-up is about 7 kHz per channel.

Synchronization of the line camera system and the hot-wire system is achieved through home designed TTL control and timing interfaces. For the present setup, the line camera provides 256 scans per data file, giving 256 x 7 samples of hot-wire data per file. A communication link allows transfer of data files between the Nicolet computer and the IBM XT computer for subsequent analysis.

Calibration Procedures. The hot-wires were calibrated according to King's Law (i.e. $E^2 = A + B\, U^{.43}$) for the velocity range 1 m/s to 15 m/s. Each wire was calibrated at nine different known mixtures of propane and air such that a smooth variation in B with concentration could be fitted to a second degree polynomial. The calibration constant A was found to be insensitive to concentration. The overheat ratios for the individual wires were close to 1.8 and the average frequency response was 13 kHz.

During the course of calibrating the hot-wires, it was discovered that by scaling and normalizing the values of B (which are different for different wires) as a function of concentration, it is possible to derive a universal polynomial fit for the variations in B with concentration. This finding suggests that a vastly simplified calibration procedure can be employed, which only requires that each wire be calibrated at the pure gas conditions. This new calibration procedure is being evaluated further.

The line-scan camera system is calibrated by recording the Rayleigh light scattering intensities from pure gases before each run.

Experiment. As a demonstration of the new diagnostic system, an experiment was conducted to investigate the mixing behavior of a turbulent axisymmetric jet of propane flowing into a slow coflow of air (about 0.16m/s). Simultaneous measurements of concentration and velocity were made along a line aligned along the radial direction. In addition to providing a severe test for the new experimental system. this experiment also offered an opportunity to study the entrainment properties of the large scale structures in a turbulent flow with density variations. The diameter of the jet nozzle was 6.35 mm, and the Reynolds number was 3960. Additional details cocerning the flow and optical systems can be found in reference [3]. An Argon ion laser (15 W, 488 nm) was used. The hot-wires were located about 2 mm downstream of the laser beam. This separation between the laser beam and the hot-wires is accounted for by the inclusion of a lag or delay time when reducing the hot-wire results using the concentration data.

Sample Results. Figure 2 shows an example of the simultaneously recorded time traces of axial velocity, U, and mole fraction, X, at $z/r_0 = 22.05$, $r/r_0 = -3.74$ and recorded at 358 Hz. Significant correlation of concentration variations and the fluctuating velocity is seen. Careful study of such records has revealed frequent occurrence of pockets of fluid with high concentration but with low velocity excursion. This observation is probably related to the common observation that in the mean, the concentration profile of a jet is wider than its velocity profile.

Figure 3 shows time averaged velocity and concentration profiles respectively for the normalized axial distance of $z/r_0 = 22.05$. Two different sampling frequencies were used. Scatters of about 10% are seen. This is attributed to the relatively short data records. The reasonably smooth variation in the mean velocity profile offers some degree of confidence on the proper working of the present technique.

Measurements at locations further downstream were also obtained. Both U_0/U and X_0/X (subscript $_0$ denotes conditions at the nozzle exit) at the jet centerline are found to increase linearly with axial distance. The hyperbolic fall-off behavior of concentration and velocity is typical of such flows.

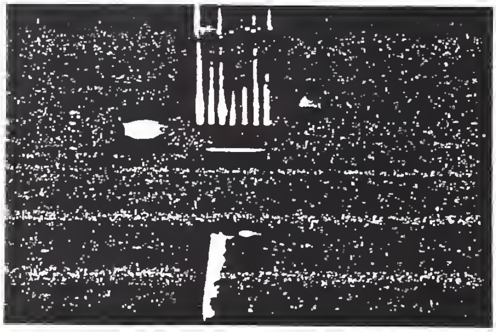
Conclusion. The preliminary set of tests show that the present experimental technique is capable of providing multi-point real-time simultaneous measurements of concentration and velocity in turbulent flow systems. When coupled with sophisticated conditional sampling analysis techniques (to be developed in the future), this new diagnostic technique will be a powerful tool for studying the entrainment and mixing properties in turbulent flows. This technique is applicable to a wide range of flows where the complicating effects of density variations or buoyancy are present.

References

1. Pitts, W. M., McCaffrey, B. J. and Kashiwagi T., "A New Diagnostic Technique for Simultaneous, Time-Resolved Measurements of Concentration and Velocity in Simple Turbulent Flow Systems," paper presented at the Fourth Symposium on Turbulent Shear Flows. Karlsruhe, W. Germany (Sept. 12-14).

2. Pitts, W. M., "Development of a Line Camera for Real-Time Measurements of Concentration in Turbulent Flow Fields." The 5th International Congress on Applications of Lasers and Electro-Optics Technical Digest, 1986.

3. Pitts, W. M. and Kashiwagi, T., "The Application of Laser-Induced Rayleigh Light Scattering to the Study of Turbulent Mixing," J. Fluid Mech. Vol.141, pp. 391-429, 1984.



Photograph 1. Arrangement of the hot-wire array with respect to the laser beam.

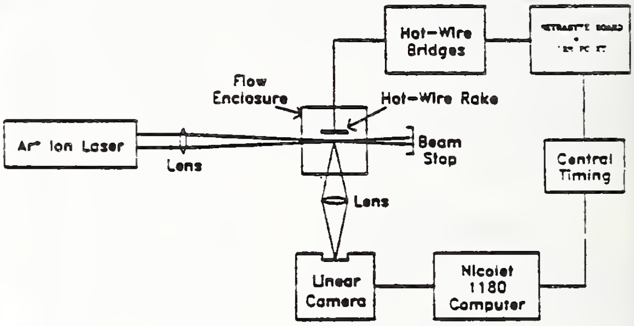


Figure 1. Schematic of the apparatus lay-out.

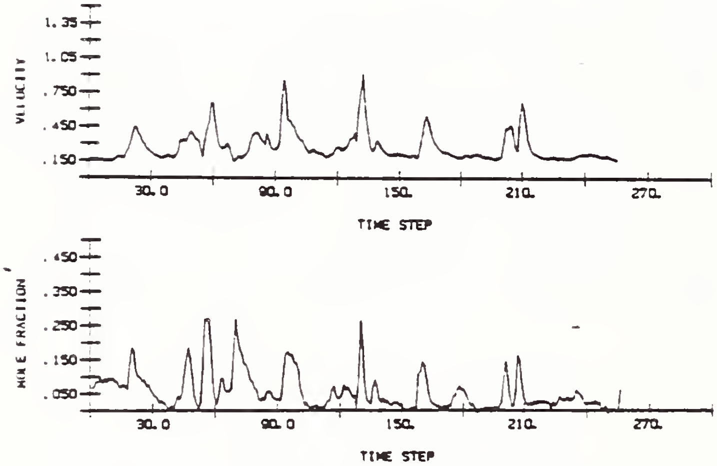


Figure 2. Simultaneously recorded time traces of the axial velocity and concentration.

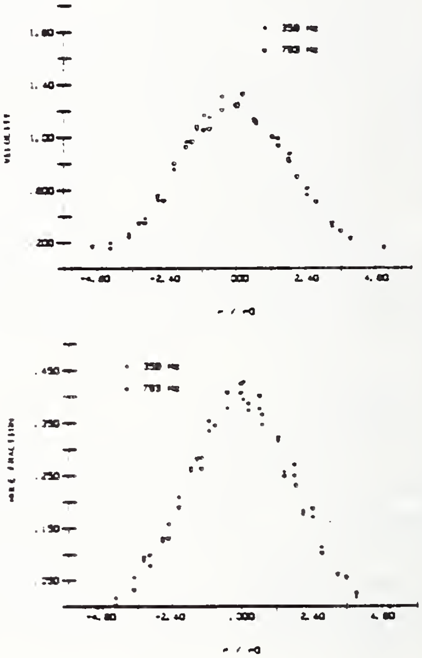


Figure 3. Radial profiles of the mean velocity and concentration at $z/r_0 = 22.05$.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: The University of Maryland (College Park)

Grant No.: 70NANB5H0517

Grant Title: Kinetics of Agglomerate Formation

Principal Investigator: Professor James W. Gentry
Department of Chemical & Nuclear Engineering
University of Maryland
College Park, MD 20742-2111

Other Professional Personnel: Mr. Roberto Samson, Graduate Fellow
Mr. Thomas Cleary, Graduate Fellow

NBS Scientific Officer: Dr. George Mulholland

Technical Abstract:

Introduction. The objectives of this study are to relate the properties of aerosols consisting of clusters formed from combustion with the operating variables of the burner. Specifically, the study focuses on the diffusion coefficient and aerodynamic diameters of the soot agglomerates. We plan to measure these properties of the clusters and relate them to their physical structure as determined by electron microscopy.

The study represents a continuation of the work of Roberto Sampson(1). The 'fractal dimension' of soot clusters was computed using four different computational models and the mass concentration of soot was related to the hydrocarbon fraction in the fuel. The data on the clusters obtained from electron micrographs were consistent with the clusters being fractals.

The study described here is a continuation of this work. It focuses on the in-situ measurement of the diffusion coefficients of the clusters. Described in this paper are the experimental design, the analysis of data, and the preliminary experimental measurements.

Experimental Design. The diffusion coefficient (D) of particles in a gas can readily be obtained by measuring the particle concentration before and after long, circular tubes (length L_t and diameter d_t) as a function of flow rate (Q). It is assumed that the collected particles are fixed on the walls of the channel and that the flow in the tubes is laminar. The fractional penetration is given by closed form expressions in terms of a single variable (the reciprocal of the Peclet number). This variable for a circular cluster of channels (diameter d_A and porosity ε) is given by

$$\phi = \pi \varepsilon \left(\frac{d_A}{d_t}\right)^2 \frac{L}{Q} D$$

The diffusion coefficient is the product of two terms the Stokes-Einstein diffusion coefficient and the Cunningham correction for non-continuum effects. For spherical particles D is approximately equal to

$$D = \left(\frac{kT}{3\pi\eta d}\right)\left(1 + \frac{0.2}{d_p\,(\text{microns})}\right)$$

For clusters and indeed for non-spherical particles in general, the analogous expressions are not known.

An experimental difficulty in diffusion coefficient measurements is that the functional relation between the penetration and has two dissimilar zones. For large ϕ ($\phi > 0.2$) the separation is sharp and the diffusion battery is an excellent instrument. For small ϕ ($\phi < 0.05$) the separation is broad and the instrument is not effective in determining size distributions.

The glass capillary array design(2) used in this study is suitable for diffusion coefficients between 3×10^{-3} and 7×10^{-6} cm^2/sec. These values correspond to spherical particles between 4 and 400 nm. The battery consists of 4 to 6 stages which can be placed in line either individually or grouped. Flow enters a circular chamber approximately 5 cm in diameter and 2 cm in height through the side of the chamber. The flow passes through the GCAF at the bottom of the stage. The penetration is determined as the ratio of concentrations through the filter and through a blank stage. The particle concentration is measured with a TSI continuous flow condensation nuclei counter.

Data Analysis. Measurements of the diffusion coefficients of clusters present two classes of problems - the aerosol is polydisperse and the aerosols are not isometric. The difficulty of the second type is that the signals in measurements are frequently ambiguous. We have developed two procedures or algorithms which can be applied to the analysis of clusters. The first procedure designed for measuring polydisperse aerosols requires measurements of the fractional penetration or collection efficiency over a wide range of penetrations. The method called the apparent size method(3,4) has been successfully applied to narrowly distributed combustion aerosols, particles with adsorbed layers of hydrocarbons, and the electrical mobility of asbestos fibers where the data are limited to the size distributions before and after the filter. The analogs in the case are the clusters before and after the diffusion battery.

The apparent size (diffusion coefficient) method is based on a plot of the apparent size as a function of experimental penetration. The apparent size is the diffusion coefficient of a hypothetical, monodisperse distribution whose fractional penetration computed from theory or empirical correlations matches the experimental value of penetration at the same conditions (i.e. flow rate). This formulation has three advantages over alternative approaches:

(1) It provides a sensitive, graphic display of the degree of experimental error and provides an indication of systematic errors.

(2) The mean value of the curve $< \text{Ln}\,\bar{D} >$ is the log mean diffusion coefficient of the distribution. This remarkable result for $< \text{Ln}\,D >$ is an experimental result independent of an assumed functional form for the distribution while the log mean diffusion coefficient depends only on the size

distribution function.

(3) The intercept as the penetration approaches one is proportional to the variance.

The unambiguous determination of two parameters is an efficient procedure for characterizing the size distribution of an aerosol and the relation of its properties to combustion variables.

The second algorithm supposes that the size distribution before and after the diffusion battery and the overall penetration are known. The principal idea is that the penetration $Pt(X_a)$ at a size X_a can be expressed by

$$Pt(X_a) = \frac{\left(\sum_{i}^{N} h(x_i - x_a, \lambda)\right)_{\text{after}}}{\left(\sum_{i}^{N} h(x_i - x_a, \lambda)\right)_{\text{before}}}$$

where $h(y,\lambda)$ is a non-negative function equal to 1 at $y=0$ and collapsing to a δ-function for an asymptotic value of λ. The representation includes the commonly used histogram method as a special case.

Its advantages are that it can be used with small samples. It can also be used with particles characterized by multiple variables such as asbestos fibers (diameter and length) or clusters (number of primary particles and radius of gyration).

Experimental Results. Described in the paper are the measurements of the diffusion coefficients and 'aerodynamic diameters' of soot clusters formed from the combustion of ethane and acetylene. The cluster size - number of primary particles - was found to depend on the hydrocarbon composition of the fuel. By controlling the fuel composition the combustion aerosol could pass through the entire range from detectable, but not visible, to the long sooty threads associated with acetylene combustion. In the diffusion battery work discussed here, the focus is on the smaller particles.

The base experiment consists of combustion in a diffusion burner. The aerosol is diluted and passed through (i) an inertial impactor stage and/or (ii) a diffusion battery stage. The penetration is the ratio of aerosol concentration through a GCAF disc and a blank stage. The aerosol concentrations were measured with a condensation nuclei counter. Experimental measurements without the impactor stage could cover the range from their formation to approximately 0.1 μm.

One thrust of the experiment is to determine the drag on the clusters. In a prior study the fractal dependence of such small clusters was measured by electron microscopy. If the drag had a (-1/F) dependency with the number of primary particles rather than (-1/3) one would expect to see a significant decrease in the mean diffusion coefficient and an increase in the variance for relatively small clusters.

Diffusion coefficients measured as a function of flow rate as well as limited measurements with electron microscopy are reported.

Reports and Papers:

I. Journal Articles, Book Chapters, etc.

1. Samson, R.J., G.W. Mulholland and J.W. Gentry, "Structural Analysis of Soot Agglomerates", Langmuir, 3, 272 (1987).

2. Samson, R.J., G.W. Mulholland and J.W. Gentry, "Analysis of Soot Agglomerates and Their Physical Properties", Aerosols: Formation and Reaction, ed. H. Fissan, Pergamon, 413-16 (1987).

II. Technical Presentations

1. Cleary, T., R. Samson, G. Mulholland and J. Gentry, "The Relationship Between Structure and Aerodynamic Measurement for Clusters", presented at GAeF Annual Meeting, Hanover, BDR, Sept. (1987).

2. Samson, R.J., G.W. Mulholland and J.W. Gentry, "Analysis of Soot Agglomerates and Their Physical Properties", 2nd International Aerosol Conference, Berlin, Sept. (1986).

3. Samson, R.J., G.W. Mulholland and J. Gentry, "Structural Analysis of Soot Agglomerates", Symposium on Fine Particles: High Temperature Synthesis, Atlanta, GA, June 15-18 (1986).

III. Other Reports

1. Gentry, J., G. Mulholland, R. Samson and T. Cleary, "Methodology for Fractal Analysis of Combustion Aerosols and Particle Clusters", Aug. (1987).

2. Samson, R., M.Sc. Thesis, University of Maryland (1986).

FIRE SCIENCE AND ENGINEERING DIVISION

ENGINEERING METHOD DEVELOPMENT
CENTER FOR FIRE RESEARCH
FY 87

Professional Personnel

Harold E. Nelson, Senior Research Engineer
Peter Lee, Cooperative Student

Program Objectives

To expedite the transfer of scientifically-based technology instruments to the practicing fire protection engineering community and similar groups.

Scope

The work addresses the development of engineering systems for design application and the demonstration of the feasibility through examples of use. The prime examples of use to date have been in fire incident reconstruction.

Activities

There are two principle activities.

A. Fire Protection Hazard Analysis and Facility Assessment System

This is a three-year project currently sponsored by NBS and the General Services Administration to develop rational engineering methods. The methods are designed to be usable by practicing fire protection engineers in appraising fire safety of buildings and evaluating the impact of specific design proposals for improving fire safety.

A prime tenant of this project is to develop the least sophisticated, fastest responding analysis procedures that produce an adequate and dependable analysis of fire hazard impact. Many of the procedures being incorporated are built around algebraic computations and simple fire growth models. Factors of safety are being included to compensate for the uncertainties involved. The initial scope addresses the development and growth of fire and fire products in any one story of a subdivided building, including leakage from that floor into other space (such as stairwells). It considers pre- and post-flashover fires, fire detection, sprinkler response, emergency evacuation, and areas of refuge.

The program disk FIREFORM presents a portion of the routines involved.

B. Fire Incident Reconstruction

Where appropriate, the procedures for the engineering analysis system are being tested and demonstrated in analysis and reconstruction of fire hazard incidents. To date, two such analyses have been made, one has been reported, a paper on the other is in clearance.

These two fires were the December 31, 1986 fire in the Dupont Plaza Hotel in San Juan, Puerto Rico and the December 15, 1985 fire in a hospice in southern Michigan. Both fires involved violent flashovers that produced excess pyrolysis conditions. In the case of the Dupont Plaza, the amount of combustible pyrolysis products transported from the room of origin was massive (estimated in the range of 6-7,000 g/s). As these products vented, they found air and converted to flame. In that fire, the majority of the deaths occurred as the occupants were swept by this flame.

Conversely, in the hospice fire, the fire vented to the outside and into an internal corridor that essentially had no vents to the outside. In this latter case, venting to the outside maintained the temperature in the room of fire origin keeping the rate of pyrolysis high. That vented into the corridor, however, appeared to quickly consume the available oxygen and move the combustion reaction sharply towards carbon monoxide. It is believed that very high concentrations of carbon monoxide (probably in excess of 50,000 parts per million) quickly invaded those other patient rooms open to the same corridor.

In late summer of 1986, a test was conducted in the NBS corridor to approximate the conditions believed to have occurred in the hospice. Figure 1 is a plan of the test corridor. The fire (5 MW propane burner) was positioned in the space immediately adjacent to the hood. This sustained flashover. The fire was continued until a steady state in both temperature and carbon monoxide production occurred in the corridor. Data was taken in each of the rooms. Figure 2 is a plot of the rate of energy release that occurred in the fire and the conditions that occurred in the most remote room. These readings demonstrate the consumption of oxygen, the production of carbon monoxide, the drop of the interface, and the relatively low rise in temperature. This appears to be very indicative of the type of conditions likely to occur in small to modest size corridors exposed to a flashed over room that in turn is vented to the outside.

Publications

Nelson, H.E., An Engineering Analysis of the Early States of Fire Development - The Dupont Plaza Hotel and Casino - December 31, 1986, NBSIR 87-3560, 1987.

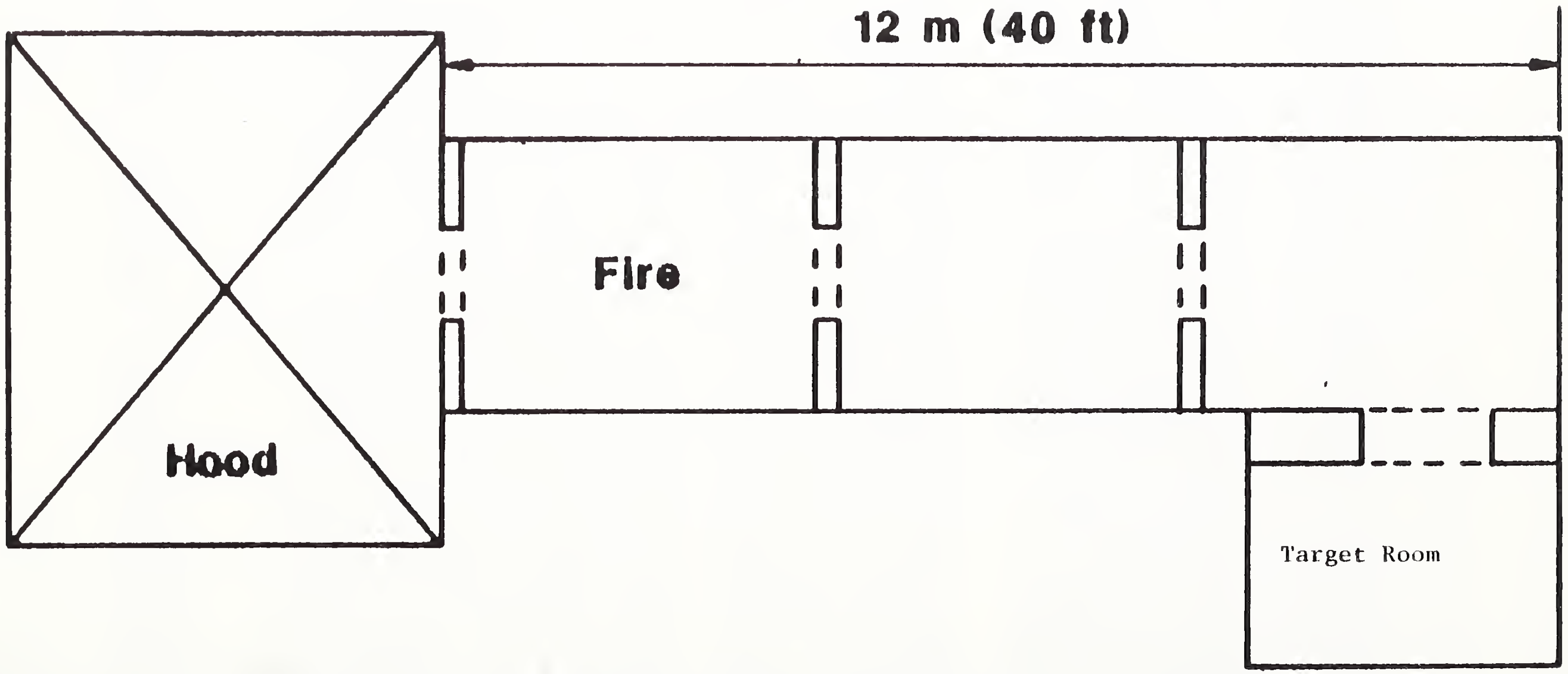


Figure 1. NBS Test Corridor (As Configured for Test)

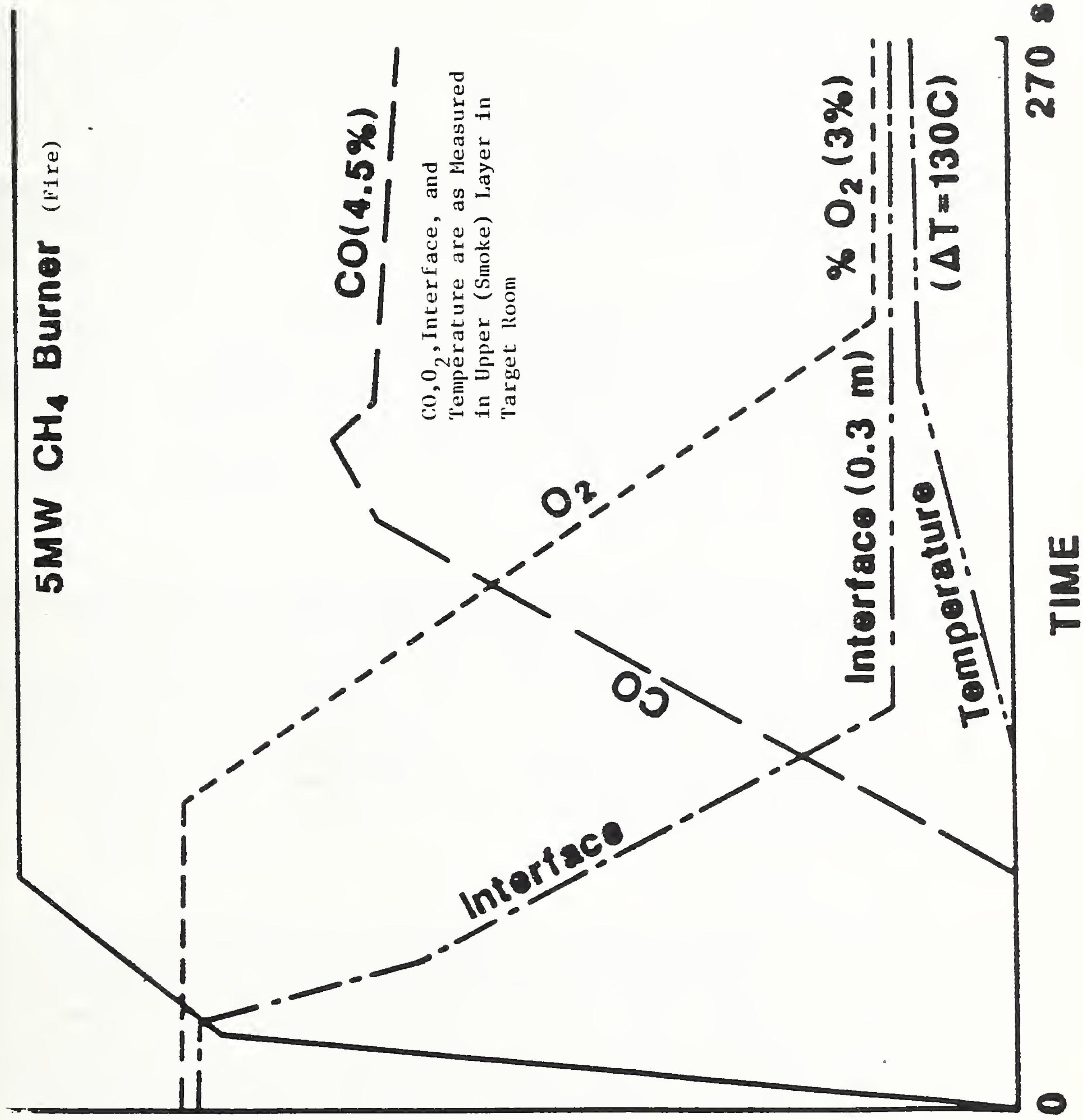


Figure 2. Test Results

COMPARTMENT FIRE MODELING RESEARCH
CENTER FOR FIRE RESEARCH
FY 87

Professional Personnel

Leonard Y. Cooper, Head
Henri E. Mitler, Physicist
John H. Klote, Mechanical Engineer
William Davis, Physicist
Glenn P. Forney, Computer Scientist
Kevin Greenaugh, General Engineer
Vahid Motevalli, Guest Worker (Univ. of Maryland)

Program Objectives

(1) Develop, maintain, improve and provide assistance in the use of Compartment Fire Model computer codes.
(2) Develop and establish the validity of new and improved analytic/computational compartment-fire-phenomena submodel algorithms for use in compartment fire simulations.
(3) Develop, maintain, and enrich a catalog of well-documented submodel algorithms and subroutines for general use in compartment fire models.

