FIRE RESISTANCE OF INDUSTRIAL FLUIDS

George E. Totten
Jürgen Reichel
EDITORS

ASTM STP 1284

STP 1284

Fire Resistance of Industrial Fluids

George E. Totten and Jürgen Reichel, Editors

ASTM Publication Number (PCN)
04-012840-12

ASTM
100 Barr Harbor Drive
West Conshohocken, PA 19428-2959

Library of Congress Cataloging-in-Publication Data

Fire resistance of industrial fluids / George E. Totten and Jurgen
Reichel.
p. cm. -- (ASTM special technical publication ; 1284)
"Papers presented at the symposium of the same name, held in
Indianapolis, IN on 20 June 1995 ... sponsored by ASTM Committee D02
on Petroleum Products and Lubricants"--Foreword.
Includes bibliographical references and index.
ISBN 0-8031-2041-9 (alk. paper)
1. Fire testing--Congresses. 2. Hydraulic fluids--Testing-
-Congresses. I. Totten, George E. II. Reichel, Jurgen, 1938-
III. American Society for Testing and Materials. Committee D-2 on
Petroleum Products and Lubricants. IV. Series.
TH9446.H9F57 1996
621.2--dc20 96-4044
CIP

Photocopy Rights

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by the AMERICAN SOCIETY FOR TESTING AND MATERIALS for users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of $2.50 per copy, plus $0.50 per page is paid directly to CCC, 222 Rosewood Dr., Danvers, MA 01923; Phone: (508) 750-8400; Fax: (508) 750-4744. For those organizations that have been granted a photocopy license by CCC, a separate system of payment has been arranged. The fee code for users of the Transactional Reporting Service is 0-8031-2041-9/96 $2.50 + .50.

Peer Review Policy

Each paper published in this volume was evaluated by three peer reviewers. The authors addressed all of the reviewers' comments to the satisfaction of both the technical editor(s) and the ASTM Committee on Publications.

To make technical information available as quickly as possible, the peer-reviewed papers in this publication were prepared "camera-ready" as submitted by the authors.

The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution to time and effort on behalf of ASTM.

Printed in Scranton, PA
March 1996

Foreword

This publication, *Fire Resistance of Industrial Fluids,* contains papers presented at the symposium of the same name, held in Indianapolis, IN on 20 June 1995. The symposium was sponsored by ASTM Committee D2 on Petroleum Products and Lubricants. George E. Totten of Union Carbide Corporation in Tarrytown, NY and Jürgen Reichel of Deutsche Montan Technologie (DMT) in Essen, Germany presided as symposium chairmen and as the editors of the resulting publication.

Table of Contents

Overview

Industrial fires caused by the use of flammable fluids such as mineral oils may lead to devastating loss of human lives and property. Therefore, many industrial processes such as underground mining, steel rolling, die casting, aerospace, and others require the use of fluids that provide substantially greater fire resistance than those attainable with mineral oils. In fluid power applications, this need has led to the development of various classes of fire-resistant hydraulic fluids which include polyol ester, phosphate ester, water-in-oil and oil-in-water emulsions, high-water-based fluids, and water-glycol hydraulic fluids. Although these and other types of fire-resistant hydraulic fluids are now available, the degree and mechanism of fire resistance that each provides is not the same. From the viewpoint of insurance underwriters, labor organizations, government regulation, and the industry itself, it is becoming increasingly critical to be able to determine appropriately the relative fire resistance provided by the use of a particular fluid in a specific industrial process. This typically cannot be done with the use of a single fire resistance test, particularly the various spray flammability tests that have been traditionally used by various organizations in the United States and Europe.

It has been nearly 30 years since a symposium focusing on fire resistance testing of industrial oils in general, and hydraulic fluids in particular, has been held. Since that ASTM symposium, which was held in 1966, there have been considerable developments in testing procedures for modeling fire risks involved with a particular industrial process and for discriminating the fire resistance offered by a particular hydraulic fluid. This is reflected by the institution of a new fire resistance testing procedure used by Factory Mutual Research Corporation and by the different fire resistance testing procedures required by the 7th Luxembourg Report.

This symposium will provide a forum for the discussion of the current and future global status of fire resistance testing of industrial oils, primarily hydraulic fluids and turbine oils. Four specific areas will be covered: fundamental principles, historical and current testing methodologies and limitations, spray flammability tests, and new test methods.