Scope

The work focuses on the development of benchmark computer codes(s) which would be useful in simulating the phenomena which occur in compartment fire scenarios. The term "benchmark computer code" is intended to connote a well-documented computer code which: a) is based on physics and numerics of proven reliability; b) is numerically robust; and c) is user-friendly in the sense that it can be used with relative ease by researchers and professional fire safety practitioners, and that it can be transferred to and used with computer hardware readily available to the fire science/technology community.

Projects and Recent Publications

1. Compartment Fire Models

The Consolidated Compartment Fire Model (CCFM) Computer Code. The main focus of the Group is to develop generic and applications-specific software for a well-documented, user-friendly, modular and easily updated CFR Consolidated Compartment Fire Model (CCFM) Computer Code. This software will be used to implement applications of the CCFM which address particular needs of CFR and the Fire Science and Technology communities. CCFM development will be based on and will consolidate the advances of the past decade of progress in zone-type compartment fire modeling research, and it will incorporate the most advanced available Computer Science technology. The code will pass through a series of useable development stages to be designated as CCFM applications. The first of these is a prototype application CCFM.HOLE. This code simulates the environment which develops during a fire in a single constant area room with a single, arbitrarily placed, near-uniform-elevation vent, or horizontal slit, of arbitrary area. Arbitrarily high room pressures are allowed, e.g., fire in a hermetically sealed compartment. The second CCFM application will involve a multi-room code, and it is planned that subsequent CCFM advances will build on this.

FIRST. This NBS code is a consolidation of several adanced versions of the original, single-room Harvard 5 code. The code was completed this year and is being issued with a Users' Guide. FIRST will be used as a testbed for new fire-growth algorithms which are now under development. It is also being used as a working tool for carrying out single-room compartment fire analyses.

The NBS/Harvard 6 Multi-Room Code. This CFR-enriched, advanced version of the original Harvard 6 code was used to simulate results of previously reported full-scale, multi-room fire experiments. Comparisons between simulated and measured fire-generated environments were reviewed.

A Model to Simulate the Effects of Roof Vents, Sprinklers, and Their Interactions. A new computer code is under development which will be useful in analyzing the responses and effects of roof vents, sprinklers, and their interactions during compartment fire-generated environments.

"Fire Growth in Combat Ships," NBSIR 86-3451, J.A. Rockett.

"The NBS/Harvard Mark VI Multi-Room Fire Simulation," J.A. Rockett and M. Morita, Fire Science Technology, Vol. 5, No.2, 1985, pp 149-163.

"A Plan for the Development of the Generic Framework and Associated Computer Software for a Consolidated Compartment Fire Model Computer Code," G.P. Forney and L.Y. Cooper, NBSIR 86-3500.

"How Accurate is Mathematical Fire Modeling?" H.E. Mitler and J.A. Rockett, NBSIR 86-3459.

"A Program for the Development of a Benchmark Compartment Fire Model Computer Code," L.Y. Cooper, J.A. Rockett, H.E. Mitler and D.W. Stroup, presented at the ASTM International Symposium on Mathematical Modeling of Fires and Related Fire Test Methods, Dec. 3, 1986 and to be published in the Proceedings.

"User's Guide to FIRST, A Prototype Benchmark Single Room Fire Model," H. E. Mitler and J. A. Rockett, NBSIR 87-3595.

"The Compartment Fire-Generated Environment and Smoke Filling," L.Y. Cooper, to be published in the Fire Protection Engineering Handbook.

"Comparisons of NBS/Harvard VI Simulations and Full-Scale, Multi-room Fire Test Data," J.A. Rockett, M. Morita, and L.Y. Cooper, NBSIR 87-3567, and submitted for outside publication.

"Fire in a Room with a Hole: A Prototype Application of the Consolidated Compartment Fire Model (CCFM) Computer Code," Cooper, L.Y. and Forney, G.P., presented at the 1987 Technical Meeting of the Eastern Section of the Combustion Institute and published in the Proceedings.

2. Compartment-Fire-Generated Flow Dynamics, Flame Spread/Growth and Heat Transfer: Submodel/Algorithm Development and Verification.

The purpose of this project area is to carry out research toward an understanding of compartment fire phenomena which are critical to the advancement of newly developing compartment fire models. The critical objective here is to develop results which can be expressed in the form of concise algorithms and associated modular computer subroutines which are readily useable in zone-type compartment fire model computer codes, in general, and in the CCFM, in particular.

Flow Dynamics, Heat Transfer, and the Response of Fire Safety Devices. This work involves experimental and theoretical activities leading to the development and validation of algorithms for simulating compartment fire-generated flow dynamics and heat transfer and the response of fire safety devices to the fire-generated environment. The ability to simulate such phenomena is neccessary for reliable predictions of the compartment fire environment. This is the environment which defines the impact of the compartment on fire growth development and which determines the extent of hazard. Progress has been made in a variety of these areas and this is indicated by the titles in the list of papers and reports which follow below.

Wall Fire Growth. The purpose of this work is to develop and validate experimentally an alogorithm which predicts the fire behavior of a burning wall in a compartment. A first-order model involving steady burning of non-charring solids has been completed and is now being implemented into FIRST.

Smoke Control and HVAC Systems. This work involves experimental and mathematical modeling activities leading toward a capability of simulating the effect of HVAC smoke control systems on the spread of fire-generated environments in multi-room facilities. An algorithm for the simulation of a simple fan-duct subsystem is being developed which will be implemented in a relatively early CCFM application.

Cigarette Fire Safety. A preliminary study on the fire safety of cigarettes has been completed. This work involved the development of mathematical models of the smoldering of cigarettes on furniture. The objective of the work was to use modeling to establish the propensity for furniture ignition of a particular cigarette configuration and furniture composition.

"The Buoyant Plume-Driven Adiabatic Ceiling Temperature Revisited," L.Y. Cooper and A. Woodhouse, Journal of Heat Transfer, Vol. 108, pp 822-826, 1986.

"Thermal Response of Unconfined Ceilings Above Growing Fires and the Importance of Convective Heat Transfer," L.Y. Cooper and D.W. Stroup, Journal of Heat Transfer, Vol.109, pp.172-178, Feb., 1987.

"Measurements of the Transient Temperature and Velocity Profiles in Ceiling Jets," V. Motevalli, C.H. Marks, B. McCaffrey and L.Y. Cooper, presentated at the 1986 Technical Meeting of the Eastern Section of the Combustion Institute and published in the Proceedings.

"Ceiling Jet-Driven Wall Flows in Compartment Fires," L.Y. Cooper, NBSIR 87-3535, to be submitted for outside publication.

"An Experimental Study of the Transient Thermal Response of Unconfined Ceilings Above Fire Plumes," A. Woodhouse, C.H. Marks and L.Y. Cooper, presented in Sessions on Heat and Mass Transfer in Compartment Fires at the 2nd ASME-JSME Thermal Engineering Joint Conference and published in the Conference Proceedings.

"Heat Transfer in Compartment Fires Near Regions of Ceiling Jet - Wall Impingement," L.Y. Cooper, NBSIR 86-3307, presented at the 1987 ASME/AIChE National Heat Transfer Conference and published in Conference Proceedings.

"Test Results and Predictions for the Response of Near-Ceiling Sprinkler Links in Full-Scale Compartment Fires, Cooper, L.Y., and Stroup, D.W., in Division review, NBSIR 87-3633 and to be submitted for outside publication.

"Before the Smoke Clears - Heat and Mass Transfer in Fires and Controlled Combustion," Kennedy L.A., and Cooper, L.Y., Mechanical Engineering, Vol. 109/No. 4, pp62-67, April 1987.

"The Effect of Cigarette Characteristics on the Ignition of Soft Furnishings - Chapter 5: Modeling Ignition," Mitler, H.E, Davis, W., and Day, D., to appear as a NBS Special Publication.

"Computer Model of a Smoldering Cigarette," H.E. Mitler and W.D. Davis, to be presentated at the 1987 Technical Meeting of the Eastern Section of the Combustion Institute and published in the Proceedings.

"Algorithm for the Mass-Loss Rate of a Burning Wall," H.E. Mitler, to appear as a NBSIR and submitted for outside publication.

"A Computer Model of Smoke Movement by Air Conditioning Systems (SMACS)," Klote, J.H., submitted for outside publication.

"The Influence of Vortex Pairs on Mass Transfer by Pulsatile Flow," Klote, J.H., submitted for outside publication.

"An Overview of Smoke Control Technology," Klote, J.H., NBSIR 87-3626 and submitted for outside publication.

"Fire Safety Inspection and Testing of Air Moving Systems," Klote, J.H., to appear as a NBSIR.

"Experiments of Piston Effect on Elevator Smoke Control," Klote, J.H. and G.T. Tamura, presented at ASHRAE Symposium, July 1, 1987, and to be published in ASHRAE Transactions.

"An Analysis of the Influence of Piston Effect on Elevator Smoke Control," Klote, J.H., submitted for outside publication.

Heat and Mass Transfer in Compartment Fires, Cooper, L.Y. and Farouk, B., Editors, Proceedings of four sessions on Heat and Mass Transfer in Compartment Fires in Volume 1 of Proceedings of the 2nd ASME-JSME Thermal Engineering Joint Conference, American Society of Mechanical Engineers, New York, NY, March 23-27, 1987.

"Methods to Calculate the Response Time of Heat and Smoke Detectors Installed Below Large Unobstructed Ceilings," Evans, D.D. and Stroup, D.W., Fire Technology, 22, pp. 54-66, 1986.

"Evaluating Thermal Fire Detection Systems [English Units]," Stroup, D.W., Evans D.D. and Martin, P., NBS Special Publication 712, April 1986.

"Development of an Automated Probe Positioner for Measurements in Fire-Generated Plumes and Ceiling Jets," Stroup, D.W., NBSIR 86-3379.

3. Compartment Fire Model Catalog of Submodel Algorithms and Associated Computer Subroutines

This work involves the maintenance and enhancement, through the development of improved and additional entries, of a Catalog of Compartment Fire Model Algorithms and Associated Computer Subroutines. A first edition of the catalog has been issued and several new entries to be used in the CCFM are under development.

"A Catalog of Compartment Fire Model Algorithms and Associated Computer Subroutines," D.W. Stroup, NBSIR 87-3607.

Associated Grants

Experimental Study of the Environment and Heat Transfer in a Room Fire, Zukoski, E.E., California Institute of Technology.

Negatively-Buoyant and Penetrative Flows Generated in Enclosure Fires, Jaluria, Y., Rutgers - The State University of New Jersey.

Prediction of Fire Dynamics, J deRis - Factory Mutual Research Corporation.

Transient Heat Transfer in Ceiling Jets, Marks, C.H., University of Maryland.

COMPARTMENT FIRE MODEL GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution:	California Institute of Technology
Grant No:	NBS5 60NANB600638
Grant Title:	Experimental Study of Enviornment and Heat Transfer in a Room Fire
Principal Investigator:	Professor Edward E. Zukoski Jet Propulsion Center 301-46 California Institute of Technology Pasadena, CA 91125
Other Professional Personnel:	Professor Toshi Kubota Michael Chobotov, PhD Candidate Stephen Toner, PhD Candidate Richard Chan, PhD Candidate James Morehart, PhD Candidate
NBS Scientific Officer:	Dr. Walter Jones

Technical Abstract:

Introduction. Smoke which is produced by a fire spreading through a building can act to aid in the spread of the flame by the transport of hot and perhaps combustible gas, and can be harmful to occupants because of its temperature and toxicity or because its opacity hinders the rapid movement of the occupants through the building. Under certain circumstances, the combustion of the fuel produced in the fire can occur under conditions in which the concentration of oxygen in the ambient gas is far below normal and a fuel rich mixture can be produced which will burn later in an adjacent space and aid in the spread of the fire. We are interested in developing models for the production and movement of smoke in complex structures and have been studying several fluid dynamic processes which will be described below. These processes are difficult to describe analytically because the flows are turbulent and are strongly influenced by turbulent mixing between streams in which buoyancy forces are predominant and because the chemical processes in turbulent-buoyant flames are not understood completely.

Gravity Currents. We are investigating the flow of hot gas in gravity currents under circumstances which model the flow of hot gas along long hallways or tunnels. Our aim is to understand the influence of heat transfer on the motion of the hot gas and the subsequent

development of the ceiling layer in hallways. Gravity currents in hallways which are both horizontal and inclined up to 30 degrees below the horizontal are being investigated.

Two types of apparatus are being used: the first is a salt water-water facility which is a 2.4 meter long channel with a 15 cm square cross section. This is being used to investigate the dependence of the gravity current parameters on the Reynolds number and the inclination angle, and to determine the nature of the return flow which develops after the gravity current has impinged on a vertical wall closing the downstream end of the channel.

Flow visualization techniques are used to measure the velocity of the head of the current, the depth of the current, and the nature of the return flow. Fluorescent dye techniques are being developed to measure the concentration profiles in the flow and hydrogen bubble techniques, and to determine the velocity profiles.

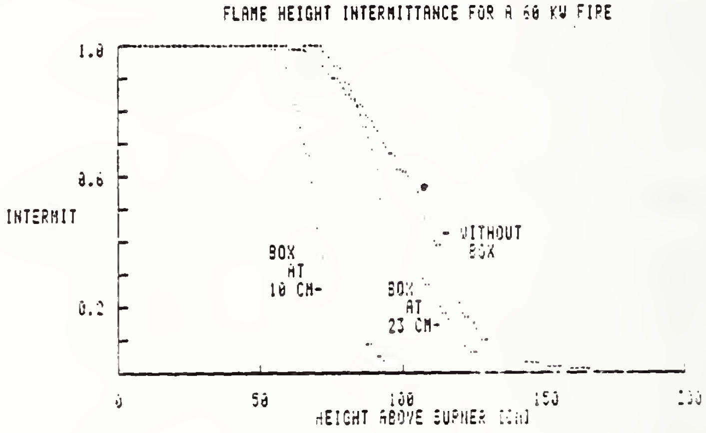
Measurements have shown several interesting features of these flows. First, when the Reynolds number of the current, based on head velocity and current thickness near the head, are greater than 6,000, the effects of Reynolds numbers are small for ratios of hall length to current depth of 100. Thus, for full scale fire situations, the influence of viscosity on the propagation of the current will usually be negligible. Second, the velocity of the head of the current is surprisingly independent of the inclination angle of the hallway over the whole range of angles from 0 to 90 degrees. Third, the return flow in the hallway occurs as a wave on the interface between the current and the ambient fluid which brings the current to a stop at the wave front without violent mixing. For deeper currents, the return flow fills more than 50% of the channel.

Finally, we have found that the depth and frontal velocity of the current are dependent on the method used to introduce the current into the channel. In contrast to the prediction of several idealized flow models that the maximum current depth which leads to a steady flow is helf the channel height, much deeper currents can be formed when the current is introduced with sufficient momentum. This process is being studied now.

The second apparatus is an air facility 8.6 m long and 0.5 m square. This apparatus and the experimental results obtained in it are described in detail in the papers by Chobotov et al and will only be very briefly reviewed here. Experiments in this apparatus have shown that the rate of heat transfer between the current and the ceiling is much higher than rates calculated for forced convection over flat plates because of a buoyancy controlled instability in the wall boundary layer. The rates are high enough to reduce the overheat in the hot gas to very small values within a length corresponding to 50 times the current depth. The effect on the velocity of the head is smaller but the influence of the heat transfer could lead to a strongly stratified hot gas layer in long hallways.

Combustion in Two-Layer Models: We are also studying the products of combustion and flame geometries produced by large buoyancy-controlled diffusion flames which extend from a lower layer, which contains unvitiated air, into a upper layer which contains products of combustion mixed with air. The results of these tests are described in detail in Toner et al (1986) and which give results based on a steady state flow from the plume into the upper vitiated layer.

The influence of the vitiated layer on the flame length has been found to be negligible when the fuel-air ratio of the gases which burned to form the upper layer is less than stoichiometric. However, when the fuel-air is greater than stoichiometric. the flame length decreases approximately as expected because of the reduction in the heat released in the flame.



Typical data are shown in the accompanying figure where the intermittency values are plotted against height for flame lengths measured in free air and with the level of the interface between air and the vitiate layer at 23 and 10 cm. The fuel-air ratio of the gas which formed the vitiated layer were 0.76 and 1.92 for the latter two cases.

In accidental fires which often develop over a few minutes, the steady state will rarely be reached and in general the gas in the upper layer will contain much more oxygen, i.e., will have a much lower fuel-air ratio, at a given time than the gas entering the layer through the fire plume. We are examining this situation at the present time in a new hood which is 2 m on a side and 1.25 meters deep, and which is equipped with a gas supply system which will allow us to control the oxygen or fuel flow to the upper layer independent of the fuel-air ratio of the plume gas.

Reports and Papers

1. E. E. Zukoski, "Heat Transfer in Unwanted Fires," presented at Joint ASME-JSME Meeting on Heat Transfer, Hawaii, March 1986.

2. E. E. Zukoski, "Summary Report, Fire and Smoke Physics Session," UJNR Meeting, Boston, Mass., May 4-8, 1987.

3. M. Chobotov, E. E. Zukoski and T. Kubota, "Heat Transfer Effects on Gravity Currents," Density-Stratified Flow Symposium Proceedings, edited by E. J. List and G. H. Jirka, D. Reidel Pub. Co. Boston, Mass. (1987).

4. M. V. Chobotov, E. E. Zukoski and T. Kubota, "Gravity Currents with Heat Transfer Effects," Report, NBS Grant No. 60NANB6D0638, California Institute of Technology, Pasadena, CA, September 1986.

5. S. J. Toner, E. E. Zukoski and T. Kubota, "Entrainment, Chemistry and Structure of Fire Plumes," Report, NBS Grant No. 60NANB6D0638, California Institute of Technology, Pasadena, CA, September 1986.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Factory Mutual Research Corp., Norwood, MA 02062
Grant No: 60NANB5D0560
Title: Prediction of Fire Dynamics
Principal Investigators: John de Ris (617)762-4300, ext. 2850
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Other Professional Personnel: M. A. Delichatsios
H. W. Emmons (617)495-2847
G. H. Markstein
L. Orloff
NBS Scientific Officer: B. McCaffrey and H. Mitler

Technical Abstract:

This work is divided into four tasks.

Task 1. Prediction of Fires in Buildings (H.W. Emmons)

Work on four problems has been in progress this year.

1. The fire in an unfire-stopped wall space connected above and below by another open wall space was solved by a program in BASIC. It is too slow to be practical with a stable solution time step. Therefore, it is to be rewritten in Fortran and run on a Vax, but this has not yet been done.

2. The Chapter on Vent Flows for the proposed book on the "Prediction of Fires in Buildings" has been published as a project report.

3. The Users Guide to the NBS computer code, FIRST, was reviewed and a number of changes to make it more user friendly were suggested. Many of these changes have been made. The changes required in the Input Program are being made at Harvard by an advanced graduate student, Jason Harry, under the direction of the project leader.

4. Some 90 different fire cases, involving many different fires and their environment, have been run with FIRST on the Harvard Physics Vax 8600. This effort has disclosed:

a. A number of cases that will not run;
b. A number of coding errors that are being corrected at NBS.

When a fire case fails to run, it can often be "fixed" by a small change of fuel location in the enclosure or a small change of some property, e.g. Heat of Combustion or Vaporization. A frequently effective fix is a relaxation of the tolerance from .001 to a lower value, often .01. This results in only small changes in most of the output.

Publications:

Home Fire Project Report #74 - Transient Ceiling Jet
Home Fire Project Report #75 - The Flow of Gases Through Vents
Experiments with an Enclosure Fire Math Model - Submitted to 2nd Symp. (Intl) on Fire Safety Science.

Task 2. Correlation of Turbulent Flame Radiation and CO Release with Smoke Point

(L. Orloff, M.A. Delichatsios, J. de Ris)

The main objective of this task is to obtain general empirical correlations relating the radiant fraction from turbulent buoyant diffusion flames to the laminar smoke-point values at corresponding thermochemical conditions. These correlations will be tested over a range of fuel chemical compositions, inert additives to the fuel supply, fuel supply temperature, and ambient O_2/N_2 concentrations.

Theory and experiment imply that properly designed buoyant turbulent jet flame experiments can provide a quantitative bridge relating laminar smoke point measurements of a fuel to its turbulent wall fire radiation. It is also possible that we can extend the results to model large-scale burning using laboratory experiments in enriched O_2 atmospheres, and predict burning rates in vitiated atmospheres. This concept of radiation modeling with buoyant jet flames requires highly precise and reliable radiation measurements that link to the independently measured wall fire radiation and smoke points. In order to verify the models described here, these radiation measurements must be reproducible in other laboratories. These requirements merit particular attention, and are discussed below.

Our modeling analysis indicates that turbulent wall fire flames and turbulent buoyant jet flames will have the same local enthalpy versus fuel concentrations provided the respective mixed fuel gases and supplied fuel have identical compositions and temperatures. We find that the composition of wall fire gases adjacent to the wall can be simulated in jet fire experiments by mixing a fraction $B_c/(B_c+1)$ of the unburned gaseous fuel with a fraction $1/(B_c+1)$ of cooled combustion gasses created by preburning this fuel with its stoichiometric mass of oxidant, with corrections for completeness of combustion. A new premixed burner will shortly be installed to permit verification that effects of wall cooling on flame radiation can be simulated in the present buoyant jet study, and consequently, by smoke point measurements.

Another aspect of the present study arises from the need for a better scientific understanding of how rate of heat release (RHR) calorimeters can be used for simulating enhanced flame radiation effects in large-scale fires. In general fires exhibit a scale effect of increasing radiative feedback relative to convection. Currently there is a lack of information to guide the RHR small-scale studies in prescribing the amount of externally imposed radiation needed to supplement the enhanced radiative feedback induced by enriched O_2 ambients. The range of vitiated and enriched O_2 burning behavior that can be investigated in this study has been extended by installation of nitrogen and oxygen supplies to permit variation of the ambient oxygen concentration between 15 and 30 percent. This modification allows a more direct comparison with smoke point measurements obtained in O_2/N_2 atmospheres by reducing the complicating thermochemical effects of CO_2 and H_2O that would arise from vitiation with actual products of combustion. The experiment includes a furnace exhaust that can be supplied to the fire environment for subsequent study of the more realistic vitiation environment.

Buoyant jet flames in open laboratories are subject to ambient disturbances that induce unpredictable effects on their radiative output. There appears to be no effective way to ensure a highly quiescent open laboratory environment with adequate air supply and absence of radiative heating from the surrounding walls. In this study we use a water-cooled 1.2 m diameter enclosure with a highly quiescent measured air supply filtered through the floor and a precisely controlled rate of exhaust.

A series of baseline measurements were carried out with systematic variation of several experimental parameters in order to gauge their effect on flame radiation. These parameters include: ambient air flow velocity in the immediate vicinity of the flame; overall air supply rate in terms of the stoichiometric combustion requirement; removal of soot fallout from the burning of carbon-rich fuels; and fuel supply temperature.

Radiation measurements of laminar-to-turbulent transitional flames (5-8 kW) revealed a significant dependence on the air supply rate. Visual inspection suggests that the co-current flow affects the transition height by generating or damping entrained vortex flows. These transition variations in turn appear to affect soot production and oxidation processes.

Co-flow was substantially reduced by (1) restricting the air supply through the enclosure floor to 30 times the stoichiometric requirement for complete combustion, which reduces its co-flowing velocity component; and (2) centering a water-cooled black circular plate below the nozzle to impose primarily horizontal air entrainment characteristic of burning in the open. Radiant fraction measurements and visual inspection of the flow for six different fuels indicate that these procedures insure stable, axisymmetric flames that are not sensitive to minor variations in the air supply rate.

Aspiration of outside air through the enclosure walls, for example through electrical and fuel ports introduces disturbances that cause the flame to lean, meander, and exhibit flame height fluctuations. These disturbances have been eliminated by tight regulation of the air supply blower and the exhaust so that the ambient pressure inside the enclosure is in equilibrium with the surrounding laboratory.

The radiation from carbon-rich fuels such as acetylene appears to be sensitive to fallout of agglomerated soot particles which screen the radiative output. This interference is reduced by increasing the exhaust rate while maintaining the desired level of air supply. The high value of radiant fraction obtained for this fuel is ascribed to its high flame temperature and soot production rate. Flame radiation was also found to be slightly sensitive to fuel supply temperature. The gaseous fuel filters through a bed of 2 mm diameter stainless steel balls before exiting at the nozzle lip. This flow-smoothing bed receives radiative feedback from the flames, which can result in fuel supply temperatures controlled by feedback radiation. A regulated fuel preheater was built into the burner to maintain the fuel at 60°C, which reduces heat exchange between the bed and fuel supply.

Task 3. Wall Fire Flame Radiation (G.H. Markstein, J. de Ris)

The objectives are extensions of previously established relationships for fire radiation to fires burning on vertical walls, comparison of the results with existing analyses of wall burning, and development of improved models of wall burning based on experimental findings. As in other related work, the significance of studies of fire radiation rests on the fact that in many fires energy transfer from the flame to the fuel and to the surroundings occurs predominantly by thermal radiation. The rate of fire growth and the spread of fire to new fuel elements depends critically on this energy transfer, and its quantitative assessment is thus essential for predicting fire behavior.

In the present task, wall fires of solid fuels are simulated by burning gaseous hydrocarbon fuels on a water-cooled vertical porous metal surface under steady-state conditions. The burner is subdivided into a number of panels of equal height, so that the simulated pyrolysis height can be varied by the choice of the number of fuel-supplying panels. In addition, the limiting case of zero pyrolysis height can be studied by supplying the fuel from a slot burner at the base of the wall.

Fuel is supplied to the burner by electronic flow controllers, and the heat transferred to each panel is determined from the temperature rise of the cooling water, measured by differential thermocouples. The total radiant emission from the fire is measured with a wide-view-angle radiometer employing a spectrally flat thermopile sensor. In addition, the vertical distribution of radiant power per unit height emitted by narrow horizontal slices across the width of the fire is measured with a scanning slit radiometer. The scan along the height of the fire is obtained by the use of an electromagnetically deflected plane front surface mirror operated in a linear ramp mode. A fast-response spectrally flat pyroelectric sensor is used in this instrument. A new version of this instrument, providing improved signal-to-noise ratio and vertical resolution by the use of spherical-mirror optics, is now undergoing evaluation.

Initial work under this task was performed with a previously developed burner[1] consisting of six 380-mm wide and 220-mm high sintered-metal panels topped by a 520-mm high metal plate. Since the fine-grained sintered metal of the burner was susceptible to clogging by soot, the work was restricted to ethane, which produces relatively small amounts of soot. A new burner incorporating various design improvements has been assembled, and work with this burner is about to begin. One important new feature is the use of an outer layer of coarse-grained sintered metal that is expected to prevent permanent clogging by soot, so that future work can be extended to fuels of greater sooting tendency than ethane. The height of the individual panels has been reduced to 127 mm to provide improved resolution of the simulated pyrolysis height. As another new feature, heat transfer instrumentation has been incorporated in the metal plate above the burner panels.

Although the data obtained previously with the old burner are of a preliminary nature, they nevertheless provided valuable results[2] which have recently been examined in greater detail to establish correlations for the radiant fraction of heat release rate χ_R and for the vertical distribution of radiant flux to the wall, $\dot{q}''(Z)$. For theoretical reasons, the convective B-number B_c, given by

$$B_c = \frac{\dot{m}''}{\dot{q}''_c} \left[\frac{\Delta H_c (\chi_A - \chi_R)}{S \chi_A} - C_p (T_s - T_\infty) \right]$$

was used for correlating the radiant fraction χ_R, where $\dot{q}''_c$ is the convective heat-transfer rate to the fuel surface and $\dot{m}''$ is the mass transfer of the fuel from the surface, χ_A is the fraction of fuel that participates in the flame reaction, and S the stoichiometric oxidizer-to-fuel mass ratio. For the present data, incompleteness of combustion was not considered ($\chi_A = 1$); thus, the previously determined total B-numbers were converted into convective B-numbers by the expression

$$B_c = B \frac{1 - \chi_R}{1 - \chi_{R,\mathrm{loss}}}$$

where $\chi_{R,\mathrm{loss}}$ is the radiative fraction of the heat transferred to the fuel-supplying portion of the wall burner, which was determined from the scanning data.

A plot of radiative fraction χ_R vs $1/(1 + B_c)$ is shown in Fig. 1. The values of L_p are simulated pyrolysis lengths, corresponding to supply of fuel by one, two, or three burner panels, respectively. The data point for $L_p = 0$ represents results obtained with a slot burner placed at the base of the wall, corresponding to $B_c = \infty$.

The choice of the abscissa, $1/(1 + B_c)$, was based on theoretical arguments which show that it represents the concentration of combustion products present at the wall surface.[3] In agreement with this theoretical argument, the figure shows a linear decrease of χ_R with $1/(1 + B_c)$.

For correlating data of radiant flux to the wall, $\dot{q}''(z)$, derived from scanning-radiometer measurements, a normalization by $\chi_R\, \dot{Q}'/L_f = \dot{Q}'_R/L_f$ was chosen, where $\dot{Q}'$ is the total heat-release rate per unit burner width, $\dot{Q}'_R$ its radiative portion, and L_f the flame height. This choice was made so that the area under plots $\dot{q}''(z)\, L_f/\dot{Q}'_R$ vs normalized height z/L_f is equal to 1/2 due to the fact that one-half of the total emitted radiant power is absorbed by the wall for an optically thin fire.

It was found, however, that use of the expression for flame height previously adopted both on theoretical grounds and from the experimental scanning data,

$$L_f = 0.059\, (\dot{Q}')^{2/3} \qquad (1)$$

gave poor agreement among the normalized flux data for different values of total heat release rate, even for constant pyrolysis height L_p. The agreement was greatly improved by using, instead, the empirically selected expression

$$L_f = 0.17\, (\dot{Q}')^{1/2} \qquad (2)$$

A partial reason for the failure of eq (1) to correlate the scanning data properly may lie in the fact that it was obtained by using 50 percent intermittency with a fairly large threshold value as the criterion for flame length, while a criterion based on the approach of $\dot{q}''_R$ to zero seems more appropriate for the present purpose.

Figs. 2 to 5 show normalized plots of radiant flux vs height for the slot burner and for one, two and three fuel-supplying panels (L_p = 0, 220 mm, 440 mm and 660 mm, respectively). The data correlate well among each other for each of the values of L_p. In addition, it was found that they can be matched closely by beta distributions

$$F(x) = x^{n-1}(1-x)^{m-1}/2\ B(n,m)$$

where $B(n,m) = \Gamma(n)\Gamma(m)/\Gamma(n+m)$,

with empirically chosen best-fit values of n and m. As a consequence of the flattening of the distributions, the values of n and m decrease with increasing L_p. The ratio of m/n also decreases with increasing L_p, reflecting the shift of the maximum of $\dot{q}''$ to higher values of z/L_f.

Further relationships can be deduced from the plots, Figs 2-5. The initial increase associated with the rate of soot formation can be seen to be roughly linear with the same slope for all runs. Equal slopes for the dimensionless plots implies that the dimensional slope $d\dot{q}''/dz$ is proportional to χ_R, with a constant factor for all runs. A mean value

$$(d\dot{q}''/dz)_{initial} = 164\ \chi_R\ kW/m^3$$

has been determined from the data, and a plausible explanation in terms of initial rate of soot formation has been advanced.[3]

The burnout of soot in the upper portion of the flame also can be represented by a simple correlation. For any given threshold value, $\dot{q}''(z) = t$, the corresponding heights z(t) were found to correlate well with the expression

$$z(t) = 0.17\ \dot{Q}'^{1/2} - i(t) \qquad (3)$$

Thus, the flame-length expression, eq (2), was further confirmed as the asymptotic limit for vanishing intercept i(0) = 0. A plot reflecting this relationship for a particular value of threshold t is shown in Fig. 6. It was also found that the intercept i(t), for thresholds t in the range from 4 to 14 kW/m^2, is a linear function of t.

The various relationships discussed above, and their significance, are being further investigated and it is planned to extend the correlations to the data to be obtained with the new burner. The results will also be compared with existing theoretical models of wall-fire combustion[4-7] and will be used for possible modification of such models, as well as for extension to wall fires of correlations between flame radiation and fuel smoke points.[3,9]

Concurrently with the study of wall fires, measurements of smoke points and of radiant emission from laminar diffusion flames have been performed. This continuing work, which is also partly supported by the Gas Research Institute, is of interest for the wall-fire study in connection with correlations between flame radiation and smoke points and is also of importance for the study of turbulent flames under Task 2.

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9. Markstein, G.H., "Radiant Emission and Smoke Points for Laminar Diffusion Flames of Fuel Mixtures," 21st Symposium on Combustion, Munich, Aug. 1986.

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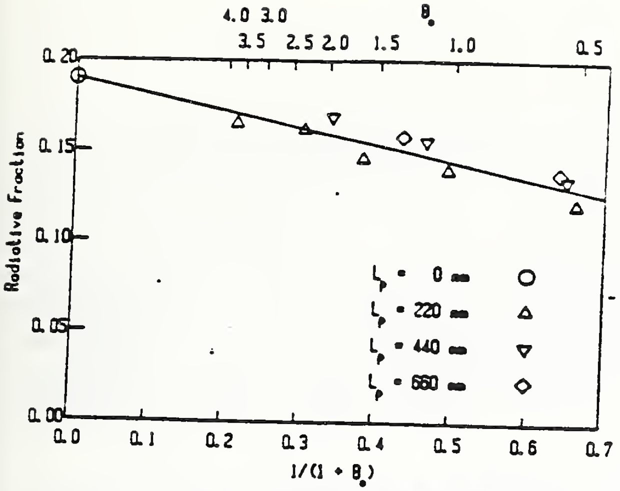

Fig. 1. Ethane wall-fire radiative fraction vs $1/(1+B_c)$ (B_c = convective B number, L_p = pyrolysis height)

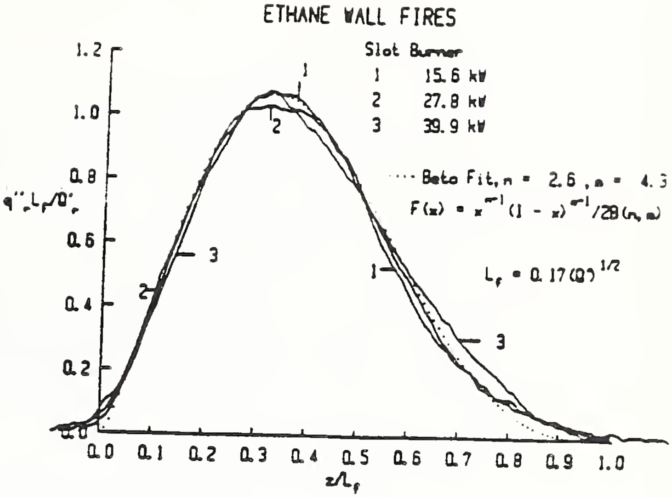

Fig. 2. Normalized plot of radiant flux vs height. Fuel released from slot burner at base of wall

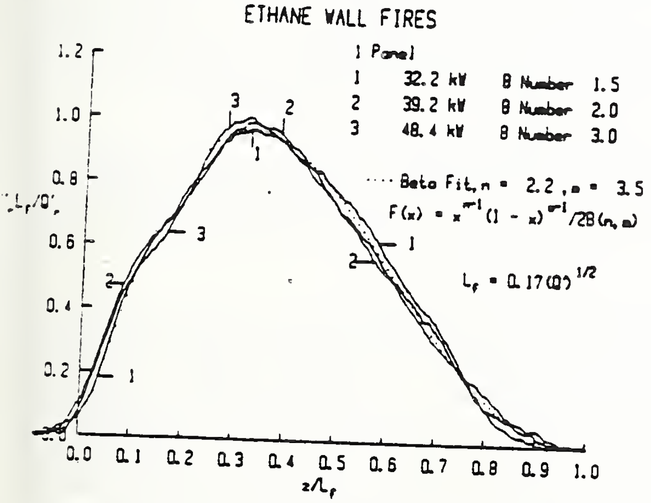

Fig. 3. Normalized plot of radiant flux vs height. Fuel released from one panel (L_p = 220 mm)

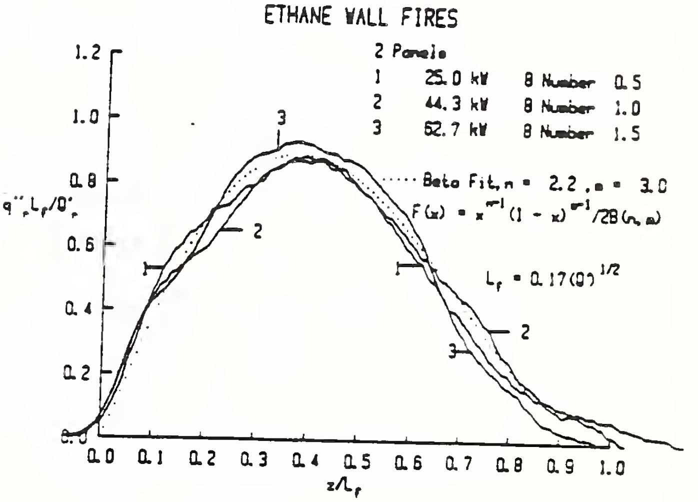

Fig. 4. Normalized plot of radiant flux vs height. Fuel released from two panels (L_p = 440 mm)

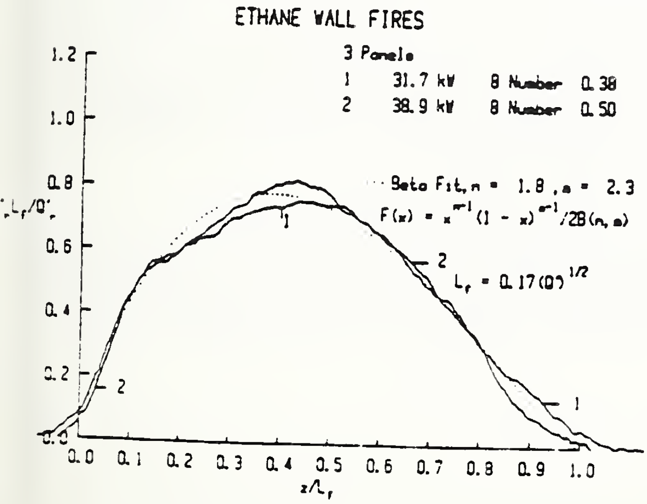

Fig. 5. Normalized plot of radiant flux vs height. Fuel released from three panels (L_p = 660 mm)

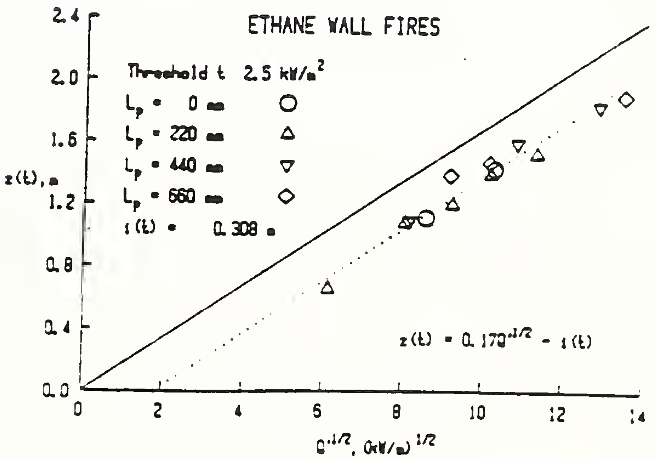

Fig. 6. Flame height for radiant flux threshold of 2.5 kW/m² vs $Q'^{1/2}$

Task 4: Dynamics of Charring Wall Fires

(M.A. Delichatsios, K. Saito, R.L. Alpert, M.K. Mathews)

Mathematical models for the prediction of upward flame spread rates as well as the prediction of critical conditions for flame spread require two key material properties: 1) the transient generation rate and heating value of the pyrolysis vapors emerging from the material, and 2) the flame radiation from the burning of the pyrolysis gases. It has been the objective of this task to improve on current techniques for predicting transient pyrolysis of materials and to provide sufficient information for calculating the radiant feedback in a fire situation, based on fundamental radiation properties of the pyrolysis gases from any material.

To achieve these objectives, we have assembled a comprehensive program which consists of a new flammability apparatus and a methodology to interpret and analyze the experimental data on transient pyrolysis and flame radiation. Emphasis has been given to charring materials because they have a transient pyrolysis history even when exposed to a constant heat flux. For noncharring materials (e.g. PMMA), a steady rate of pyrolysis can be readily measured or calculated by using a heat of gasification and pyrolysis temperature.

We have completed the construction of a sophisticated experimental apparatus carefully designed to obtain accurate measurements for the transient pyrolysis rate of charring materials as well as for the flame radiation from the burning of their pyrolysis gases.

A systematic set of 56 experiments was run in this apparatus by our summer scientist, Professor K. Saito. Measurements of weight loss and temperatures at four locations inside the samples were recorded. In this phase, quartz heaters were used for generating the external heat flux which was calibrated for a range of 1 to 17 W/cm^2. Four different materials were used; black PMMA, two types of particle board and Douglas Fir wood. The measured weight loss was fitted by a rational ratio of third or fourth order polynomials for better representing the local slope (i.e. pyrolysis rate) and curvature of the experimental data trend. For illustration, Figures 1a and 1b show the weight loss and pyrolysis rate and the temperature measurements for particle board 12 cm in diameter and 1.9 cm thick, exposed to a heat flux of 5.2 W/cm^2. These data are currently being analyzed(1) based on our previous semi-analytical and numerical models. The next phase of experiments will involve the application of a cone-radiant source for generating the external heat fluxes. These measurements will provide information on the effects of spectral characteristics of the source on the transient pyrolysis of materials.

Finally, in conjunction with concomitant efforts by NBS, we have outlined a comprehensive model(2) for the burning and upward flame spread on charring materials in wall fires. Perhaps an important outcome of this work is that upward flame spread rates (dx_p/dt) may be correlated by the following expression:

$$\frac{K_w^2 \pi (T_p - T_s)^2}{4 \alpha_w \dot{Q}_{ch}'^{4/3}} \frac{dx_p}{dt} = \chi_R^2 \, \mathrm{fcn} \left(\chi_R \frac{\Delta H_c}{\Delta H_v}\right)$$

This equation illustrates directly the main parameters which control upward flame spread; namely wall thermal properties (K_w, α_w, T_p), heat release rate ($\dot{Q}'_{ch}$), radiant fraction (χ_R) and a material flammability number ($\chi_R \frac{\Delta H_c}{\Delta H_v}$).

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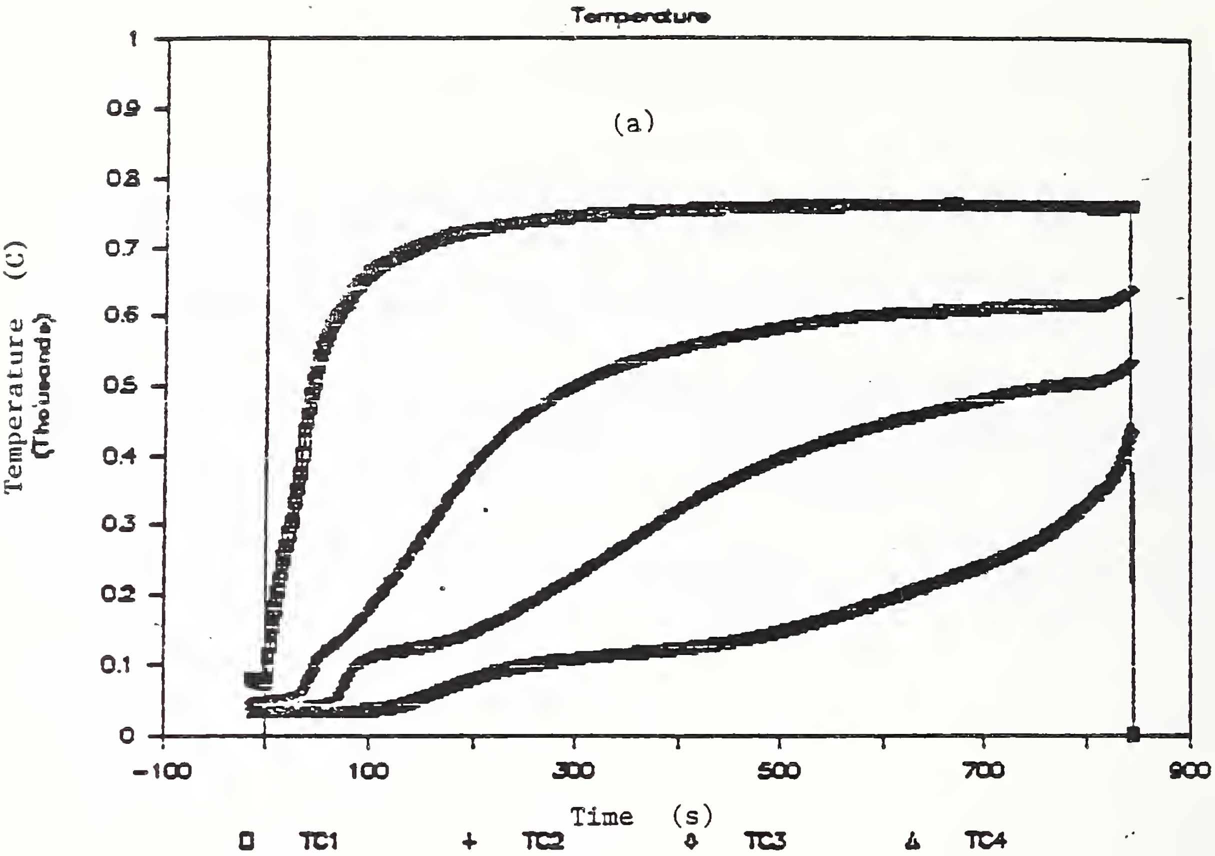
2. Delichatsios, M.A., "An Outline for a Comprehensive Model for the Burning and Upward Flame Spread on Charring Materials in Wall Fires," FMRC report, and paper submitted for presentation at the Eastern Section of the Combustion Institute, Nov. 1987, NBS.



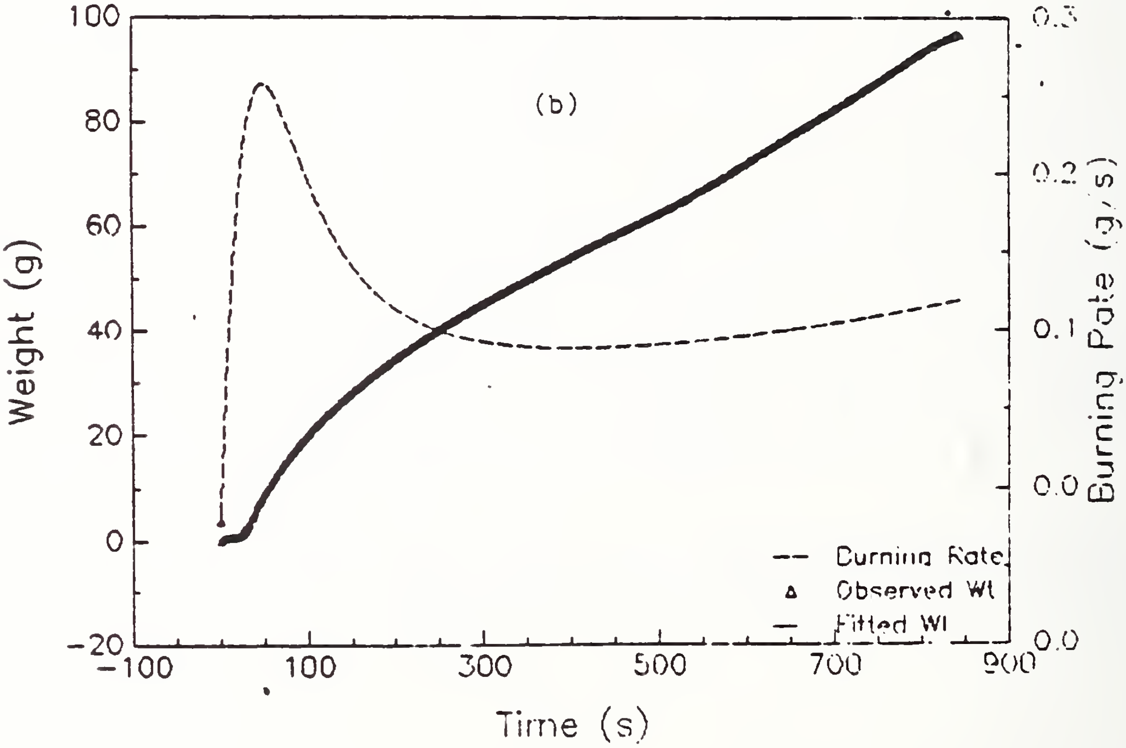


Fig. 1 Temperatures at the front surface, 6 mm, 12 mm deep and at the back surface (Fig. 1a) and weight loss and pyrolysis rate (Fig. 1b) of a charring particle board exposed to a uniform flux of 5.2 W/cm^2.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY87

Institution:	Rutgers, The State University of New Jersey New Brunswick, New Jersey
Grant No.:	NB83NADA4047
Grant Title:	Negatively Buoyant and Penetrative Flows Generated in Enclosure Fires
Principal Investigator:	Professor Yogesh Jaluria Department of Mechanical & Aerospace Eng. Rutgers, The State University of New Jersey New Brunswick, New Jersey 08903 Telephone: (201) 932-3652
Other Professional Personnel:	K. Kapoor (Post-Doctoral Fellow) A. Abib (Ph.D. Student)
NBS Scientific Officer:	Dr. Leonard Y. Cooper

Technical Abstract:

Introduction. The objective of this project is to carry out a detailed experimental investigation on the negatively buoyant and penetrative flows that arise at the early stages during the growth of a compartment fire. In particular, negatively buoyant jets in an extensive environment simulate the ceiling jet driven wall flow and also the buoyancy-induced flow adjacent to the walls of an enclosure. Following the establishment of the two zones typical of such fires, these wall flows penetrate across the interface, become negatively buoyant and rise toward the interface. Extensive measurements have been taken on negatively buoyant wall jets in an extensive isothermal medium, as well as on their penetration in a two-layer stably stratified environment. Correlating equations have been developed for the penetration depth, heat transfer and entrainment into the flow, to provide inputs for the zone model analysis of compartment fires.

Negatively Buoyant Wall Jets. The penetration depth δ_p, the total entrainment into the flow, given in terms of the total flow rate $\dot{m}_{out}$ in the reverse flow, the heat transfer flux to the wall q and the velocity and temperature fields have been determined experimentally. Details on the experimental system and on the results obtained are given in the listed publications. It is found that these results can be well correlated in terms of the Richardson number $Ri = g\beta(T_o - T_\infty)D/U_o^2$, where D is the width of the jet at the discharge, U_o the average discharge velocity, T_o the jet discharge temperature, T_∞ the ambient temperature, g the gravitational acceleration and β the coefficient of thermal expansion.

Several correlations have been derived. Some of the important ones, for negatively buoyant wall jets, are:

$$\delta_p/D = (1.88-14.1\Delta T/T_o) + (2.6-8.56\Delta T/T_o)Ri^{-0.6} \quad \text{for } 0 < Ri \leq 1.0 \qquad (1)$$

$$\begin{aligned} \dot{m}_{out}/\dot{m}_{in} &= 38.6\ Ri^{0.878} && \text{for } 0 < Ri \leq 0.06 \\ &= 13.1\ Ri^{0.491} && \text{for } 0.06 < Ri \leq 0.3 \qquad (2) \\ &= 8.75\ Ri^{0.177} && \text{for } 0.3 < Ri \leq 0.6 \end{aligned}$$

$$Nu_D = \frac{hD}{k} = 0.5 + [0.268-3.46\Delta\tilde{T}/T_o]Ri^{-1.12} \quad \text{for } 0 < Ri \leq 1.0 \qquad (3)$$

where T_o is in K, Nu_D is the Nusselt number, $\dot{m}_{in}$ is the mass flow rate at the jet inlet, h the heat transfer coefficient, k the thermal conductivity of the fluid, $\Delta T = T_p - T_\infty$, T_p being the wall temperature, and $\Delta\tilde{T} = T_o - T_p$. For an adiabatic wall, the penetration depth had been found to be well correlated by the expression

$$\delta_p/D = 4.424\ Ri^{-0.389} \quad \text{for } 0 < Ri \leq 1.0. \qquad (4)$$

All the above correlations were found to represent the data quite closely, with correlation coefficients of order 0.95. Some of these correlations have been applied to typical enclosure fires. The results obtained have been found to be physically realistic. The effects of these flows were confirmed to be significant in the transport mechanisms that underlie enclosure fires.

Penetrative Wall Flows. An experimental arrangement was designed and fabricated to obtain a stably stratified two-layer environment in an enclosed region. Figure 1 shows the typical temperature profiles in the enclosure. It was found that the temperature levels, the height of the interface and the sharpness of stratified region between the two essentially isothermal regions could be varied by controlling the temperature and flow rate of the low-velocity hot air flowing through a wide diffuser into the tank at the top. Both a downward heated jet and the buoyancy-induced flow adjacent to a cooled plate were considered and the penetrative convection studied in such a two-layer environment.

Figure 2 shows the downward penetration of a two-dimensional heated jet discharged at the top of the upper zone. The flow penetrates across the interface into the lower zone, becomes negatively buoyant and rises toward the interface. The corresponding penetration depth δ_p is shown in Fig. 3 and the results obtained are compared to those for a jet in an isothermal environment. Clearly, the upper zone temperature T_u is more appropriate for correlating the data than the lower layer temperature $T_L = T_\infty$. The penetration of the buoyancy induced wall flow due to a cooled surface is shown in Fig. 4. Again, the flow becomes negatively buoyant in the lower zone and rises toward the interface, ultimately flowing out of the enclosure. The velocity and thermal fields associated with these flows have also been measured in detail. The resulting transport between the two zones because of these wall flows can thus be determined.

This work is presently being continued and correlating equations are being derived to characterize the experimental results on penetration. These equations will then be applied to typical enclosure fires to determine the resulting effects at the early stages of fire growth, particularly in predicting mass and energy transport rates. The results obtained so far have indicated the considerable importance of the wall effects and the need to incorporate these into existing models for an accurate prediction of the changing environment in a compartment fire.

Reports and Papers

1. Jaluria, Y., " Buoyancy-Driven Wall Flows in Enclosure Fires," Proc. 21st Symp. (Int.) Combust., Combust. Inst., Pittsburgh, PA, 1987, in press.

2. Jaluria, Y. and Kapoor, K., "Effect of Wall Flow at the Early Stages of Fire Growth on the Mathematical Modeling of Enclosure Fires," Proc. ASME/JSME Thermal Engg. Conf., Hawaii, 1, 395-401, 1987.

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4. Abib, A.H. and Jaluria, Y., "Numerical Simulation of the Buoyancy-Induced Flow in a Partially Open Enclosure," ASME Winter Ann. Meeting, Boston, Dec. 1987, to be presented.

5. Kapoor, K. and Jaluria, Y., "An Experimental Study of the Generation and Characteristics of a Two-Layer Thermally Stable Environment," submitted for publication.

6. Kapoor, K. and Jaluria, Y., "Heat Transfer from a Negatively Buoyant Wall Jet," submitted for publication.

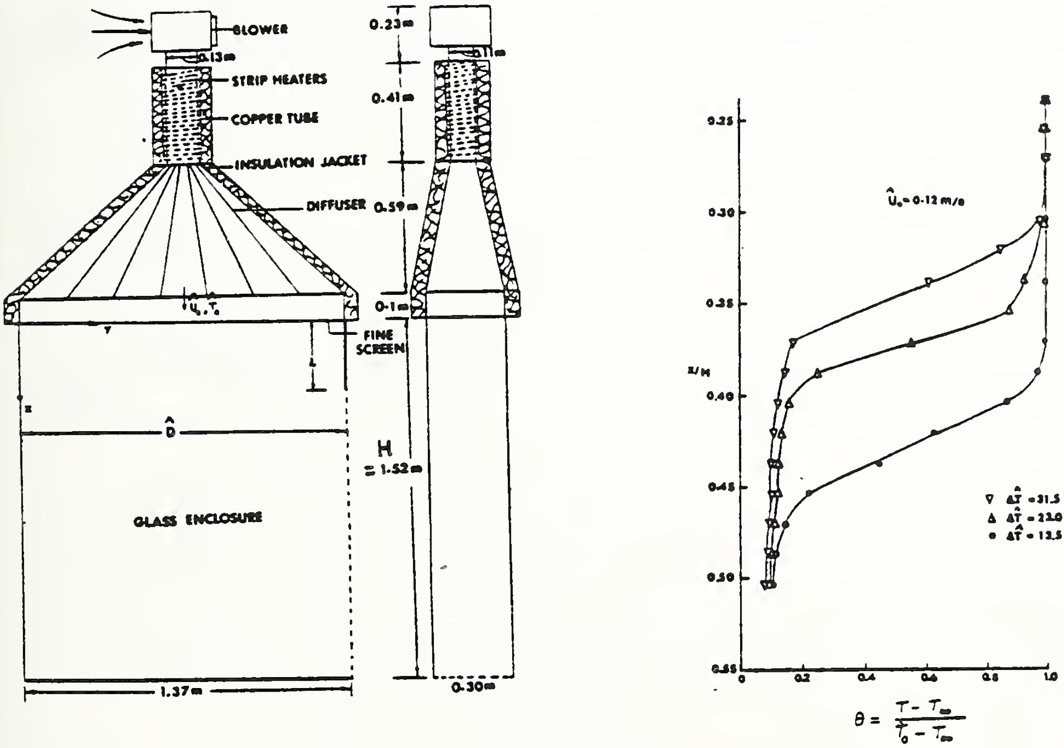

Fig. 1. Measured temperature profiles in the experimental enclosure which simulates the environment in a compartment fire.

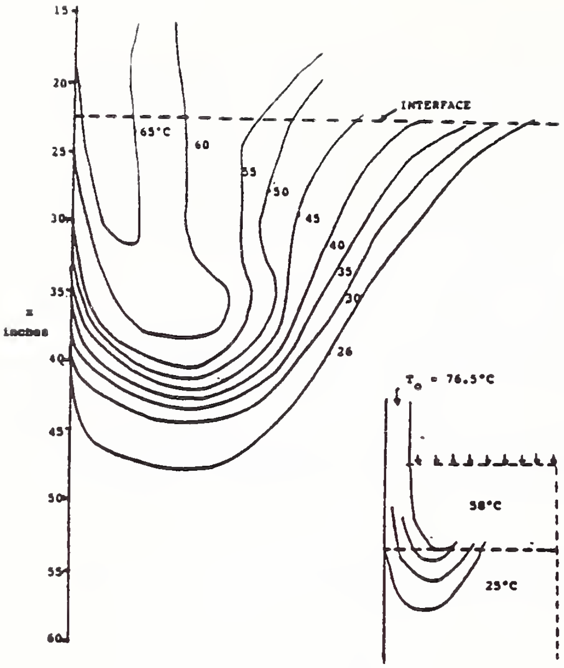

Fig. 2. Penetration of a downward, heated, wall jet in a two-layer stratified environment, in terms of the isotherms, at Ri = 0.1.

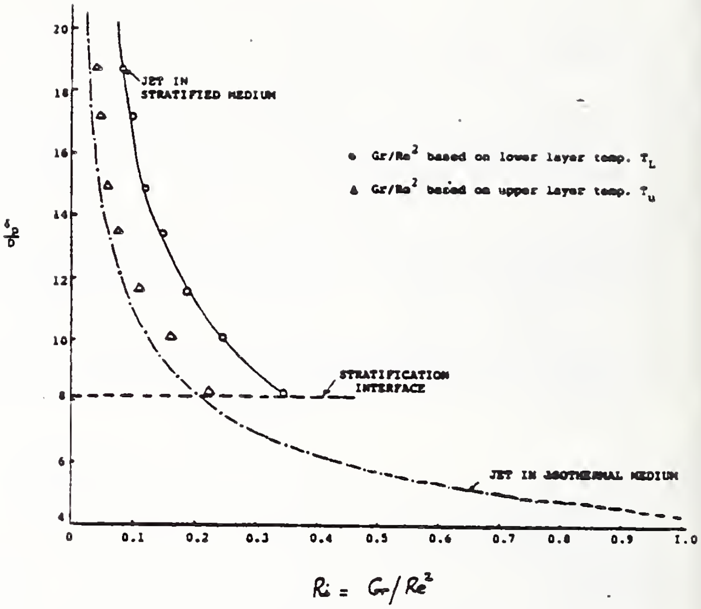

Fig. 3. Penetration depth of the wall jet in an isothermal and a two-layer stably stratified medium as a function of the Richardson number Ri.

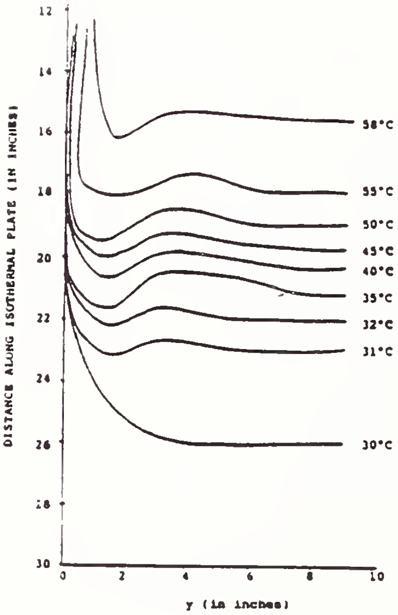

Fig. 4. Downward penetration of a buoyancy-driven flow adjacent to a cooled vertical plate at 25.2°C in a stably stratified two-layer environment, with T_u = 59°C and T_L = 27.0°C.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of Maryland

Grant No.: 70NANB5H00551

Grant Title: Transient Ceiling Jet Characteristics

Principle Investigator: Prof. Colin H. Marks
Department of Mechanical Engineering
University of Maryland
College Park, MD 20742

Other Professional Personnel: Vahid Motevalli, Graduate Student and Guest Worker; Dr. Bernard McCaffrey, NBS

NBS Scientific Officer: Dr. Leonard Y. Cooper

Technical Abstract:

Introduction. Measurements of the transient temperature and velocity characteristics of ceiling jets caused by a fire plume impinging on a ceiling are described here. The measurements provide a data base needed to support the development and verification of compartment fire mathematical models, and they are also needed in order to optimize the design and location of sprinklers and smoke detectors. Measurements of ceiling-jet temperatures and velocities have been made previously[1][2][3] but except for the temperature measurements of Veldman et al they have been made after the temperatures and velocities have reached steady state.

Apparatus. The apparatus consists of a heat source formed by burning a premixed amount of methane and air, an insulated fiberboard ceiling (2.13 m diameter, 1.27 cm thick), and a probe connected to a computerized data acquisition system. In the work reported herein, the ceiling is unconfined.

The velocity is obtained by determining the time that it takes for hot turbulent eddies present in the flow to be carried along by the fluid's mean motion from one position to another. This time is found by determining the time shift in the temperature-time records for a pair of thermocouples, one located a short distance downstream of the other. This technique was utilized by Cox and Chitty[4] for determining the fluid velocity in fire plumes. In

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[2] Veldman, C.C., et. al., NBS, Rpt. No. NBS-GCR-77-98, (1975).
[3] You, H.Z. and Faeth, G.M., NBS, Rpt. No. NBS-GCR-79-188, (1978).
[4] Cox, G. & Chitty, R., Combustion and Flame, Vol. 39, (1980).

addition, using the temperature-time records, the mean temperature of the fluid can be determined directly from the thermocouple pairs. The probe used to determine the fluid mean velocity and mean temperature has eight pairs of thermocouples in order to obtain measurements at eight distances from the ceiling nearly simultaneously. Details of the probe, the instrumentation and of the cross-correlation technique used to determine the time shift are described in (1,2). In order to construct complete velocity and temperature profiles it is necessary to repeat an experiment several times with the probe located at different distances from the ceiling.

Transient Temperature and Velocity. Temperature and velocity profiles have been obtained as a function of time for fire strengthes, Q, ranging from 0.5 kW to 2.0 kW for burner-to-ceiling heights, H, of 0.5 m and 1.0 m. These have been obtained at various radii, r, from the impingement point of the fire plume on the ceiling so as to provide measurements for a range of values of r/H from 0.26 to 2.0. r/H of 0.26 is just outside of the stagnation zone, and r/H of 2.0 is in the region where buoyancy forces are becoming significant. For r/H<1, the ceiling jet is driven by the momentum of the plume. The data are far too voluminous to be included in this short paper, but will be included in the annual report to the National Bureau of Standards for the grant under which this work is being supported.

Typical temperature profiles at various times for Q=2.0 kW at r/H of 0.26 and 1.0 are shown in figures 1 and 2. The temperature profiles represent the difference between the ceiling jet absolute temperatures and the temperature of the ambient. The maximum temperature in the jet occurs below the ceiling even at long times into the run when steady state has been reached. This is because the ceiling has a high emissivity (0.9) and the thus looses appreciable amount of heat by radiation to the cool surroundings. The temperature and velocity profiles are obtained by averaging the temperature measurements over 1 or 2 and 5 minutes for the transient and steady state conditions respectively. Figure 1 shows that at r/H of 0.26, measured temperature profiles do not vary significantly with time despite the increase in the ceiling temperature. At r/H=1.0, figure 2, ceiling jet temperature variation with time is much more evident. This is mainly due to the increased total heat transfer from the ceiling jet to the ceiling at larger radii. Examination of the data also shows that the steady-state values of temperature are approached more rapidly at smaller r/H. Comparison of figure 1 with figure 2 shows that the point of maximum temperature is closer to the ceiling at smaller values of r/H. This effect is more pronounced by examining the temperature profiles at different r/H values, figure 3. The velocity profiles, figure 4, on the other hand, show a boundary layer directly below the ceiling and a free jet type of flow below this layer. The maximum velocity is located at the junction of the two and based on our measurements seems to be somewhat farther from the ceiling than the point of maximum temperature. In contrast with the temperature profiles, our investigation thus far shows that the variation in velocity profiles with time is not appreciable. As would be expected, the maximum variation of temperature with time occurs at the ceiling due to the ceiling's thermal inertia; however, the maximum variation in the velocity always occurs at the point of maximum velocity. Velocity profiles at different r/H values are compared in figure 5. The profiles seem to be similar beyond r/H=0.5 and the significant change in the ceiling jet velocity occurs between r/H=0.26 and 0.5. Comparison of the steady-state velocity profiles with those obtained by Alpert show general agreement as to the magnitude of the maximum velocity and its location from the ceiling. The maximum velocity and its location reach steady state values quickly. The variations of the maximum velocity with time for r/H=0.26 and 0.5 are shown in Figure 6. It is observed that while the maximum velocity fluctuates with time, its average value appears to reach the steady-state value a short time after ignition of the fire.

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1. Marks, C.H. and Motevalli, V., "Transient Characteristics of Plume-Driven Ceiling Jets," National Bureau of Standards, Rpt. No. NBS-GCR-529, April 1987.

2. Motevalli, V., Marks, C.H., McCaffrey, B., and Cooper, L.Y., "Measurements of the Transient Temperature and Velocity Profiles in Ceiling Jets," 1986 Fall Technical Meeting of the Eastern Section of the Combustion Institute, San Juan, Puerto Rico, Dec. 1986.

3. Woodhouse, A., Marks, C.H., and Cooper, L.Y., "An Experimental Study of the Transient Response of Unconfined Ceilings Above Fire Plumes," Proc. of the 1987 ASME-JSME Thermal Engineering Joint Conference, Honolulu, Hawaii, March 1987, pp. 387-394.

4. Motevalli, V., Marks, C.H., and McCaffrey, B., "Measurement of Velocity and Temperature Profiles in Low-Speed, Turbulent Non-Isothermal Floes," Submitted for publication at the 1987 ASME Winter Meeting.

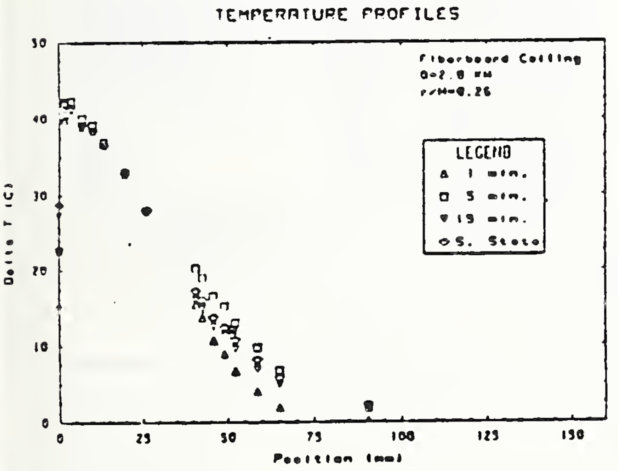

Figure 1 - Temperature Profiles
Variation with Time
2 KW Fire, r/H=0.26, H=1 m

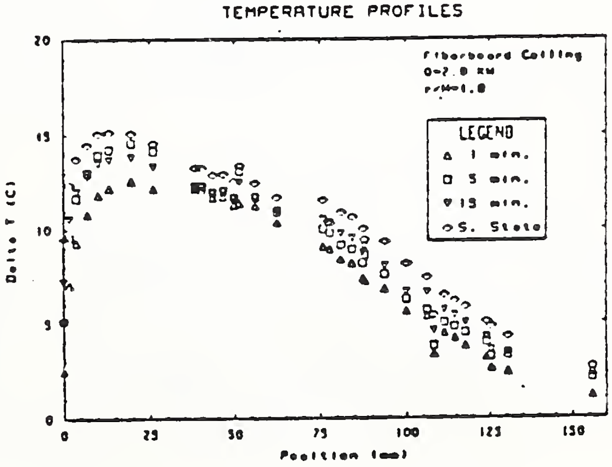

Figure 2 - Temperature Profiles
Variation with Time
2 KW Fire, r/H=1.0, H=1 m

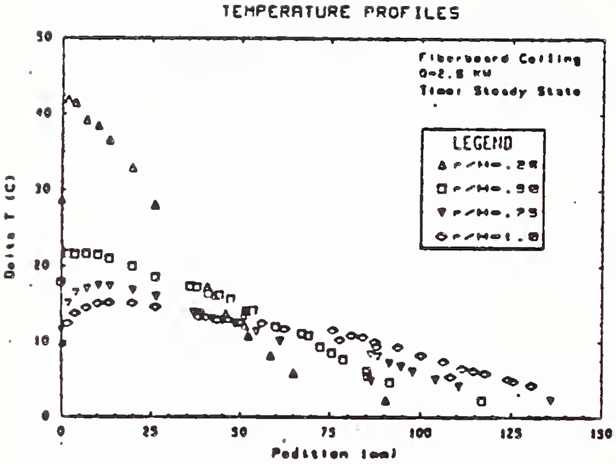

Figure 3 - Steady State Temperature Profiles at Different radii, H=1 m

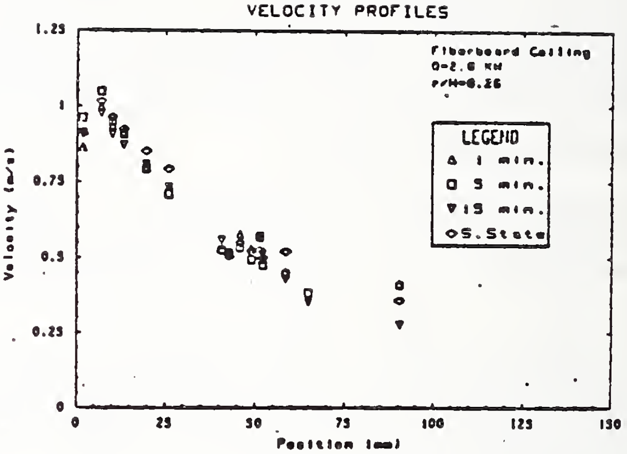

Figure 4 - Velocity Profiles variation with Time 2 KW Fire, r/H=0.26, H=1 m

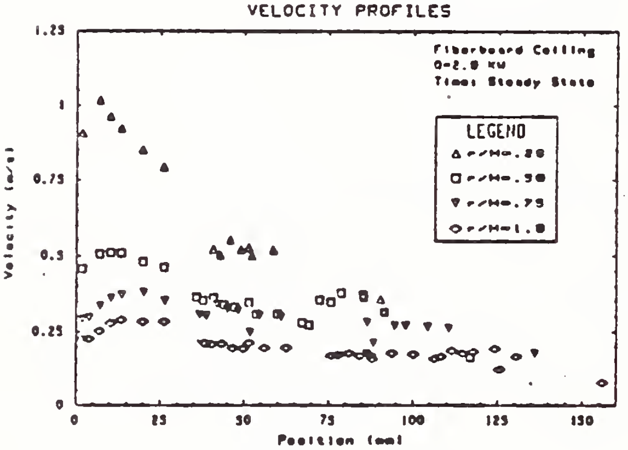

Figure 5 - Steady State Velocity Profiles at Different radii, H=1 m

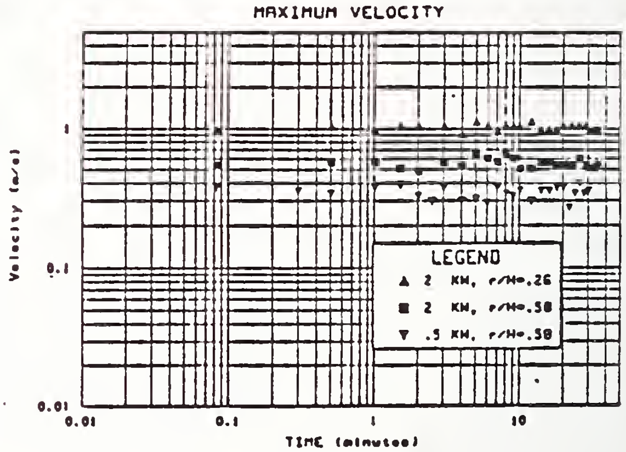

Figure 6 - Ceiling Jet Maximum Velocity Variation with Time

Fire Growth and Suppression
Center for Fire Research
FY 87

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John Rockett, Guest Researcher (USA)

Program Objectives

Through research we aim to develop predictive methods to describe the processes of growth and suppression as related to natural fire phenomena and the performance of fire safety systems.

Scope

The work addresses the processes of fire growth and decay associated with both free burning fires and fires within structures. It examines the overall dynamics of fire growth and its suppression in order to identify and understand the significant underlying processes; ignition, flame spread, burning rate, extinction, and the related transport processes. It utilizes mathematical techniques, experimental studies and correlations, and similitude methods to develop accurate predictions for realistic configurations and materials. As appropriate, it formulates and demonstrates predictive methods for specific applications.

Project Area

Suppression

Research is being conducted to understand the dynamics of fire suppression using water sprays and the overall performance of fire protection sprinkler systems. Studies include the development of predictive methods for sprinkler actuation time, measurements of crib fire suppression with water sprays, cooling of hot surfaces with water droplets, and the characterizations of sprays from commercial sprinklers.

Analysis of laboratory scale measurements collected in a cylindrical enclosure using automated probe positioning equipment showed that·time averaged plume temperatures in the upper warm layer of a two layer stratified ambient could be predicted using substitute fire source techniques as demonstrated in figure 1. These substitute fire source techniques and quasi-steady fire assumptions were used to predict maximum ceiling-jet temperatures in room fire tests of furniture items. Figure 2 illustrates the agreement between predicted ceiling-jet maximum temperatures and measured values. Figure 2 also shows data revealing the important effects of ceiling jet vertical temperature profile. Prediction of these temperature profiles is underway using the results of a program created by Guest Researcher Dr. Yamauchi from Hochiki Corporation, Japan.

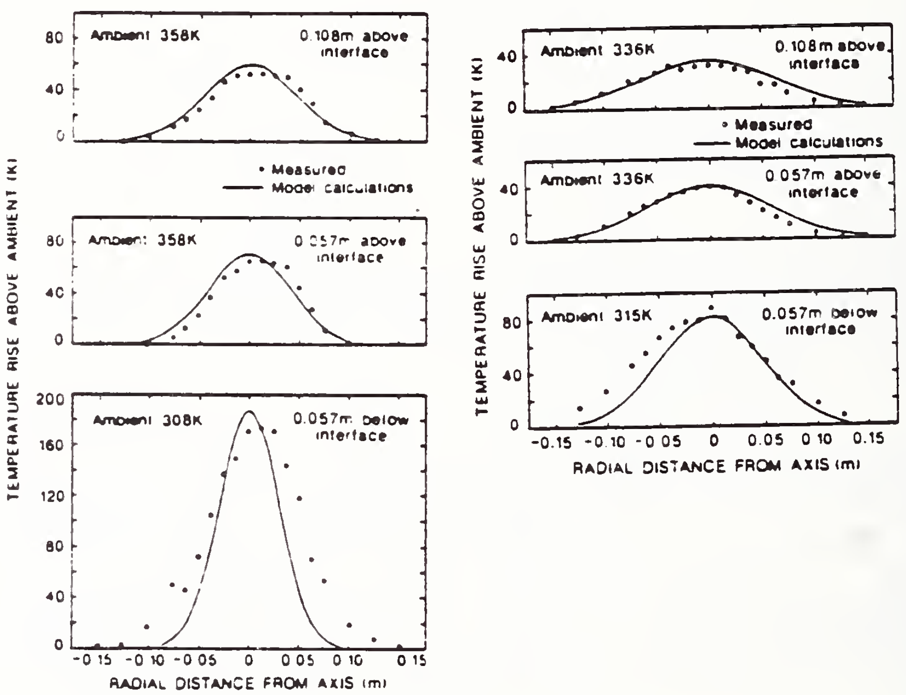

Figure 1. Measured and predicted time averaged plume flow temperature in the lower and upper layers of a stratified atmosphere. Heat source 1 KW. (Left) heat source 0.77 m below ceiling. (Right) heat source 0.97 m below ceiling.

Sprinkler and heat detector activation calculation depends on accurate prediction of gas flow temperatures and velocities and simulations of the heating of the sensing element. Guest Researcher, Dr. Beever from the UK Fire Research Station evaluated the role of conduction losses on sprinkler activation through experiments and modeling. The present findings indicate that conduction losses must be accounted for in situations of both slow fire growth and slow response hardware.

Furniture fire growth and suppression characteristics were simulated for the time range of expected sprinkler response by wood cribs in a project to examine critical water flow rates for fire extinction. Water sprays simulating sprinkler discharges over the range of water fluxes from 0.013 to 0.13 ℓ/s/m^2 were used. Preliminary results show a systematic decrease in burning rate with increased water flux. Measurements show that at low spray flux the crib burning rate is reduced but after reduction continues to grow at the same rate as observed with no water application. At large spray flux the burning rate decreases and the crib is extinguished prior to collapse.

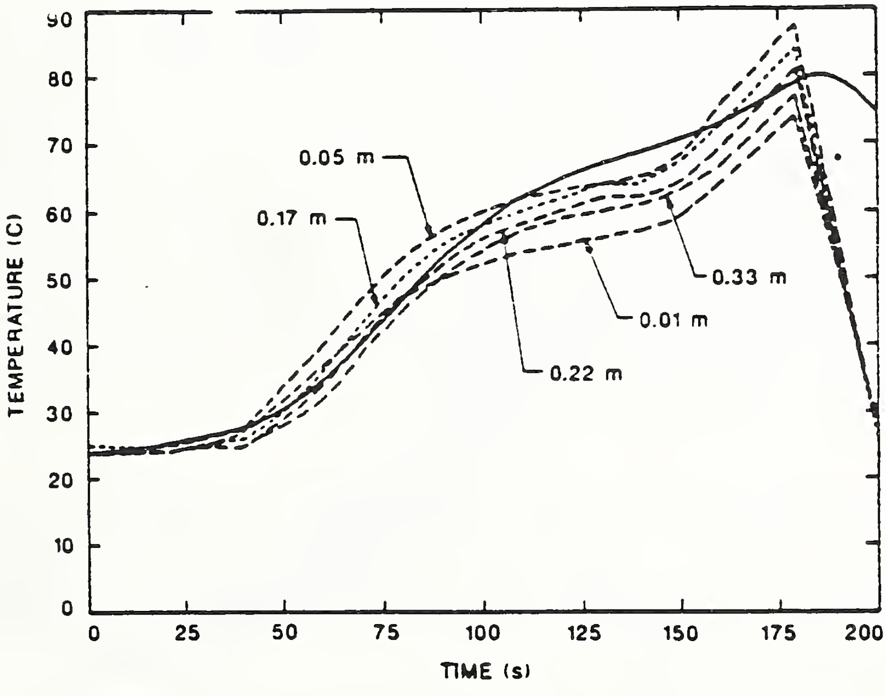

Figure 2. Predicted time dependent maximum ceiling-jet temperature based on substitute fire source method of analyzing plume flow in two-layer ambients and measured gas temperatures at the indicated distances below the ceiling.

The simple analytical representations of the shape of water droplets deposited on hot metal surfaces as segments of spherical lens have allowed calculation of total evaporation time and surface heat flux rates. Evaporation times are consistent with measurements. Modeling of similar measurements completed for a low thermal conductivity glass substrate are underway. This work is directed at the construction of a thermal model for fire extinction.

Measurement of droplet diameters and velocities in sprays from fire protection sprinklers were completed. Extensive evaluation of the data showed a preferential selection of small droplets over larger diameters in the spray by the instruments. This problem is being examined further.

An algorithm for a first order suppression model has been completed. This algorithm when coded would be capable of evaluating first order effects of sprinkler system performance in room fires. The algorithm includes a sprinkler activation section based on DETACT-QS and a spray trajectory calculation neglecting the effects of fire flow. Surfaces of fuel segments represented by rectangular solids are extinguished if exposed to calculated spray fluxes greater than a user specified critical value. Evaluation and improvement of this first order model will guide future priorities in CFR suppression studies.

Turbulent Burning

This work combines the use of theoretical, computational and experimental methods to resolve phenomena associated with turbulent reacting flows.

A mathematical model of combustion in a turbulent eddy was developed. The model consists of a local flow field characteristic of turbulence (a time-dependent stretched vortex characterized by an exact solution of the Navier-Stokes equation), a variable property convection-diffusion equation for the species mixture fraction, and an energy release controlled feedback modifying the flow. Solutions illustrating 3-dimensional transient mixing and diffusion of the mixture fraction have been obtained. This work will be extended to include finite rate chemical processes in the future. The output will be a set of computer codes describing a variety of small scale physical and chemical processes in turbulent reacting flows.

The aerodynamic theory of soot agglomerates has been developed to the point where the forces and moments on long linear chains of spherical particles of arbitrary length have been calculated using a general method applicable to agglomerates of any shape. The planned output will be a computer program yielding the forces and moments for an agglomerated particle composed of elemental spheres in any prescribed configuration. This information is needed to study soot growth mechanisms.

The mathematical model of ground level flows induced by mass fires has been completed. The results will be presented in an invited talk at the Second International Symposium on Fire Safety Science. An initial model of the process by which the multiple plumes coalesce and interact with the atmosphere has been formulated.

Fire Dynamics of Systems and Materials

Wall Fires

A series of experiments designed to characterize the fire behavior of a PMMA wall element in a reduced-scale compartment were completed. A fixed-height variable-width doorway was used to vary ventilation conditions within the compartment. Door widths ranged from 2.6 to 100 percent of the compartment width. A first-cut analysis of the results shows the mass-loss rate to be fairly linear with the oxygen and incident radiant flux proportioned over the upper and lower (layer) wall surfaces. A wall burning algorithm for use in the FIRST compartment-fire computer model was formulated as the sum of upper and lower layer mass rates as:

$$\dot{m}'' = [\dot{q}_f'' (Y_{oxu}/0.233) + \dot{q}''_{ou} - \sigma T^4{}_{vap}] (A_u/A_T L)$$
$$+ [\dot{q}_f'' (Y_{ox\ell}/0.233) + \dot{q}''_{e\ell} - \sigma T^4{}_{vap}] (A_\ell/A_t L)$$

Figure 3 shows the agreement between calculated and measured mass loss rates for PMMA wall sections.

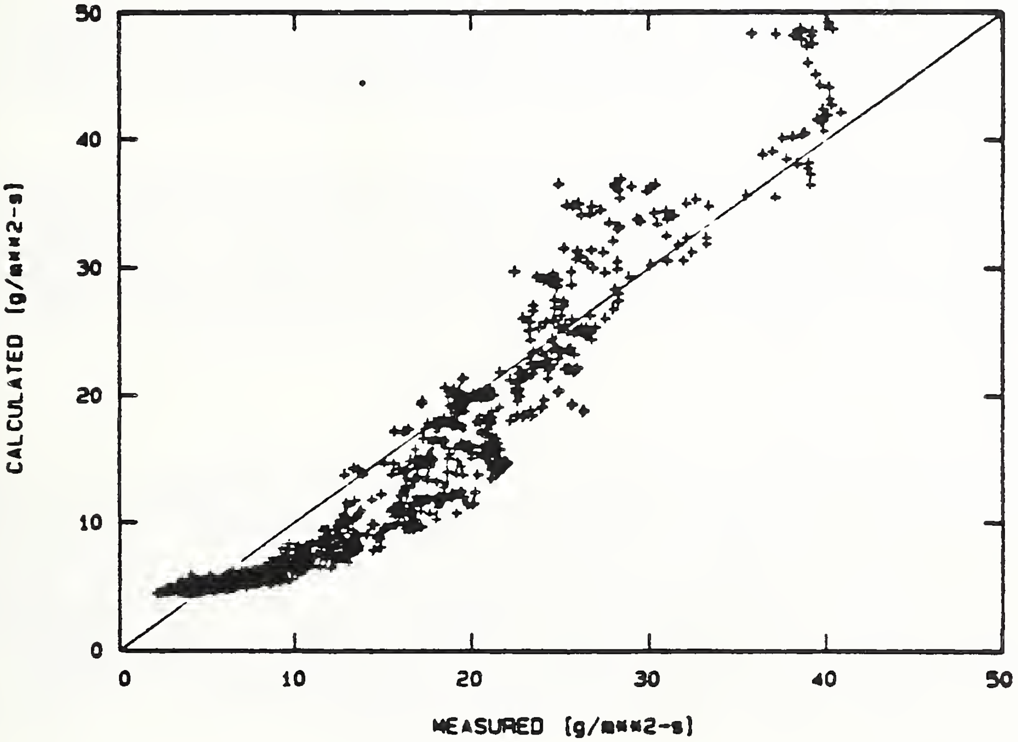

Figure 3. Comparison of calculated and measured mass loss rates for PMMA walls burning in an enclosure with variable door widths.

Flame Spread

Data for validation of material fire properties derived from the Lateral Ignition and Flame Spread (LIFT) apparatus have been collected in medium and large scale tests. In these tests horizontal and downward flame spread were measured on vertical PMMA walls radiated by a non-combustible wall heated by a gas flame sheet. The flame front position was tracked with sequenced photographs and video recordings. Thermocouples mounted at the fuel surface produced local surface temperature histories during the flame spread process. These data are the first large scale comparisons of the predictive capabilities of the LIFT apparatus.

Standardization of the LIFT apparatus and test procedure is proceeding through ASTM with the draft standard prepared for submission to the E05-22 subcommittee. ISO is planning a round robin test that may include the NBS test procedure.

Fire Driven Flows

An experimental study of burning in spaces ventilated through ceiling openings is being conducted through both compartment fire experiments and salt water analog experiments.

A 0.43 m cube laboratory-scale enclosure with variable area ceiling vents and side-wall vents was used to assess the effects of various ventilation conditions on the burning of a 0.1 m diameter ethyl-alcohol pool fire located in the center of the enclosure floor. Various combustion conditions ranging from choked and then quenched flames to strongly pulsating and finally steady fires were observed. Measurements of enclosure gas temperature and fuel mass loss rate are being analyzed.

Some 1/10 scale plexiglass models were constructed to study exchange flow rates through horizontal openings. Salt water was injected into fresh water to simulate how hot fire gases move into fresh air environment. Salt concentrations were measured by a conductivity probe at appropriate points to determine front positions as a function of time as well as flow exchange rate. Test data is being analyzed.

Fuel Pyrolysis

A holographic-interferometric technique was used to measure the transient temperature distributions within a block of fused silica exposed to a radiant heat source operating at levels typical of a fire environment. The experimental results were used to assess the accuracy of the Finlayson-Aung-Kashiwagi model for heat transfer in non-degrading transparent solids. The experimental and theoretical results were found to be in good agreement. This work represents the first steps in a program aimed at characterizing the environment in which pyrolysis products (gas bubbles) are formed and migrate in transparent thermoplastic materials subjected to a fire environment.

Associated Grants

1. Pennsylvania State University, A. Kulkarni - Vertical Wall Fire and Buoyant Plume in Two-Layer Stratified Atmosphere.

2. University of Maryland, M. diMarzo - Transient Cooling of a Hot Surface by Droplet Evaporation.

3. Michigan State University, A. Atreya - Effect of Water on Ignition of Cellulosic Materials.

4. University of California, Fernandez-Pello - Fire Propagation on Concurrent Flows.

5. University of California, P. Pagni - Fire Modeling.

6. University of Michigan, G. Faeth - Radiation from Turbulent Luminous Fires.

7. University of California, W. Yuen and W. Lick - A Study of the Suppression and Extinction of Fires by Water Sprays.

FIRE GROWTH AND EXTINCTION GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: Michigan State University

Grant Number: 60NANB5D0578

Title: Effect of Water on Ignition of Cellulosic Materials

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Lin-Shyang Tzeng, Ph.D. candidate
NBS Scientific Officer: Dr. David D. Evans

TECHNICAL ABSTRACT:

Introduction. The objective of this work is to experimentally and theoretically investigate the effect of water on the piloted ignition of cellulosic materials. This work is divided into two parts. In the first part, the effect of adsorbed water (which can be up to 30% of the oven-dry weight) on piloted ignition is being experimentally investigated in a controlled atmosphere combustion wind tunnel as a function of sample moisture content, external radiation, gas speed and gas composition. A fundamental-theoretical model with finite rate gas and solid phase chemical kinetics is also being developed. In the second part, transient cooling of the surface of a hot porous solid by impingement of water droplets is being experimentally investigated by using an instrumented porous ceramic block. This work will be useful in determining the onset of ignition and subsequent fire growth rate under different relative humidity conditions. It will also provide information on the water application rate required to contain the fire growth.

Experimental Work. The experimental apparatus used for investigating the effect of adsorbed moisture and environmental variables (e.g. external radiation, wind speed and oxygen concentration) on piloted ignition is shown in Figure 1. The heart of this apparatus is a controlled atmosphere and controlled radiation combustion wind tunnel. To control the gas composition, metered amounts of oxygen (or nitrogen) are mixed in the air stream. These gases are metered by critical nozzles and mixed by using high speed opposed jets. The resulting mixture is slightly above the atmospheric pressure before it enters the tunnel test section. The tunnel exhausts into a 2'x2'x3' metal chamber whose pressure is maintained slightly below atmospheric by an exhaust fan. The exhaust opening is controlled to obtain atmospheric pressure in the test section. This minimizes any leaks into or out of the tunnel. After the test section, the products of combustion are mixed in a heated exhaust section and a representative gas sample is pumped via. heated sample lines to the gas analysis equipment where the concentration of major species (CO_2, CO, H_2O, O_2, and total hydrocarbons [HC]) are measured as a function of time. Transient measurements of weight loss, temperature in the gas and in the solid phase are also made for different levels of external radiation.

Prior to the experiments the samples are conditioned in a temperature and humidity controlled chamber. This chamber (Model TH-3, BMA Inc.) has a controllable humidity range of 10 to 98% RH ± 2% RH and a controllable

temperature range of 10 to 85°C. The moisture content of the sample is then determined by the difference between its "dry" and "wet" weight. Before conditioning, the test samples are instrumented by fine wire thermocouples on the surface and in-depth. After conditioning the instrumented samples are placed on the weighing table with their top surface flat along the tunnel base and exposed to the radiant heaters. The products of thermal decomposition in the boundary layer flow across an electrically heated wire and the time required for piloted ignition of the sample is noted.

Low Heat-Flux Moisture Desorption Experiments. First, a set of experiments are being conducted to quantify the rate of moisture desorption from the wood samples. Preliminary results of these experiments are very encouraging. They also serve as a test of the capability of the entire experimental apparatus. Figures 2a,b,c and d show various measured quantities plotted against time for an experiment conducted at 1 W/cm^2 on a sample that was at equilibrium with the laboratory air (50% RH and 22°C). Figure 2a shows the external heat flux along with the front and back surface temperatures of the 1.5" thick wood sample. During this experiment N_2 with less than 0.1% H_2O and O_2 was used as the main gas flow in the tunnel. Some room air (with 20.9% O_2 and 1.47% H_2O) was allowed to leak into the tunnel in order to increase the response time and accuracy to the dew-point hygrometer. The amount of leakage was calculated from the measured O_2% in the gases and from the knowledge of N_2 flow rate measured by the critical nozzle. Figure 2c shows the measured O_2 concentration in the gases and production of CO_2 during the decomposition process. Figure 2b shows the meared weight loss during the experiment along with the production rate of water vapor which is roughly 90% of the total weight loss for this low heat flux experiment. The remaining 10% consists of CO_2, CO and total hydrocarbons which are shown in Figures 2c and 2d. It is very encouraging to note that the instantaneous mass balance over the entire duration of the experiment is with ± 5%. It is also evident that water is a significant part of the total weight loss, especially in the initial stages of thermal decomposition where piloted ignition is expected to occur.

Water Droplet Experiments. Work on studying the effect of water droplets on transient cooling of a porous solid is also underway. The objective is to simulate a porous material like wood. Thus, an inert porous ceramic sample has been cast around a matrix of thermocouples. Castable MgO (KF-95) was used for this purpose since it has excellent water absorption properties and its high temperature thermophysical properties (up to 1200°C) are fairly well known. The location of the thermocouples prior to casting was measured to within ± 0.1 mm. However, the confidence in their location inside the casting is only ± 0.5 mm because of the uncertainties introduced during the casting process and shrinkage. Attempts at determining the thermocouple locations radiographically by using X-rays, have thus far not been successful.

Theoretical Model of Piloted Ignition. In a study of piloted ignition of cellulosic materials (Ref. 1) it was shown that a gas-phase energy balance at the instant of ignition enabled the determination of (i) the critical fuel mass flux for ignition, (ii) the critical surface temperature for ignition, and (iii) the ignition time. An experimentally measured premixed flame temperature of extinction was one of the key parameters in the balance equation. A premixed flame temperature was used because it was believed that the initial ignition process occurred through a premixed flame. An extinction temperature was used because the application of the pilot always produces local temperatures higher than the ignition temperature in the gas; thus, the limiting conditions governing sustained flaming are those of extinction. A very convenient experimental result is the near constancy of extinction temperature for most hydrocarbon fuels (near 1550°k, see Ref. 1). Since most of the analysis concentrated on processes occurring in the solid phase, the above gas-phase analysis was mostly phenomenological. However, the formulas obtained for the mass volatilization rate compare very well with previous results (Ref. 2).

Analytical-Numerical Solution Algorithm for the Gas-Phase Equations of Combustion. An operator-splitting procedure was formally developed, in which a (thermal) model equation was analyzed by Green's functions, and shown to be separable in the limit of large Damkohler number. Thus, the calculation of the temperature at the following time step may be separated into two parts. First, the solution of a (spatially) locally homogeneous explosion problem, expressed as a balance between the transient and reaction terms in the energy equation. The duration of the explosion is brief and enables use of the calculated increment of temperature as a modified initial condition. Second, the solution of a homogeneous (no reaction term) convection-diffusion equation, in which the local temperature increments are now redistributed throughout the field. The numerical solution algorithm developed under this formulation is shown by comparison to other schemes to be extremely fast and stable. Detailed discussions of these comparison are presented [see previous progress reports], and where it is shown that the scheme performs well both for premixed and diffusion flames.

One-Dimensional Model of Piloted Ignition. The numerical scheme discussed above is used to integrate the equations for a one-dimensional piloted gas phase flame near a porous fuel wall. The calculations show the initial development of a premixing region, the subsequent propagation of two premixed flame fronts, one toward the fuel surface, the other toward the oxygen side, and the eventual development of a stable diffusion flame. The steady state calculations agree with the theoretical predictions of previous steady-state analyses (Ref. 3). The ignition process is shown to be highly dependent on the premixing process, and therefore the location of the pilot flame [see the discussion of the theoretical model of piloted ignition]. Quenching of the premixed flame by the cold wall just after the ignition spark is the major reason that the theoretically-predicted steady-state flames are not attained. This also explains the "cold flashes" discussed in Ref. 1. When the pilot flame is moved away from the wall, closer to the asymptotic ($t \to \infty$) flame location, sustained flaming is more likely to occur. Comparison of numerically and theoretically calculated flame locations and flame temperatures are in excellent agreement (± 1%).

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1. Atreya, A. and Wichman, I.S., "Heat and Mass Transfer during Piloted Ignition of Cellulosic Solids," 2nd ASME-JSME Thermal Engineering Joint Conference, 1987.

2. Wichman, I.S. and Atreya, A., "A Simplified Model for the Pyrolysis of Charring Materials," accepted for publication in Combustion and Flame (1987).

3. Liñán, A., "The Asymptotic Structure of Counterflow Diffusion Flames for Large Activation Energies," Acta Astronautica, 1, pp. 1007-1039 (1974).

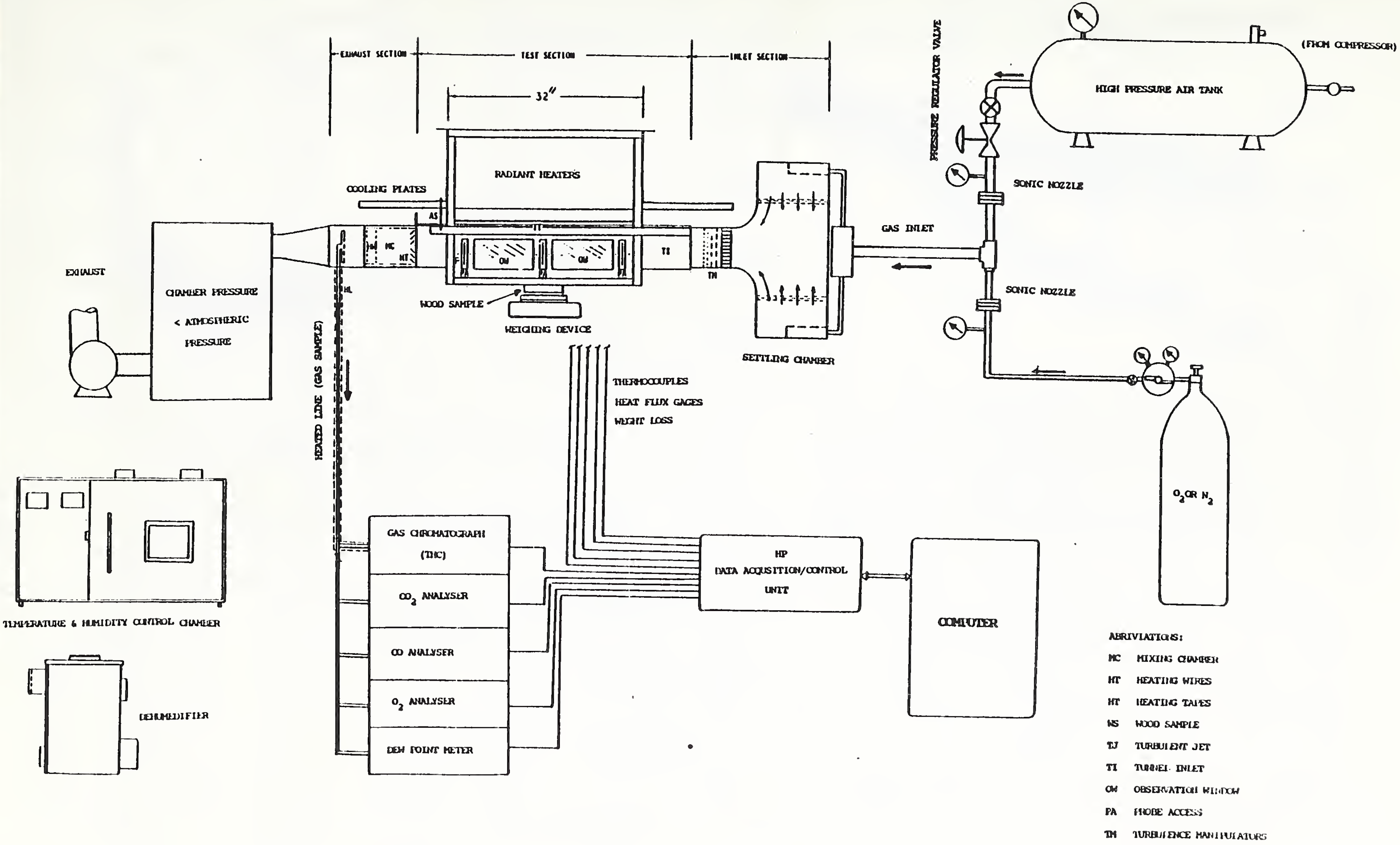

FIGURE 1 EXPERIMENTAL APPARATUS

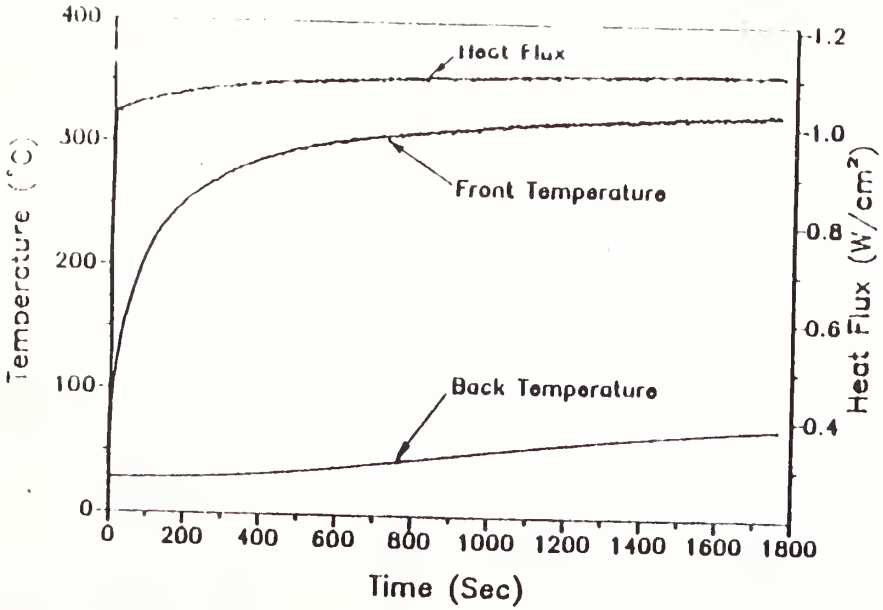

Fig. 2a External Heat Flux and Front & Back Surface Temperatures.

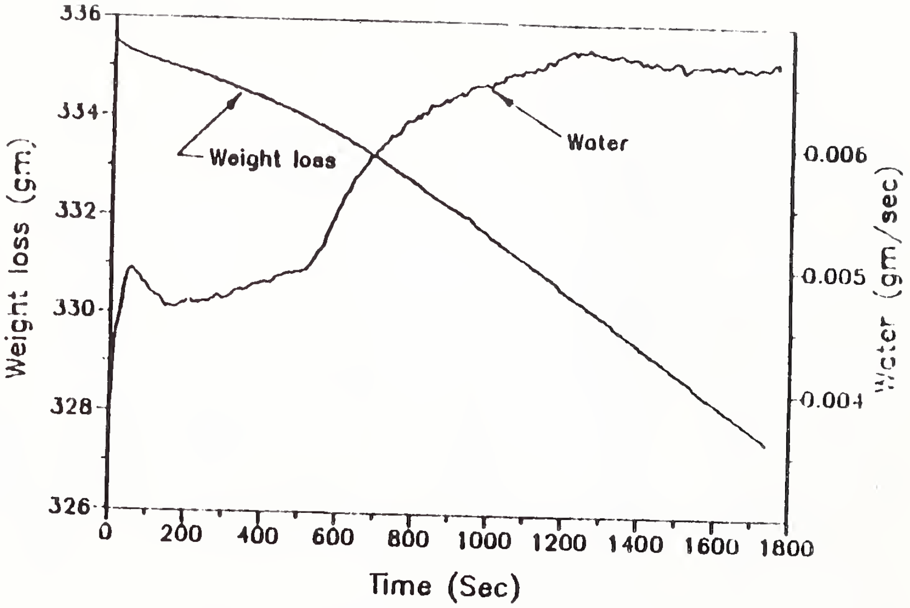

Fig. 2b Sample weight loss and H_2O production rate.

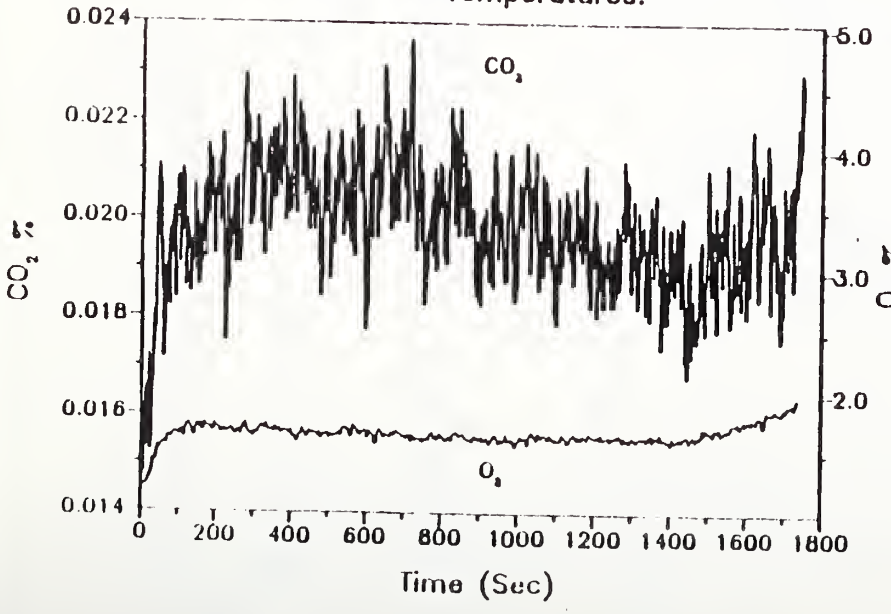

Fig. 2c Co_2 Production rate and O_2 in the tunnel gases.

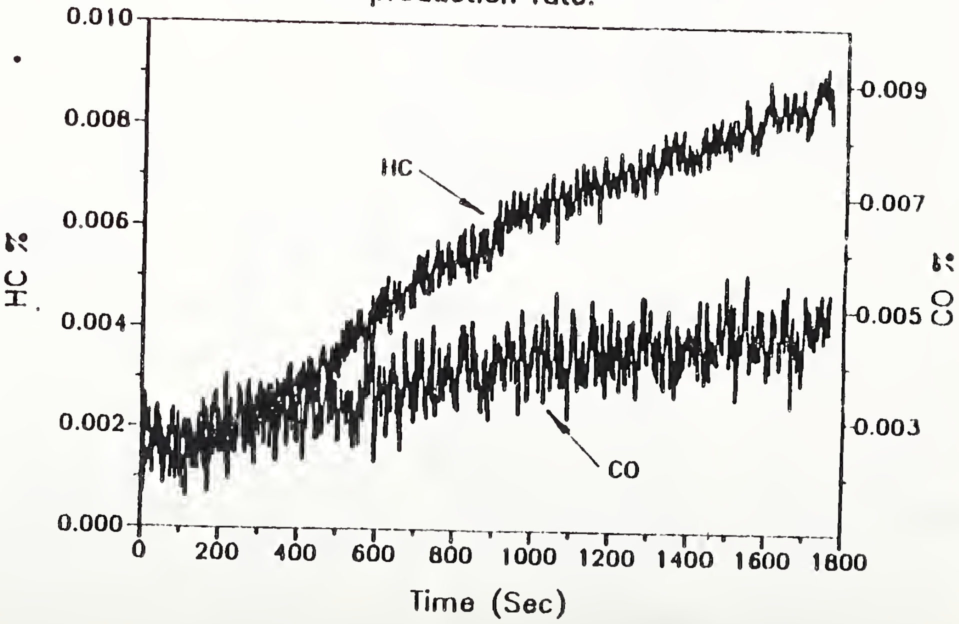

Fig. 2d Hydrocarbon and Co production rate

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: The Pennsylvania State University

Grant No.: 60NANB4D0037

Grant Title: Vertical Wall Fire in a Two-Layer Stratified Atmosphere

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NBS Scientific Officer: Mr. Ken Steckler

Technical Abstract:

Introduction. In a typical compartment fire, the interior atmosphere becomes stratified with a hot, oxygen-deficient layer of gases on the top and a relatively cool, oxygen-rich layer of fresh air on the bottom. The overall objective of this investigation is to study the effect of the stratified ambient atmosphere on the vertical wall fire. We are specifically interested in finding out how the burning rate and the flow of gases are affected. Further, we wish to determine whether a linear superposition of results based on studies assuming nonstratified ambient conditions is adequate for predicting behavior of wall fire in a stratified atmosphere. In the past year, we simulated various types of stratified ambient conditions surrounding burning vertical walls in a small scale apparatus and studied their effect on local burning rates.

Also, in an indirectly related project, we conducted experiments to study behavior of a buoyant jet in a two-layer stratified atmosphere. These experiments, and their outcome, are reported in a paper which is listed below.

Wall Fire Experiments: The experimental setup and the procedure for simulating a stratified atmosphere surrounding a vertical, flat sample of polymethylmethacrylate, and the technique of determining local burning rates, were described in the last year's report.

Figure 1 shows measured temperature (at three different times from the start of a run) and oxygen mass fraction data at various heights for a set of runs (Set 1). For this specific stratified atmosphere in front of the samples, the local burning rates were evaluated in at least four different runs which are shown in Figure 2. The measured burning rate gradually decreases with the distance from the leading edge, x. Overall, the burning rate is considerably less than the burning rate measured for the uniform ambient atmosphere having an oxygen mass fraction, $Y_{O\infty}$ = 0.233. The solid line, denoted by $Y_{O\infty}(x)$, represents the predicted burning rate obtained using the temperature and oxygen mass fraction data set of Figure 1 as boundary conditions in our previously developed mathematical model. The solid line denoted by $\overline{Y}_{O\infty}$ indicates the theoretical results from our mathematical model using a constant value of $Y_{O\infty}$ for $0 \leq x \leq L$, where L is the total height of the sample. This value represents a height-averaged, i.e., bulk mean, value of measured oxygen mass fraction shown in Figure 1. The broken curve with crosses is based on the burning rate data measured by Kulkarni and Sibulkin (Combustion and Flame, 44, 1982) at a fixed height of 4 cm from the leading edge. They measured local burning rate for vertical, flat PMMA slabs in an ambient atmosphere having different (but constant over $o \leq x \leq L$) values of $Y_{O\infty}$. The broken curve is generated from their data by first selecting a distance from the leading edge, (say 3.5 cm); finding out the $Y_{O\infty}$ at this distance from the present data in Figure 1 (at 3.5 cm, it is 0.21); and then reading the burning rate at this $Y_{O\infty}$ from their experimental data curve (at $Y_{O\infty}$ = 0.21, they measured $\dot{m}''_w = 0.88 \times 10^{-2}$ kg/m s). Thus, the broken curve in Figure 2 thus represents a linear superposition of data obtained from several $Y_{O\infty}$ = constant (uniform ambient atmosphere) runs. A very important point must be noted here. It has been shown that the measured limiting oxygen concentration for PMMA vertical slabs (of the same scale and same configuration as the present experiments) is 0.18; i.e., a PMMA slab can not sustain burning in atmospheres having $Y_{O\infty}$ less than 0.18. A linear superposition of experimental results would indicate that as soon as $Y_{O\infty}(x)$ drops below 0.18, there would be extinction. This means that (according to Figure 1) for x>5 cm the burning rate should drop to zero, as shown by the broken curve in Figure 2.

In our experiments, we observed that the PMMA samples continue to burn vigorously over the entire height with the conditions of stratification shown in Figure 1. The fact that the samples burn at the trailing edge, despite having $Y_{O\infty}$ = 0.025 at that height, shows that there must be a very strong influence of the upstream, oxygen-rich layer on the downstream, even up to the trailing edge. A simple linear combination of results obtained from experiments conducted in the uniform ambient atmosphere is not sufficient to explain the behavior of a burning surface in a stratified atmosphere. Another contributing factor for continued burning near the trailing edge of the sample where $Y_{O\infty}$ is well below 0.18 may be the enhanced radiation from the upper, hot layer. However, the upper layer gas temperature and the temperature of the surrounding plates in the present experiments was less than 300°C. A simple calculation would show that such a low temperature cannot add sufficient radiation to sustain a vertical wall fire at $Y_{O\infty}$ = 0.025. Therefore, the major mechanism must be the convection of oxygen from lower layer to upper layer for sustaining the vertical wall fire in a stratified atmosphere.

Figure 3 shows another set of stratification conditions (Set 2). The measured local burning rate at these conditions is shown in Figure 4.

Again, the mechanism of convection of oxygen from the lower layer to the upper layer is confirmed. The agreement of theoretical results using the bulk mean value $Y_{O\infty}$ and the data is purely coincidental here.

The present experimental study clearly shows that in the case of a vertical burning wall in a room having stratified atmosphere, the lower layer has a strong effect on the wall fire and must be given careful consideration in room fire modeling. Because the present study was performed on a small scale, effects of turbulence must be studied before results can be extended to full scale.

<u>Reports and Papers</u>

1. A. K. Kulkarni, and J. J. Hwang, "Vertical Wall Fire in a Stratified Atmosphere", <u>Proceedings of the 21st International Symposium on Combustion</u>, August 1986 (in press).

2. A. K. Kulkarni, H. R. Jacobs, and J. J. Hwang, "Similarity Solution for Natural Convection Flow over an Isothermal Vertical Wall Immersed in a Stratified Medium", <u>Int'l. J. Heat and Mass Transfer</u> <u>30</u>, pp. 691-698 (1987).

3. A. K. Kulkarni and S. L. Chou, "Turbulent Natural Convection Flow over a Vertical Wall in a Stratified Medium", 1987 National Heat Transfer Conference, <u>ANS Proceedings</u>, pp. 216-223, (1987).

4. A. K. Kulkarni and J. J. Hwang, "An Experimental Study of Vertical Wall Fire in a Stratified Atmosphere", Proceedings of the 1987 Fall Technical Meeting, The Combustion Institute, pp. 21.1-21.4, (1987)

5. J. J. Hwang and A. K. Kulkarni, "An Experimental Study of Vertical Wall Fire in Stratified Atmosphere". Submitted to <u>International Journal of Experimental Heat Transfer, Thermodynamics, and Fluid Mechanics</u>.

6. A. K. Kulkarni and F. Murphy, "Buoyant Jet in a Two-Layer Stratified Medium", to be presented at the International Symposium on Natural Circulation, 1987 ASME Winter Annual Meeting, Boston, Massachusetts.

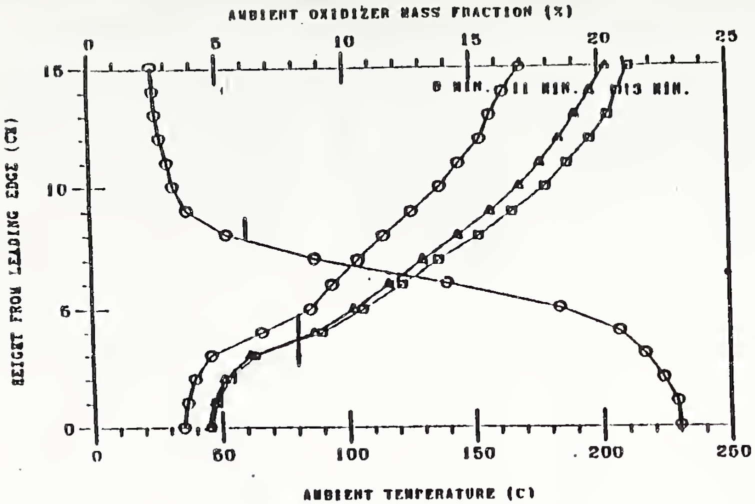

Figure 1. Profiles of temperature and oxidizer mass fraction for a certain set of experimental conditions (set 1). The height-averaged oxidizer mass fraction is $\bar{Y}_{O,\infty}$ = 0.11.

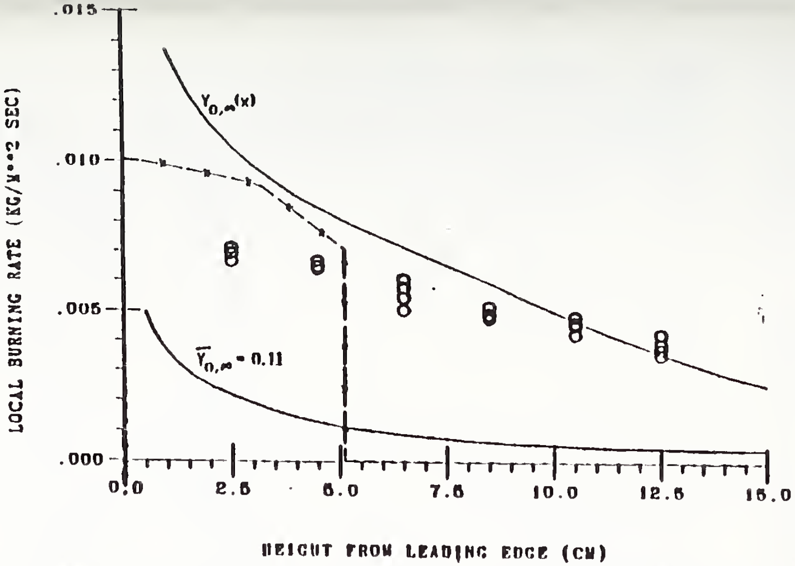

Figure 2. Local mass burning rate data for stratification conditions shown in Fig. 1 (circles). $Y_{O,\infty}(x)$ denotes our predictions with boundary conditions of Fig. 1. $\bar{Y}_{O,\infty}$ denotes the predictions for an average (constant) value of $Y_{O,\infty}$ for the data set in Fig. 1. Also, data of Kulkarni and Sibulkin (1982) are shown by broken line.

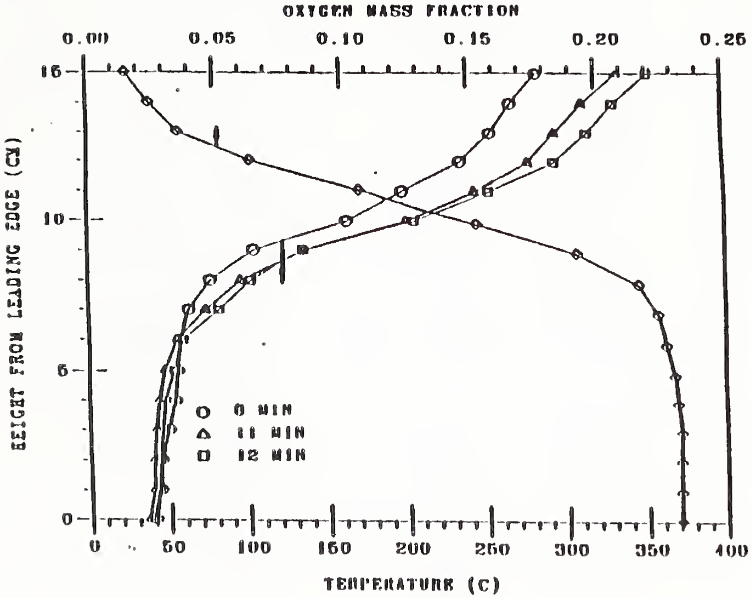

Figure 3. Profiles of temperature and oxidizer mass fraction for a certain set of experimental conditions (set 2). The height-averaged oxidizer mass fraction is $\bar{Y}_{O,\infty}$ = 0.17

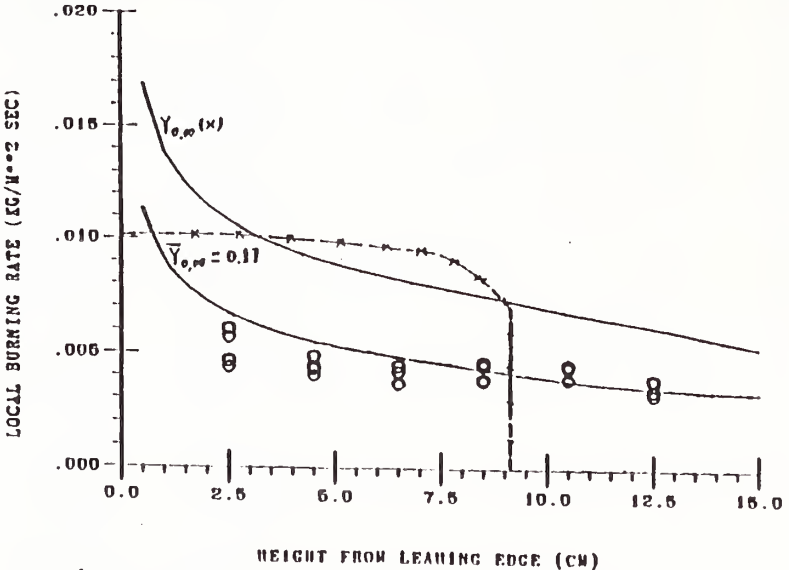

Figure 4. Local mass burning rate data for stratification conditions shown in Fig. 3 (circles). $Y_{O,\infty}(x)$ denotes our predictions with boundary conditions of Fig. 3. $\bar{Y}_{O,\infty}$ denotes our predictions for an average (constant) value of $Y_{O,\infty}$ for the data set in Fig. 3. Also, data of Kulkarni and Sibulkin (1982) are shown by broken line.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of California, Berkeley

Grant No.: 60NANB5D0552

Grant Title: Fire Modeling

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NBS Scientific Officer: Dr. Howard Baum

Technical Abstract:

The overall goal of this project is to develop chemical, physical and mathematical models of the detailed combustion phenomena which control a fire's growth. Our emphasis recently has been on accurate descriptions of boundary layer flames and on measurement and prediction of the soot volume fraction, f_v, in a variety of flames and on the role of f_v in determining the fire radiation.

Combusting Boundary Layers:

In order to interpret f_v measurements in free and forced boundary layers, accurate temperature and velocity fields are needed. (See e.g. Smyth, K.C. et al. Combustion and Flame, 62, 1985, pp. 157-181). The classic solutions of boundary layer diffusion flames neglected phenomena such as fuel cracking, property variations, buoyancy and radiation and, therefore, produced profiles that are not adequate for soot formation modeling. These analyses add those effects (1-4).

The fact that predicted temperature profiles significantly overestimate measured temperatures between the fuel surface and the flame (5) even when soot radiation is negligible, as shown in Fig. 1, implies that endothermic fuel cracking is important. Therefore, we have included a pyrolysis reaction, $Y_{F1} \rightarrow Y_{F2}$, in our analyses. Fast

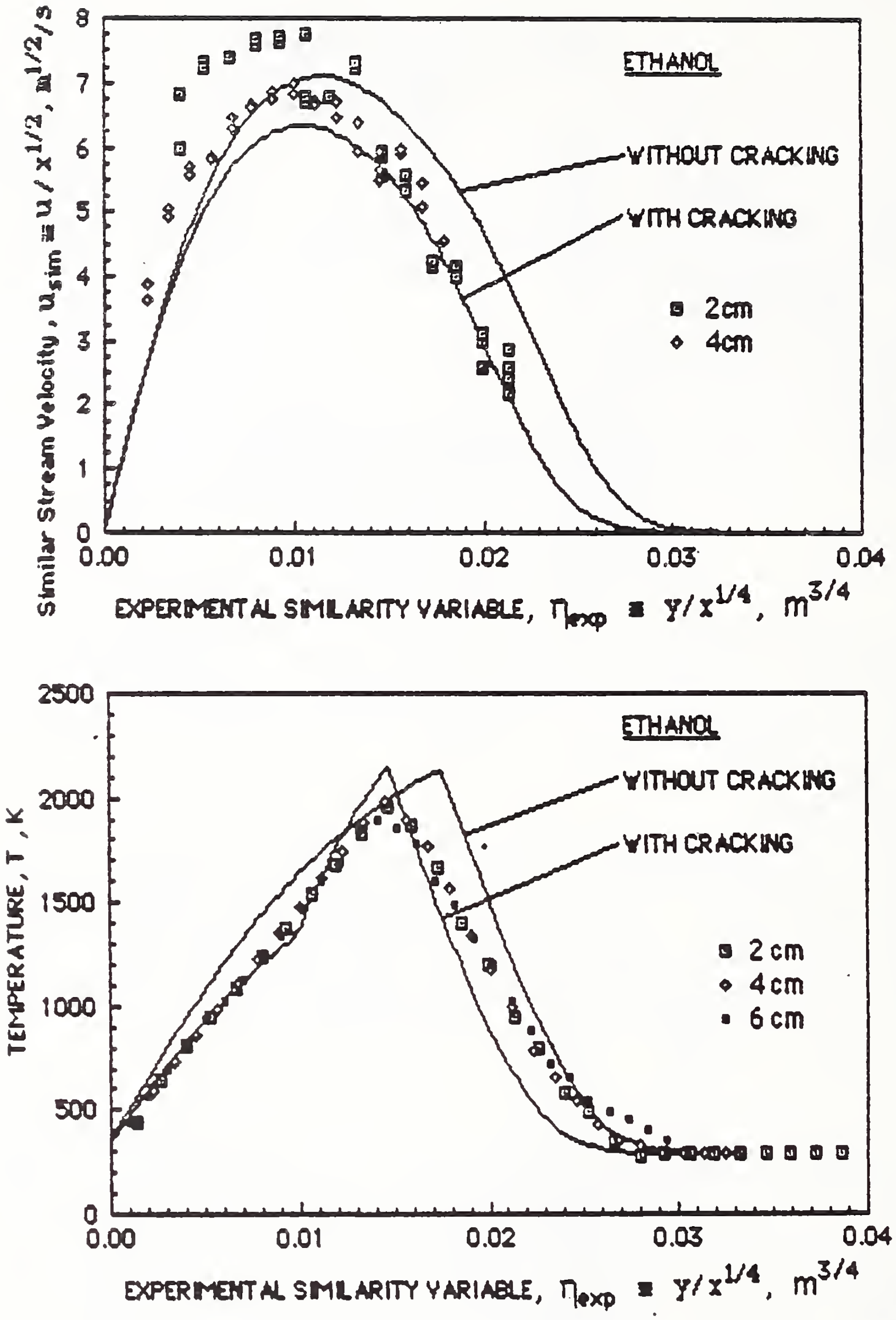

Fig. 1 Comparison of experimental (5) and theoretical streamwise velocity and temperature profiles for ethanol. Experimental velocities are for 2 cm and 4 cm downstream. Experimental temperatures are for 2 cm, 4 cm and 6 cm downstream. The theoretical curves are shown with and without thermal cracking.

kinetics are assumed so that a fuel cracking sheet exists inside the flame sheet as shown in Fig. 1. In the future these sheets will be expanded using activation energy asymptotics. Similarity solutions are still possible provided the Shvab-Zeldovich variables are redefined to include the cracked fuel product, Y_{F2}, as will be discussed for the free case in the Meeting of the Eastern Section of the Combustion Institute held simultaneously with this year's Annual Conference.

Fire Radiation:

In flame radiation, the most important and least known parameter is f_v, the soot volume fraction, defined as the volume occupied by soot per unit of flame volume. Previous summaries have described a multi-wavelength laser extinction technique for in-situ measurement of the local flame f_v in free and forced boundary layers as well as in pool fires. Detailed experimental comparisons are underway with alternative single-wavelength scattering/extinction measurement methods, by my student, Valerie Lyons, at NASA Lewis Research Center. Good progress has been made and this project should come to a conclusion during this grant period.

Limited data on small pool fire mean soot volume fractions suggest f_v scales with optical thickness, κL, as

$$f_v/f_{v_{max}} = 1.5(\kappa L)^{1/3} \quad , \kappa L \leqslant 0.3$$

$$f_v/f_{v_{max}} = 1 \quad , \kappa L \geqslant 0.3$$

If this correlation holds for all fuels, it will permit scaling of the mean f_v in pool fires to any size from a single measured f_v. The apparatus described in Ref. 6 is being reconstructed to perform additional experiments to evaluate the correlation.

Other studies related to fire are underway at Berkeley with separate support in the areas of smoldering (7,8,9) and self-heating to ignition (10). These projects were required due to the slow, continuous attrition of CFR grant support. A review paper for the Second International Symposium on Fire Safety Science is in preparation. We are also assisting the Publications Committee in planning the publication (11) of the Proceedings of the Second International Symposium.

Reports and Papers:

1. J.A. Ang, "Perturbed Boundary Layer Diffusion Flames," Doctoral Dissertation, Mechanical Engineering Department, University of California-Berkeley, November 1986.

2. T.G. Mataga, "Thermal Cracking and Variable Properties Effects on Free Boundary Layer Diffusion Flames," Master of Science Thesis, Mechanical Engineering Department, University of California-Berkeley, December 1986.

3. J.A. Ang and P.J. Pagni, "Forced Flow Boundary Layer Flames with Thermal Cracking," Combustion and Flame, to appear, 1988.

4. T.G. Mataga, J.A. Ang and P.J. Pagni, "A Two Sheet Model for Fuel Pyrolysis and Reaction," Paper No. 17, Eastern Section of the Combustion Institute-1987 Fall Technical Meeting, November 2-6, 1987.

5. J.A. Ang, P.J. Pagni, T.G. Mataga, J.M. Margle and V.J. Lyons, "Temperature and Velocity Profiles in Sooting Free Convection Diffusion Flames," AIAA Journal, to appear late 1987/early 1988.

6. S. Bard and P.J. Pagni, "Spatial Variation of Soot Volume Fractions in Pool Fire Diffusion Flames," Fire Safety Science - Proceedings of the First International Symposium, pp. 361-369, Hemisphere Publishing Co., New York (1986).

7. S.S. Dosanjh, J. Peterson, A.C. Fernandez-Pello and P.J. Pagni, "Bouyancy Effects on Smoldering Combustion," Acta Astronautica, 13, pp. 689-696, 1986.

8. S.S. Dosanjh and P.J. Pagni, "Forced Countercurrent Smoldering Combustion," Proceedings of the 1987 AMSE-JSME Thermal Engineering Joint Conference, P.J. Marto and I. Tanasawa, eds. Vol. 1, pp. 165-173, 1987.

9. S.S. Dosanjh, P.J. Pagni and A.C. Fernandez-Pello, "Forced Cocurrent Smoldering Combustion," Combustion and Flame, 68, pp. 131-142, 1987.

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11. C.E. Grant and P.J. Pagni, eds., Fire Safety Science - Proceedings of the First International Symposium, Hemisphere Publishing Co., New York (1986).

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of California, Berkeley

Grant No: NB83NADA4020

Grant Title: Fire Propagation in Concurrent Flows

Principal Investigator: Professor A.C. Fernandez-Pello
Department of Mechanical Engineering
University of California
Berkeley, CA 94720

Other Professional Personnel: B. Amos, Doctoral Graduate Student
L. Zhou, Doctoral Graduate Student

NBS Scientific Officer: Dr. H. R. Baum

Technical Abstract:

A research program is being conducted to study the mechanisms controlling the spread of flames over the surface of a solid combustible in an oxidizing gas flow. The objective of the research is to provide fundamental information about the spread of fire for its use in the development of models of fire growth in rooms, and of test methods of the flammability of materials. Because of the varied mechanisms involved in the flame spread process, the research program encompasses a number of studies covering different physical phenomena, from the ignition of a gasifying surface to the extinction of a spreading flame.

Research performed during this reporting period includes two theoretical studies. One is a numerical analysis of the ignition of a combustible solid that is vaporizing in a stagnation point air flow due to an externally applied irradiance perpendicular to the solid surface. The analysis considers the cases when ignition is caused by absorption of radiation by the vaporized fuel (high irradiances) or by heat transfer to the gas from the elevated temperature vaporizing surface (charring material). The second study is a numerical analysis of the influence on the spread of flame over a thick combustible solid of the velocity and oxygen concentration of a flow opposing the direction of spread. Both studies provide relevant information about the mechanisms leading to the establishment of a flame and its spread over a solid combustible surface.

Ignition of a Vaporizing Combustible Solid:

In this work, an analysis is developed of the ignition of a vaporizing flat combustible solid and of the subsequent establishment of a diffusion flame over it, in a stagnation point oxidizing gas flow. The gasification of the solid is produced by an external radiant flux applied perpendicular to the surface. Two sources of ignition are considered; one the absorption of radiation by the vaporized gaseous fuel, and the other heat transfer to the gas from the elevated temperature vaporizing surface. The former case applies to the ignition of a combustible that is exposed to a very high radiant intensity, and the latter to the ignition of a charring material whose char attains high temperature due to the external irradiance.

The ignition by vapor fuel absorption of radiation is modeled as follows. A planar combustible solid at its vaporization temperature is in a stagnation point air flow at ambient temperature. At the initial time the solid surface is suddenly subjected to a constant radiant flux perpendicular to the surface. The solid absorbs the radiation at its surface and immediately begins to vaporize mixing with the ambient air. The vaporized fuel absorbs some of the incoming radiation and eventually becomes hot enough to initiate the ignition of the fuel/air mixture. After the onset of ignition, the external radiation is removed and the chemical reaction is let to evolve until it becomes a self-sustained, steady, diffusion flame. In the analysis it is assumed that the absorption of radiation by the gas is independent of the temperature, but that is directly proportional to the fuel concentration. The combustion of the mixture is modeled using a one step chemical reaction of the Arrhenius type. In accordance with related stagnation point solutions, it is assumed that the normal velocity component, the temperature, and species are only functions of time and the normal coordinate.

The problem governing equations are solved numerically using an implicit method except for the temperature in the reaction rate term which is handled explicitly. A movable grid is used to track the propagation of the flame after ignition. The grid size and time steps are varied according to the characteristic lengths and times dominant during the analyzed period. A parametric study of the effect on the ignition delay time and flame structure of the radiant intensity, absorption coefficient, and flow velocity is performed for PMMA as combustible solid. A characteristic example of the predicted evolution of the temperature profile is shown in Fig. 1, for a flow velocity of 0.5 m/sc imposed at a distance of 5 cm from the surface, an irradiance of 38 w/cm^2 and an absorption coefficient of 10 m^2/kg. The predicted evolution of the temperature and species profiles shows the existence of three regimes. The first regime corresponds to the period from the instant when the external irradiance is first applied to the onset of ignition. The evaporation of the fuel causes the generation of two opposing stagnation point flows, one of fuel and the other of oxidizer, at whose interface the fuel and oxidizer mix by diffusion. During this period the fuel vapor absorbs radiation and heats up eventually causing the ignition of the mixture. After ignition, the combustion reaction propagates through the mixture away from the solid surface. This premixed propagation process leads to the generation of a diffusion flame once all the fuel ahead of it is consumed. The diffusion flame adjusts its position until finally it reaches its steady state position near the wall.

The analysis and the results for the case when ignition is caused by the high surface temperature are similar to those described above. A characteristic example of the evolution of the temperature profiles is presented in Fig. 2. It is seen that although in this case ignition occurs sooner and closer to the wall, the generation of the diffusion flame over the gasifying surface follows the same pattern as that predicted in the previous case.

Dependence on the Opposed Flow Characteristics of the Flame Spread Over a Thick Solid Combustible

A theoretical model is developed of the effect on the spread of flames over the surface of a thick solid combustible of the velocity and oxygen concentration of a gas flow opposing the direction of flame spread. In the analysis, the transient, reactive, gas phase balance equations of energy and species coupled at the interface to the solid phase energy equation are solved numerically to predict the flame spread rate and flame structure dependence on the characteristics of the flow. To simplify the analysis, the gas flow is prescribed as a constant density, Hagen-Poiseuille flow. The gas phase reaction is modeled with a one step, second order Arrhenius reaction and the solid pyrolysis with a zero order Arrhenius rate. The problem governing equations and boundary conditions are solved numerically using a finite difference, implicit, method.

A variable integration grid is used in the normal direction to accommodate the large temperature and species gradients near the solid surface. The time steps are based on the lowest characteristic time of the problem.

The calculations are made for PMMA as combustible material. In Fig. 3, the results are shown for the flame spread rate variation with the flow velocity for three oxygen mass fractions. For comparison purposes, the experimental results of Fernandez-Pello et. al. (18th International Combustion Symposium, 1981) are also included in the figure. It is seen that the analysis describes quantatively well the experiments predicting a spread rate that for a given oxygen concentration, varies with the flow velocity first increasing and then decreasing as the velocity increases. For a given flow velocity the spread rate increases with the oxygen concentration. The results of the analysis show that this behavior is the result of the interaction of two controlling mechanisms. A flame to fuel heat transfer mechanism that dominates at low flow velocities and/or oxygen concentrations and a gas phase chemical Kinetics mechanism that dominates at high velocities and/or oxygen concentrations. The discrepancies between the theoretical and experimental results are explained by the simplifications used in the model, particularly the prescribed flow, the absence of buoyancy and the one step chemical reaction.

Reports and Papers

1. Kodama, H., Miyasaka, K. and Fernandez-Pello, A.C., "Extinction and Stabilization of a Diffusion Flame on a Flat Combustible Surface with Emphasis on Thermal Controlling Mechanisms", Combustion, Science and Technology (in press, 1987).

2. Amos, B., Kodama, H., and Fernandez-Pello, A.C., "An Analysis of the Ignition by Vapor Radiation Absorption of Vaporizing Fuel at Zero Gravity", Presented at the AIAA 25th Aero. Sci. Meeting, Reno, Nevada, 1987. Submitted for publication in Acta Astronautics.

3. Amos, B.,"Ignition and Flame Propagation Studies Over a Flat Fuel Surface", Ph.D. Thesis, Department of Mechanical Engineering, University of California, Berkeley, August 1987.

4. DiBlasi, C., Cresticelli, S., Russo, G. and Fernandez-Pello, A.C., "Predictions of the Dependence on the Opposed Flow Characteristics of the Flame Spread Rate over Thick Solid Fuels". Submitted at the 2nd Int. Symp. of Fire Safety Sci., Japan, June 1988.

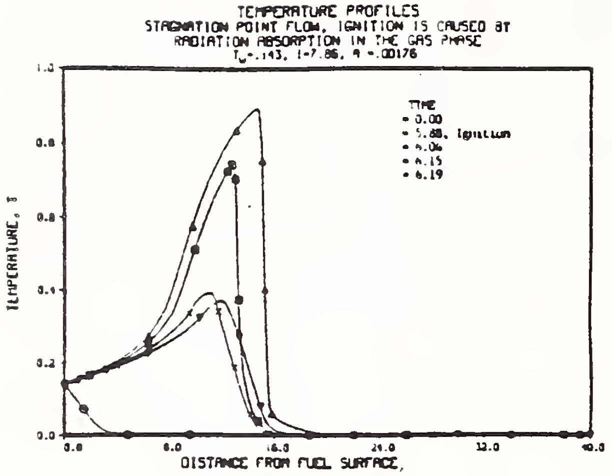

Figure 1.

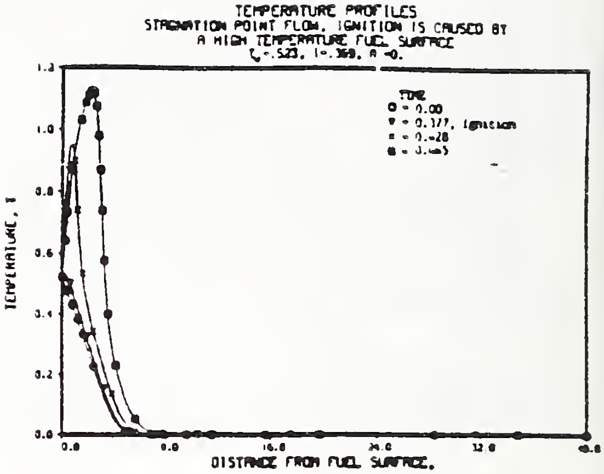

Figure 2.

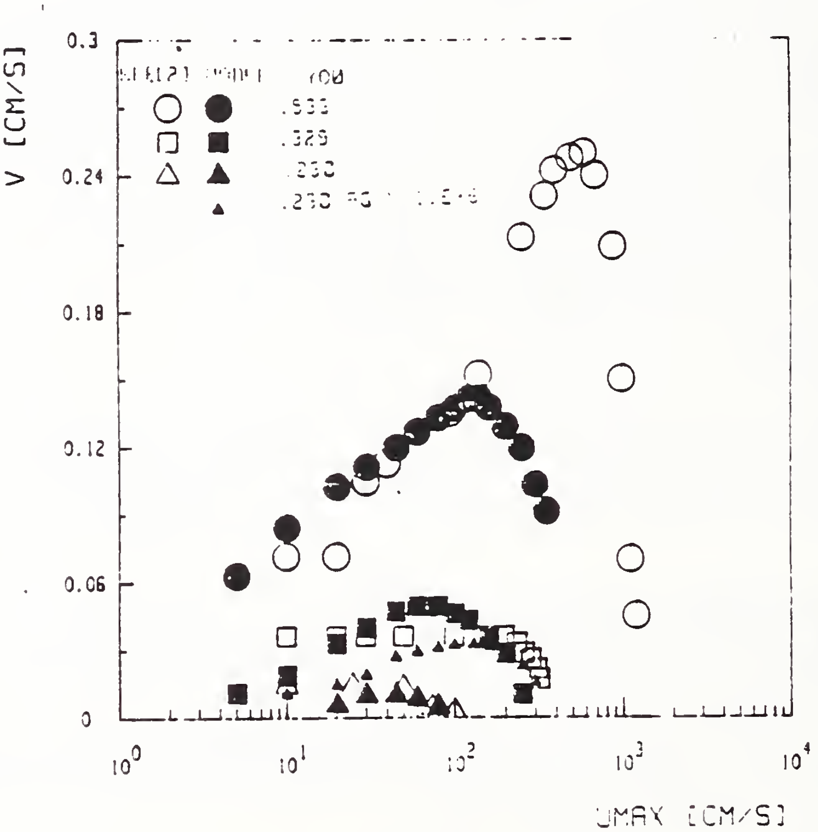

Figure 3.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: The University of California

Grant No: 60NANB6D0651

Grant Title: A Study of the Supression and Extinction of Fires by Water Sprays

Principal Investigators: Professors W. W. Yuen and W. Lick
Department of Mechanical Engineering
University of California at Santa Barbara
Santa Barbara, California, 93106

NBS Scientific Officer: Dr. Bernard J. McCaffrey

Technical Abstract

1. INTRODUCTION

The objective of this study is to determine the fundamental mechanisms by which the spraying of water leads to fire supression and extinction. During this reporting period, the research concentrated on three specific tasks: (1) the numerical modelling of the general and localized circulation in a room as dependent upon door and window openings; (2) a detailed analysis and description of the dynamics of water spray as influenced by the fluid dynamics; and (3) the thermal quenching of a flame due to the presence of chemically-inert species. The first two tasks contribute to the understanding of the "survivability" of the water sprays in a fire environment after injection. The third task contributes to the understanding of the interaction between the water droplets/vapor and the reacting species in a combustion/extinction process.

2. MODELLING OF CIRCULATION IN A ROOM WITH DOOR AND WINDOW OPENINGS

A quite general numerical model of the time-dependent dynamics of a compressible, viscous, heat-conducting, chemically-reacting mixture of gases has been developed and applied to the problem of natural heat convection in a room with door and window openings. A unique feature of the model is its treatment of the conditions at the doors and windows, where open boundary conditions (Licks, et. al. 1986, 1987). must be specified. Numerous calculations have been made and are being made to investigate the general dynamics of natural convection in a room with specific emphasis on the effects of door and window opening.

A preliminary calculation of this type, primarily to test the open boundary condition, is shown in Figures 1 and 2. A heat source at the middle of the left wall causes the air to rise and a ceiling jet to develop. On the right, the hot air escapes from the top and cool air is drawn in at the bottom. A steady-state eventually develops and it can be shown that the open boundary condition (in its nonlinear formulation) works extremely well. This type of calculation is continuing so as to investigate the effects of various flow parameters.

3. DYNAMICS OF WATER DROPLETS

The model described in section 2 is used simply to describe the general fluid dynamics. Of primary interest is the dynamics of the water droplets as influenced by the fluid dynamics and the influence of the water droplets on the fluid dynamics. A general numerical model of this interaction is being developed.

Both the fluid dynamics and the droplet dynamics are developed by an Eulerian procedure. For complex problems of droplet-fluid dynamics interaction, this seems most appropriate and numerically efficient. The basic conservation equations for the water droplets have been written in a form identical to the fluid dynamics equations used in the model described in section 2 and are presently being included in that model. In its most general form, this model can then be used to describe the dynamics of water droplets of varying sizes and the droplet's size changes as a function of evaporation and heat transfer.

4. THERMAL QUENCHING BY CHEMICALLY-INERT SPECIES

Since water is not expected to be chemically reactive with most common fuels, the supression and extinction of fire by water is primarily a thermal quenching phenomenon as noted by previous investigators (Rasbash 1962, Grove et.al. 1981, Williams 1981). A survey of the literature, however, shows that while extensive amount of data have been collected on the relative effectiveness of various gaseous/liquid agents on thermal quenching (Friedman and Levy 1963, Seshadri and Williams 1975, Kent and Williams 1975, Tucker et.al. 1981), a fundamental non-empirical theoretical study of this important phenomenon has not been reported. The development of such a theoretical model is a major objective of this research program.

A laminar diffusion flames generated by two opposing flows of fuel and oxidizer is selected as the basis of the present extinction study. The geometry is shown in Figure 3. This geometry is selected because it is one of the few cases for which conservation equations for mass, momentum and energy can be readily written from first principle with no empirical constants. Assuming constant thermophysical properties, density and a unit Lewis number, numerical and approximate solutions to this problem have been reported by many investigators (Fendell 1965, Linan 1974, Krishnamurthy et.al. 1976). Many of the reported experimental studies on extinction (Friedman and Levy 1963, Seshadri and Williams 1975, Kent and Williams 1975, Tucker et.al. 1981) were also performed on this opposing flow configuration.

The mathematical development in the previous works is generalized in the present work to allow a variation of the specific heat of the reactants and products as a function of composition and temperature. Numerical results are generated for a pure fuel stream (methane) and oxidizer streams consisting of oxygen and different inert gases of various proportions.

Typical ignition characteristics generated for three inert gaseous species (N_2, H_2O, andHe) with different specific heats are presented in Figure 4a. At 600 K, the specific heat for N_2, H_2O and He are 1.0 J/gm-K, 2.0 J/gm-K and 5.2 J/gm-K respectively. As expected, for a given oxygen mass fraction in the oxidizer stream, the mixture ignites if the dimensionless Damkohler number (which is a ratio of the characteristic time of the flow to the characteristic time of the reaction) exceed a critical value. For a given inert gas, a decrease in the oxygen mass fraction in the oxidizer stream reduces the reaction rate, the critical Damkohler number required for ignition increases. For the same oxygen mass fraction, a mixture with an inert gas of higher specific heat has a lower mixture temperature and therefore lower reaction rate. The critical Damkohler number required for ignition also increases.

Since the Damkohler number is inversely proportional to the characteristic flow velocity, numerical data presented in Figure 4a can be presented in terms of the characteristic flow velocity, u, as shown in Figure 4b. u_0 is a characteristic velocity corresponding to the ignition of an oxygen/nitrogen mixture with 50% oxygen mass fraction. It is interesting to note that Figure 4b is qualitatively similar to some experimental extinction curves. Since u_0 is the only adjustable parameter in Figure 4b, the present results suggest that measurement of the extinction curves for different inert species and oxygen mass fraction can be an effective mean in determining the various reaction constants for the reaction.

In the next reporting period, additional numerical results will be generated for other fuels and inert gases. The model will also be expanded to allow for variable density and Lewis number different from unity. Based on the model, the effect of liquid inert species on the reacting mixture will be addressed. Specifically, the fire supression/extinction characteristics of water spray will be illustrated.

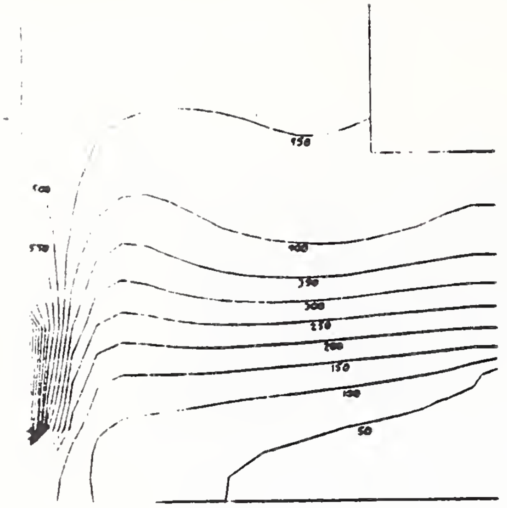

Fig. 1. Computed Isotherms in an Enclosure with a Hot Spot (1000 C) at the Wall and an Opening.

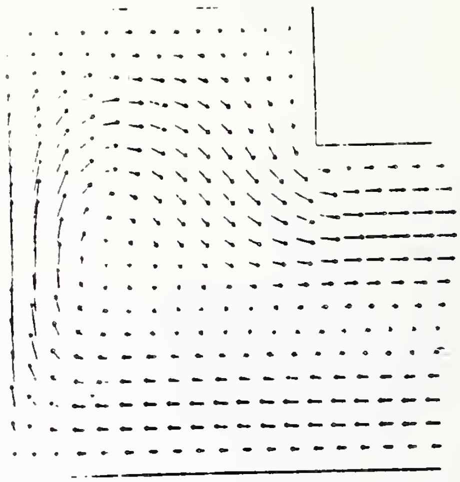

Fig. 2. Computed Flow Field in an Enclosure with a Hot Spot (1000 C) at the Wall and and Opening.

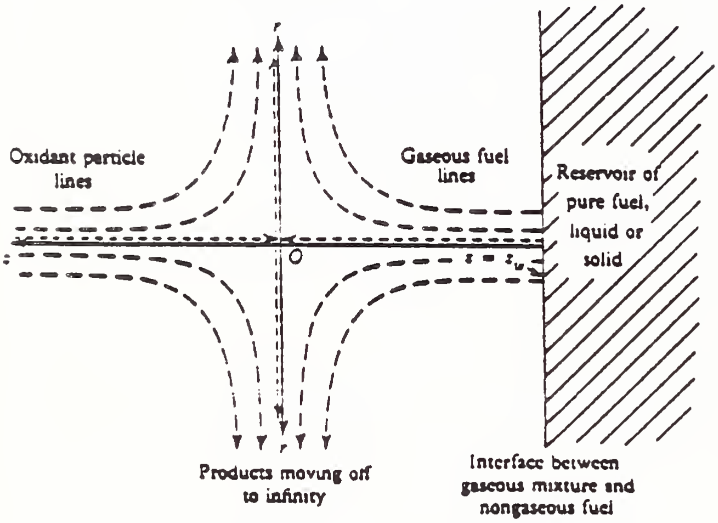

Fig. 3. Oxidant, Fuel, and Product Particle Lines in an Axially Symmetric Stagnation-Region Flow.

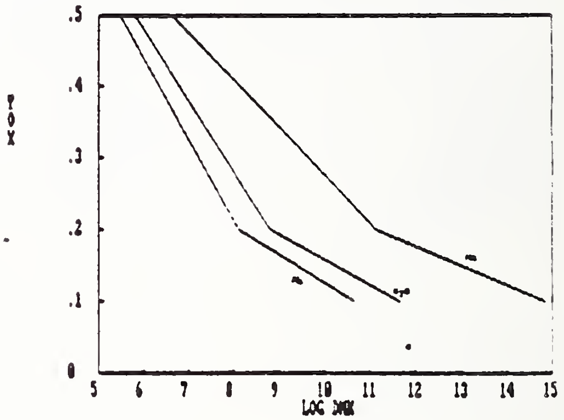

Fig. 4a. Critical Damkohler Number Required for Extinction for Oxidizer Streams with Different Oxygen Mass Fraction and Inert Gas.

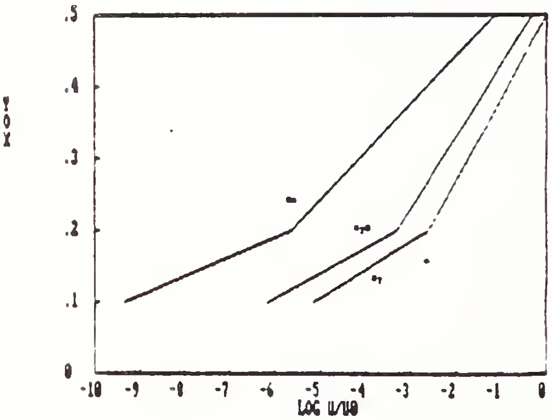

Fig. 4b. Critical Characteristic Flow Velocity Required for Extinction for Oxidizer Streams with Different Oxygen Mass Fraction and Inert Gases.

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: The University of Maryland at College Park

Grant No.: COMM 70NANBSH0525

Grant Title: Transient Cooling of a Hot Surface by Droplets Evaporation

Principal Investigator: Dr. Marino di Marzo
Mechanical Engineering Department
University of Maryland
College Park, MD 20742

Other Professional Personnel: W. H. Meng, Graduate Research Assistant
Z. Y. Wang, Graduate Research Assistant

NBS Scientific Officer: Dr. David D. Evans

Technical Abstract:

Introduction The phenomena associated with solid fuel fire extinguishment processes are related to the evaporation of water droplets deposited on hot solids. Numerous investigations address the full range of water vaporization phenomena on hot high thermal conductivity solids. More closely related to the extinguishment problem are the phenomena of evaporation on low conductivity solid. The evaporation of gently deposited droplet on Macor (a glasslike material) is described hereafter. In order to develop a complete predictive method for the cooling processes, the effect of the droplet momentum on the configuration of the water deposited on the solid surface is quantified. Finally, a methodology to extend the single droplet results to a spray is presented.

Data Collection With Macor Water droplets are gently deposited on a Macor block at various initial surface temperatures. The measured radius of the wetted area is ratioed to the radius of the spherical droplet of equivalent volume and is identified as the shape parameter β [r1]. Figure 1 shows the behavior of the shape parameter β as a function of the initial solid surface temperature for various droplet volumes. Note that each data point shown in the figure is the average of ten experimental measurements. For the purpose of the analysis, a constant value of the shape parameter β of 1.42 is used since most of the experimental data are within a plus or minus five per cent band about this value.

The evaporation time for various droplet sizes and initial surface temperatures is presented in Fig. 2. The cooling is more intense and more localized than previously measured for aluminum [1]. This means that the evaporation time for droplet deposited on Macor is longer than the time of evaporation of droplets deposited on aluminum given the same

initial solid surface temperature. The reason for this result is evident if one considers that, due to its lower thermal conductivity, the Macor exhibits lower temperatures in the droplet proximity than the aluminum. In line with this consideration it is also reasonable that nucleate boiling is suppressed up to initial surface temperatures of the Macor in the order of 160 °C while, for droplets deposited on aluminum, nucleate boiling is observed at temperatures a few degrees higher than the water saturation temperature. Indeed, if one considers the contact temperature suggested by Seki [r2] to be present under the droplet (at least at the initial contact time), it can be shown that, for an initial Macor surface temperature of 160 °C and a liquid water initial temperature of about 25 °C, the contact temperature is very close to the water saturation temperature.

Droplet Release Height and Shape Parameter An extensive data base is collected to identify the effect of droplet momentum on its configuration after impact on the solid surface. A droplet that spreads on the surface has a faster evaporation time than a droplet that spreads less. Analysis to correlate the droplet shape parameter β with the droplet impact velocity is under way. This information is paramount to extend the softly deposited droplet studies to the cooling effect of a water spray.

Multi-Droplet Cooling A multi-droplet model is developed to determine the minimum water mass needed to cool a hot surface. This calculation is the basis for the future development of a thermal model of extinction with water sprays. The model uses the single droplet experimental results obtained for aluminum [1] and is derived under the following assumptions: a) no coalescence of droplets takes place on the plate; b) a suitable frequency function can describe the distribution of droplet sizes in the spray. Therefore, a droplet size distribution function can be use to integrate the cooling effect induced by all the droplets in a spray.

The cooling effect induced by a single droplet is calculated making use of three correlations describing: the evaporation time, the shape parameter β and the maximum area of the solid surface influenced by the droplet cooling. As a result, the total maximum area of influence contributed by a spray is expressed as a function of droplet mass flow rate, initial surface temperature and two mean diameters. A criteria is proposed to determine whether or not the hot surface is cooled. That is, the ratio of the area of influence and of the surface area should be at least larger than 1.0. Experimental determination of the value of this ratio is one of the future task of this study.

In order to illustrate the model, three typical distribution functions [r3] are used to calculate the water mass required to cool a solid surface. Figure 3 shows the results of the model prediction for the Rosin-Rammler, the Nukiyama-Tanasawa and the Log-Probability distribution functions. The water mass is intended to be supplied in twice the evaporation time of the average size droplet.

Conclusions The cooling effect of a single droplet gently deposited on the surface of a Macor block is compared to the similar cooling effect on a higher conductivity solid (aluminum). Further information is provided concerning the behavior of the shape parameter β for droplets impinging on a solid surface with a given momentum. A model to extend the single droplet cooling to a spray is proposed and demonstrated for three typical spray distributions.

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r2. M. Seki, H. Kawamura, K. Sanokawa, "Transient Temperature Profile of a Hot Wall Due to an Impinging Liquid Droplet", J. Heat Transfer, 100, 176, 1978

r3. R. A. Mugele, H. D. Evans, "Droplet Size Distribution in Sprays", Ind. Eng. Chem., 43, (6), 1317, 1951

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1. M. di Marzo, A. K. Trehan, "Transient Cooling of a Hot Surface by Droplet Evaporation", National Bureau of Standards Report, NBS-GCR-86-516, 1986

2. M. di Marzo, "The Cooling Effect of a Single Evaporating Droplet on a Hot Semi-Infinite Metal Body", Annual Conference on Fire Research, NBS - Gaithersburg, MD, 1986

3. M. di Marzo, D. D. Evans, "The Cooling Effect Induced by a Single Evaporating Droplet on a Semi-Infinite Body", Proceedings of the Eastern Session of the Combustion Institute Fall Technical Meeting, pp. 23-1-4, San Juan, Puerto Rico, 1986

4. M. di Marzo, D. D. Evans, A. K. Trehan, "The Cooling Effect of a Single Droplet on a Hot Semi-Infinite Metal Body", National Bureau of Standards Interagency/Internal Report, NBSIR 87-3517, 1987

5. M. di Marzo, D. D. Evans, "Dropwise Evaporative Cooling of High Thermal Conductivity Materials", Heat and Technology, Vol. 5, No. 1-2, pp. 126-136, 1987

6. M. di Marzo, D. D. Evans, A. K. Trehan, "The Cooling Effect of a Single Evaporating Droplet on a Semi-Infinite Metal Body", Proceedings of the II ASME-JSME Thermal Engineering Joint Conference, Honolulu, Hawaii, Vol. 1, pp. 409-415, 1987

7. M. di Marzo, Z. Y. Wang, W. H. Meng, "Transient Cooling of a Hot Surface by Droplet Evaporation", Mechanical Engineering Report, No. 87-11, 1987

8. M. di Marzo, D. D. Evans, "Evaporation of a Water Droplet Deposited on a Hot High Conductivity Solid Surface", 24th ASME/AIChE National Heat Transfer Conference, Pittsburgh, Pennsylvania, in press. Also submitted to Journal of Heat Transfer, Transaction ASME

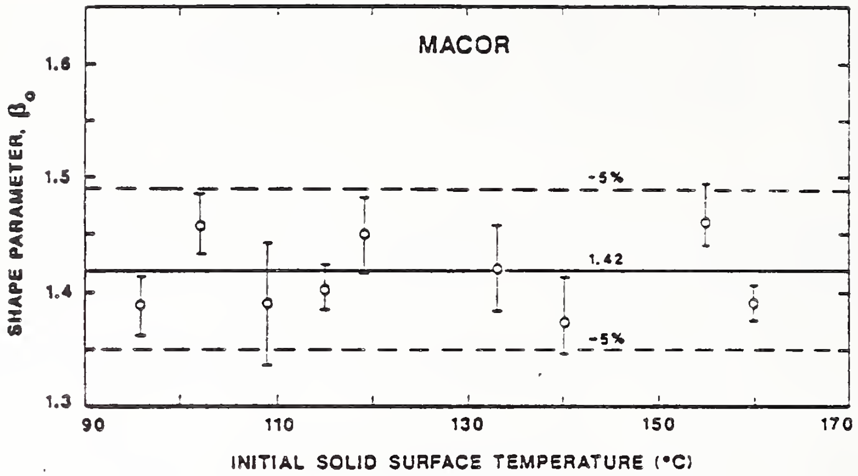

FIGURE ONE - Shape Parameter β

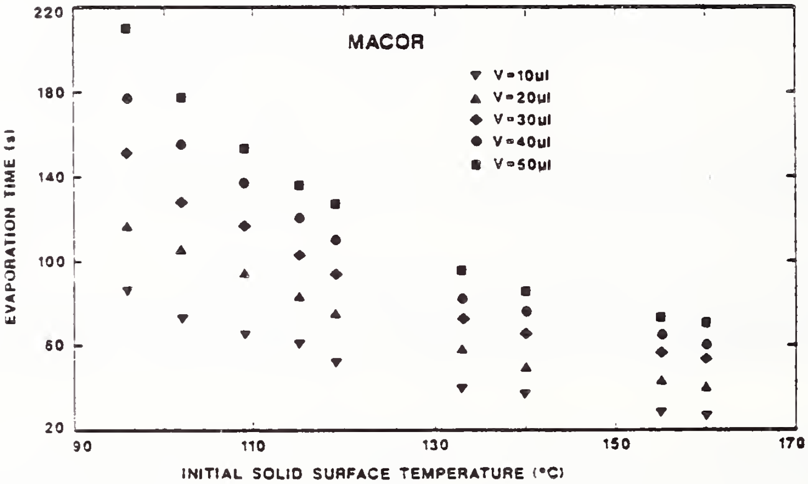

FIGURE TWO - Evaporation Time

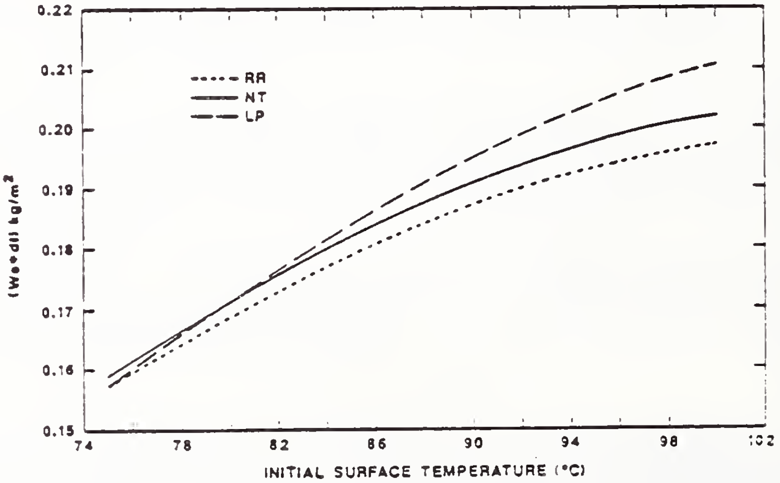

FIGURE THREE - Minimum Water Mass to Obtain Surface Cooling

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: The University of Michigan

Grant No.: 60NANB5D0576

Grant Title: Radiation from Turbulent Luminous Flames

Principal Investigator: Professor Gerard M. Faeth
Department of Aerospace Engineering
The University of Michigan
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Technical Abstract:

Introduction. The objective of this investigation is to establish methods for predicting the structure and radiation properties of unwanted fires. The main research issues involve the scalar structure of turbulent flames, and effects of turbulence/radiation interactions, emphasizing soot-containing luminous flames. Both theory and experiment are being used to study these issues, emphasizing the following two research topics: (1) the structure and radiation properties of luminous flames; and (2) turbulence/radiation interactions in nonluminous flames. Progress in each of these areas is briefly summarized in the following.

Luminous Flames. Structure calculations are based on the laminar flamelet concept, which implies that scalar properties in diffusion flames (laminar or turbulent) can be correlated solely as a function of mixture fraction (the fraction of mass at a point, irrespective of chemical compound, which originated from the fuel). Past work has shown that this is a reasonably good approximation for the concentrations of major gas species – even in luminous soot-containing flames. If the same property is true for soot volume fractions, the main scalar property of soot that is needed for radiation calculations, analysis of the radiation properties of luminous flames would be vastly simplified; therefore, this hypothesis is being examined.

Figure 1 is an illustration of the correlation between soot-volume fractions and mixture fractions in both laminar and turbulent ethylene/air diffusion flames. Measurements in laminar flames for fuel-rich conditions, reported earlier, do not correlate as well as gas species concentrations, due to

effects of finite-rate chemistry and transport of soot particles by convention and thermophoresis in a laminar environment. Nevertheless, a crude correlation of the data (denoted the soot-volume-fraction state relationship in Fig. 1) is obtained. For fuel-rich conditions, significant soot concentrations are only observed for a narrow range of mixture fractions – yielding a soot spike.

Most practical flames are sooting; therefore, work during this report period considered soot volume fractions, and their correlation with mixture fraction, in the lean (overfire) portions of turbulent diffusion flames. The findings at various points within two turbulent ethylene/air flames are also illustrated in Fig. 1. Soot reactions are quenched in the overfire region and soot particles only passively mix: a correlation based on this idea (called the soot mixing region) is also plotted on the figure. Data for the lower Reynolds number flame is correlated quite well by this plot, with departures as the soot spike is approached due to effects of turbulent fluctuations. The latter effects are predicted quite well by stochastic analysis. The higher Reynolds number flame, however, exhibits consistently lower soot-volume fractions, which are attributed to finite-rate chemistry effects. Thus, the correlation may only be appropriate for long-residence time flames: fortunately, such flames are of greatest interest for unwanted fires. Similar results were obtained for acetylene; however, the correlation exhibited much less scatter in the lean region.

Applications of the soot volume fraction state relationship for calculations of radiation properties are illustrated in Figs. 2 and 3. Predictions are based on the soot-volume-fraction state relationship illustrated in Fig. 1, using either mean properties along a radiation path, or a stochastic method which allows for effects of turbulent fluctuations. Predicted monochromatic transmittivities for a turbulent ethylene/air flame, illustrated in Fig. 2, exhibit little effect of turbulent fluctuations, and are in reasonably good agreement with measurements. This is very encouraging, since the results were obtained using a single soot-volume-fraction state relationship for all points in the flame.

Typical predicted and measured spectral radiation intensities, for the same ethylene/air flame, are illustrated in Fig. 3. In this case, there are significant differences between mean property and stochastic predictions, indicating effects of turbulence/radiation interactions. The two methods of prediction tend to bound the data, and represent effects of position reasonably well, which is very encouraging. The stronger effect of turbulent fluctuations on emission than absorption suggests that the nonlinearity of the Planck function is mainly responsible for turbulence/radiation interactions.

Present findings concerning the correlation between soot volume fractions and mixture fraction suggest potential for the laminar flamelet concept for soot volume fractions. However, only a limited range of test conditions has been considered and measurement uncertainties (shown as brackets in Fig. 1) are high. Current work is attempting to rectify these deficiencies, concentrating on the overfire region. A range of burner geometries, fuel burning rates, and fuels are being considered; emphasizing buoyant flames which are representative of unwanted fires.

Nonluminous Flames. Past work concerning turbulence/radiation interactions has been limited to effects of turbulent fluctuations on mean radiation levels. A stochastic approach has been developed which shows some promise for predictions of mean radiant intensities and heat fluxes (see Fig. 3). The objective of present work is to extend these concepts to provide predictions of radiation fluctuations, probability density functions, and the temporal properties of flame radiation (as represented by temporal spectra). Findings will provide a better fundamental understanding of turbulence/radiation interactions, while temporal properties of flame radiation are relevant directly to the design of fire detectors.

Hydrogen/air flames exhibit interesting effects of turbulence/radiation interactions and satisfy flamelet concepts for scalar properties with good accuracy; therefore, work has begun with this flame system, using flame conditions that were studied earlier. The new measurements involve time-resolved spectral radiation intensities and mixture fractions along various paths through the flames, although only radiation measurements have been completed thus far.

Some typical radiation measurements are illustrated in Fig. 4. The temporal power spectral densities of narrow-band spectral radiation intensities (4.8 nm slit width at a wavelength of 2491.1 nm) are illustrated. Two flames are considered, with the power spectral densities, E, and frequencies, f, normalized by the local flame centerline velocity, $\bar{u}_c$, the height above the burner, x, and the rms spectral radiation fluctuation intensity, i'_λ. In these coordinates, the high-frequency end of the spectra of both flames are the same, suggesting an inertial-like regime for radiation, where $E \sim f^{-2}$.

The low frequency behavior illustrated in Fig. 4 is very different for the two flames. The high Reynolds number flame has a flat energy-containing region, while the low Reynolds number flame exhibits a distinct peak at $fx/\bar{u}_c = 0.3$, which corresponds to an actual frequency of 10 Hz. The latter behavior is probably more representative of unwanted fires, which are generally very buoyant and often exhibit pulsitile behavior.

Radiation measurements are continuing, considering other variables: the diameter of the radiation path, the wavelength, the wavelength range, and the position in the flame. The stochastic analysis is also being extended to see if predictions of the temporal behavior of flame radiation can be made. Subsequent work will involve predictions and measurements of scalar properties along the radiation paths, and studying their relationship to radiation properties.

<u>Reports and Papers:</u>

1. M.-C. Lai, S.-M. Jeng and G. M. Faeth, "Structure of Turbulent Adiabatic Wall Plumes," J. Heat Transfer, Vol. 108, No. 4, pp. 951-959, 1986

2. M.-C. Lai and G. M. Faeth, "A Combined Laser-Doppler Anemometer/Laser-Induced Fluorescence System for Turbulent Transport Measurements," J. Heat Transfer, Vol. 109, No. 1, pp. 254-256, 1987.

3. M.-C. Lai and G. M. Faeth, "Turbulence Properties of Adiabatic Wall Plumes," J. Heat Transfer, in press.

4. J. P. Gore, S.-M. Jeng and G. M. Faeth, "Spectral and Total Radiation Properties of Turbulent Hydrogen/Air Diffusion Flames," J. Heat Transfer, Vol. 109, No. 1, pp. 165-171, 1987.

5. J. P. Gore, S.-M. Jeng and G. M. Faeth, "Spectral and Total Radiation Properties of Turbulent Carbon Monoxide/Air Diffusion Flames," AIAA J., Vol. 25, No. 2, pp. 339-345, 1987.

6. J. P. Gore and G. M. Faeth, "Structure and Spectral Radiation Properties of Turbulent Ethylene/Air Diffusion Flames," Twenty-First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, in press.

7. G. M. Faeth, J. P. Gore, S. G. Chuech and S.-M. Jeng, "Radiation from Turbulent Diffusion Flames," Ann. Rev. of Numerical Fluid Mech. and Heat Trans., Hemisphere Publishing Corp., Washington, in press.

8. J. P. Gore, G. M. Faeth, D. Evans and D. B. Pfenning, "Structure and Radiation Properties of Large-Scale Natural Gas/Air Diffusion Flames," Fire and Materials, Vol. 10, pp. 161-169, 1986.

9. J. P. Gore and G. M. Faeth, "Structure and Radiation Properties of Luminous Turbulent Acetylene/Air Diffusion Flames," J. Heat Transfer, in press.

10. G. M. Faeth, J. P. Gore and Y. R. Sivathanu, "Radiation from Soot-Containing Flames," Proceedings of the 70th AGARD Symposium on Combustion and Fuels in Gas Turbine Engines, Chania, Greece, in press.

11. Y. R. Sivathanu, J. P. Gore and G. M. Faeth, "Scalar Properties in the Overfire Region of Sooting Turbulent Diffusion Flames," Combustion and Flame, submitted.

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13. Y. R. Sivathanu, J. P. Gore and G. M. Faeth, "Scalar Structure and Soot Properties in the Overfire Region of Turbulent Ethylene and Acetylene/Air Diffusion Flames, Proceedings of the 1987 Spring Technical Meeting, Central States Section of the Combustion Institute, Pittsburgh, pp. 49.1-49.4, 1987.

14. J. P. Gore and G. M. Faeth, "Radiation from Turbulent Luminous Flames," Annual Report, NBS Grant No. 60NANB5D0576, The University of Michigan, Ann Arbor, MI, 1986.

15. J. P. Gore, "A Theoretical and Experimental Study of Turbulent Flame Radiation," Ph.D. Thesis, The Pennsylvania State University, University Park, PA, 1986.

HAZARD ANALYSIS
CENTER FOR FIRE RESEARCH
FY 87

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Program Objectives

To develop predictive, analytical methods which enable the quantitative assessment of hazard and risk from fires.

Scope

The predictive methods being developed are based on numerical modeling, but also include hand calculation methods for estimating hazards, and production of design curves/tables for use by architects and engineers. To ensure use, necessary data must be readily available, and data input and presentation must be in terms readily understandable by the average professional. Thus, the projects include a strong emphasis on state-of-the-art computer graphics and computer aided design techniques.

Projects

1. Hazard Assessment

The objective of this project is to develop quantitative methods to predict the development of occupant hazard in building fires. The main thrust of the group (and the Center) this past year has been the completion and publication of the first version of the Hazard Assessment Method - HAZARD I. This consists of a three volume (1000 page) report and a set of 5 1/4 in. disks containing the software necessary to conduct hazard analyses of products used in residential occupancies. All of the software provided will operate on any IBM PC (XT or AT) or compatible computer. The programs include a scenario development guidance utility; an interactive program for inputing data to the fire model; a data base program and files of thermophysical, thermochemical, and reference toxicity data; the FAST model for multi-compartment energy and mass transport; a graphics utility for plotting data; a detector/sprinkler activation model; an evacuation model which includes human decision/behavior; and a tenability model which evaluates the impact of the predicted exposure of the occupants in terms of incapacitation or lethality from temperature or toxic gases or incapacitation by second degree burns from radiant flux exposure.

Also included in the report is a set of eight representative example cases of typical residential fires as established by two panels of outside experts. These consist of fire scenarios, selected by a panel composed of representatives of the major fire services organizations, in each of three single-family residences (three bedroom ranch and townhouse, and four bedroom two-story), which were felt to represent typical homes by a panel from the model building codes, NFPA, and the architectural community. In addition to serving as examples of the use of the system, these cases can be used as a baseline against which the change in hazard associated with products of interest can be measured, and as a resource of typical buildings for evaluating specific products, or fire scenarios for evaluating building designs and their fire protection features.

While the scope of this first hazard assessment method is limited to residential occupancies, the work necessary to extend it to other occupancy classes is underway. This first version is being introduced in order to begin the process of familiarization of the fire protection community with the method and its use in addressing the critical issues facing them. In addition, feedback from users, both positive and negative, is crucial to identify the improvements necessary to maximize the usefulness of the method in addressing these issues. This feedback is being obtained through an organized evaluation program of 100 invited reviewers representing all aspects of the international fire community.

Bukowski, R. W., et. al. HAZARD I - Vol. 1: Hazard Assessment Method (NBSIR 87-3602), Vol. 2: Representative Example Case Documentation (NBSIR 87-3603), and Vol. 3: Data Base Listing (NBSIR 87-3604), Nat. Bur. Stand. (1987).

Bukowski, R. W., A Summary of the Assumptions and Limitations in HAZARD I, Proceedings of the 9th UJNR, Boston MA., (1987).

2. Risk Assessment

A new effort was initiated this past year with funding from the private sector through the National Fire Protection Research Foundation. This three-year project builds on the Hazard Assessment method by adding a means of identifying the scenarios (a scenario generator) which involve a product in any way and, as such, will influence its associated risk. The probabilities of these scenarios derived from NFIRS data are used to weight the outcome predicted by HAZARD, and summed to obtain a measure of the fire risk of that product.

The first phase of the project required the development of a proposed calculation method and its demonstration on two products - upholstered furniture in residential occupancies and carpet in office occupancies. The second phase (for FY 88) is to finalize the method based on the phase 1 experience and review, and demonstrate the refined method on several more products to be defined. The third phase is to submit the method into the engineering and code arenas for potential implementation.

Bukowski, R.W., Hall, J.R., Sekizawa, A., and Stiefel, S.W., Fire Risk Assessment: Description of Methodology, NBSIR in press.

3. Smoke Transport Modeling

The objective of this project is modeling the growth of fires and the spread of smoke and toxic gases. Interest extends from the room of fire origin to compartments which are sufficiently distant to be in the "far field" of the fire. The goal is to provide a model which allows one to generate a general description for a building, the fire to which it is subjected, and then to model the course of the fire, and generate an easily understood description of the results. A secondary objective is connecting laboratory scale experiments with full scale fire performance of materials and buildings. The thrust is to be able to predict the outcome of a fire given appropriate measurements which can be conducted in a laboratory. If successful, this application of the model will allow a great economy of scale as most materials and configurations necessary for performance testing can be done in the laboratory.

A number of major, technical improvements are underway for this model. One deals with the incorporation of a capability to simulate smoke movement throughout large buildings including simulation of the effects of HVAC systems, smoke control systems, inside to outside pressure difference, wind and smoke buoyancy. Another major improvement is the addition of a self-consistent algorithm for combustion chemistry to account for vitiated combustion and deposition of a reactive species ($HC\ell$) to surfaces.

Verification and validation are ongoing projects to check the accuracy of the model predictions. It is an important step in the acceptance of such a technique by the engineering and code communities. Recently, a series of experimental studies was completed using the NBS full scale test facility and the corresponding theoretical predictions. The present work is aimed at identifying the strengths and weaknesses of the current model prior to adding such features as ventilation systems, or self-consistent burning furniture.

The work has focused on three roots of the modeling tree. First is to develop fast and reliable numerical software. Second, we must be sure that the physical models to be incorporated are consistent and to the extent possible, complete. Third, the output must be understandable.

Jones, W.W., and DeWitt, C., Heat Transfer through Multilayer Boundaries, Fall Technical Meeting of the Combustion Institute, San Juan (1986).

4. Fire Research Information Services (FRIS)

FRIS is an on-going project. It was started in 1971 and incorporated several personal collections at the National Bureau of Standards (NBS), as well as the Fire Council collection. Over the years it has grown and now contains approximately 30,000 reports, books, journal articles and conference proceedings. (On the average, 1500 items are added to the collection each year.) It reflects the programmatic needs of the Center for Fire Research, as well as developing a national and international fire research collection for use by NBS staff, researchers, fire departments, fire science students and the fire community at large.

One of the major obstacles in fire research has been accessing fire research information. Although the FRIS collection is one of the most complete, it only has been a manual system and, therefore, not readily accessible to the fire research community. To remove this obstacle, FRIS has begun to automate its collection and the online bibliographic database is called FIREDOC. All new bibliographic records are added to FIREDOC. Retrospective input is being completed by modules; the current year being entered is 1984. People interested in using the database may telephone (301)975-6862 for information.

For interested people who cannot come to the FRIS, an extensive interlibrary loan program is carried out with participating libraries throughout the United States. For more information on this program, you may write to us at the National Bureau of Standards, Building 224, Room A252, or contact us by telephone: (301)975-6860.

Jason, Nora H. FIREDOC Users Manual. Nat. Bur. Std. (U.S.) NBSIR 87-3562. September 1987.

Jason, Nora H. FIREDOC Vocabulary List, 2nd Edition. Nat. Bur. Std. (U.S.) NBSIR 87-3545. April 1987.

Jason, Nora H. Fire Research Publications, 1985. Nat. Bur. Std. (U.S.) NBSIR 87-3555. April 1987.

Associated Grants

1. University of California, G. Apostolakis - Fire Risk Analysis Methodology.

HAZARD ANALYSIS GRANTS

CENTER FOR FIRE RESEARCH
NATIONAL BUREAU OF STANDARDS
FY 87

Institution: University of California Los Angeles

Grant No.: 60NANB6D0649

Title: Fire Risk Analysis Methodology

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Technical Abstract

The objective of this work is to develop a methodology for the assessment of the types and frequencies of initiating events for the quantification of fire risk in buildings. At present, the building types being most closely researched are those which are in the category 'residential occupancies', nominally one and two level houses. Within this building category, a major hazard to life-safety are fires which involve upholstered furniture. Upholstered furniture can be involved in fire in three general ways: initially ignited by 1) smoldering (e.g., cigarette ignition), or 2) flame (e.g., match ignition) or (3) secondarily ignited from heat transfer from a fire already in progress. While a large amount of statistical evidence is available on fires which have already occured (building/room of fire origin, types of materials first involved, etc.), of interest is the change in the nation's overall fire risk due to a new product for which no statistical evidence is available. We are interested in the adaptation of available statistics to a new product, coupled with the use of mathematical ignition modeling and results from laboratory fire tests, to be utilized to predict the ignition behavior of new products for estimating changes in fire frequency and ultimately fire risk due to those products.

Fire Occurance Statistics. The large amount of data available for fires which have occured allows us to make good inferences as to what some of the major factors affecting ignition are. For upholstered furniture, cigarettes and small flames are major ignitors contributing to the occurance of fires. One major fire data base (NFIRS) can provide us with frequency estimates of the form

$$fr(\text{ignitor } i \mid \text{fire ocurred on item } j) \qquad (1)$$

where fr(A|C) is the frequency of event A given that event C has occured. Thus, since the frequency with which ignitor i contacted, but did not ignite item j is not available to us, we cannot explicitly estimate the frequency of a specific ignitor contacting an item. The value given in (1) might be used to apply to a new product if that product will not have enough market share of item i to affect the statistical base, but the reliability of this assumption is not known at this time. Presently, a method for using laboratory ignition results to update the available data to new products is being sought.

Mathematical Ignition Modeling. The detail to which mathematical modeling of ignition phenomenon will be useful to us is restricted by the projected availability of data. To predict differences in ignition properties purely from a mathematical model would require lengthy modeling of the physical, heat transfer, and chemical interactions and it is not reasonable to suppose that a new product manufacturer would be able to supply such data, nor would it be easily attainable by experiment for a variety of new products. Our approach is to utilize a simplified heat transfer model along with basic experimental input to predict ignition properties in more general situations. Appropriate ignition criteria such as surface temperature, average solid temperature, mass pyrolyzate loss rate, etc. are being considered and ultimately, the type of criteria used may depend on the material being analyzed.

Consideration also needs to be taken of physical processes, such as shrinking or cracking, which may greatly affect the ignition properties of a composite surface such as a vinyl covered polyurethane cushion. An event-tree type logic structure may be useful to incorporate these effects, since they can occur systematically in time (heating, cover melting, cushion igniting, etc.) Development of requisite models for small-flame ignition is currently being instituted.

Other Work. Throughout this modeling effort, the incorporation and quantification of relevant uncertainties is important. Addition of the final model(s) into existing hazard models is also of concern. Since a risk model is probabilistic and usually a hazard model is a deterministic, physical analysis model, attention is being given to making the results from the initiating event analysis useful as input to the hazard model.

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report was prepared for distribution at the Combined Meetings of the Eastern Section: The Combustion Institute and the Annual Conference on Fire Research, November 2-5, 1987. It contains descriptions of the internal programs of the Center for Fire Research as well as extended abstracts of grants for fire research sponsored by the Center for Fire Research.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

cellulose; charring; combustion; fire models; flame spread; ignition; polymers; smoke; soot; toxicity

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