Two fundamental aspects of fluid flammability will be discussed. One is the often ignored issue of the potential toxicity of fluid combustion byproducts that may be formed. The second aspect of fire resistance testing that will be discussed in detail is modeling and characteristics of pool fire burning which is important when the fire risk potential of fluid leaks and spills must be considered.

To provide a thorough treatment of fire resistance testing, an overview and analysis of the various hydraulic fluid testing procedures, including traditional and current testing procedures, have been reported. The objective of these reviews is to identify the limitations and deficiencies of these various tests. All of these tests model only one type of fire risk, for example, spray ignition or pool fire burning. Thus, it is usually necessary to use two or more tests to provide an adequate assessment of the fire risk that may be encountered. However, many of these tests, although they have been used for many years, do not adequately reflect the fire risk involved with the use of a particular fluid. The inability of these tests to discriminate adequately fire risk will be discussed in the various papers presented here.

Fortunately, very significant advances have been made in the testing of the fire risk potential of hydraulic fluids. Two tests that are currently being promoted for this purpose are the Factory Mutual Research Corporation "Spray Ignition Parameter" test, which will become one of the primary fire resistance testing procedures in the United States, and the "Relative Ignitability (RI)-Index" derived from the newly developed Buxton Test, which will become one of the primary testing procedures required in Europe. The testing procedures for both tests and the results obtained for various types of aqueous and nonaqueous hydraulic fluids will be discussed.

Most of the tests require large volumes of fluid and often can only be conducted by relatively few laboratories (often at high cost). With few exceptions, the reproducibility of these tests is relatively poor and many do not adequately model the actual relative fire risk encountered. Therefore, the identification of much smaller scale, lower cost methods for characterizing fire resistance offered by a particular hydraulic fluid is of great interest. The potential use of two calorimetric testing procedures for the evaluation of hydraulic fluid fire resistance will be discussed here.

From these papers, it is clear that significant gains have been made in modeling and quantifying the relative amount of fire resistance exhibited by a hydraulic fluid. Incorporation of the more recently developed testing procedures into harmonized national and international standards will become increasingly important with globalization of safety standards. One of the most significant results of this conference may be the possibility for harmonizing global fire resistance testing standards.

George E. Totten

Union Carbide Corporation
Tarrytown NY; symposium
chairman and editor.

Jürgen Reichel

Deutsche Montan Technologie (DMT)
Essen, Germany; symposium
chairman and editor.

Introduction

Common industrial fluids include: mineral oils, synthetic hydrocarbon blends, and chemical compositions formulated with additives to achieve properties required for specific applications. Potential fire resistance and environmental and toxicological properties of these fluids are composition dependent.

In hydraulic fluid power systems, power is transmitted and controlled through a liquid under pressure within a closed circuit. Petroleum oils are the most commonly used hydraulic fluid. Petroleum oils are also commonly used for turbine governor controls and other hydraulic systems in electrical power stations.

Some applications demand a greater degree of fire resistance than afforded by petroleum oils. In these situations, fire-resistant fluids may be used. Fire resistance is defined by the ability of the fluid to ignite and propagate flame. Fire resistance properties vary widely among the types of fluids. Examples of fluids commonly used for their fire-resistant properties include: phosphate esters, polyol esters, thickened water/glycols, and high water base and invert emulsions.

However, fire-resistant fluids are not completely inflammable. They may present some degree of fire risk. The hazard will be especially serious if those fluids are used either in close or explosion-prone environments such as those present in underground mining applications or in highly safety sensitive areas such as the aerospace industry. Fire-resistant fluids are also commonly used in the steel, aluminum, and die casting industries. Therefore, the use of industrial fluids, such as hydraulic fluids, in fire- or explosion-prone areas are subject to regulations regarding the amount of fire resistance that they must provide.

The benefits of fluid power over electromechanical drives include: smaller size, higher energy efficiency, and ease of adjustment. All of these advantages are lost if an incident occurs in which the hydraulic fluid, under pressure, is sprayed in the presence of an ignition source resulting in a fire.

Three factors required for a fire are:

- an inflammable fluid,
- a source of ignition, and
- oxygen.

If one of these components is lacking, combustion will not occur. Sprays from a hydraulic system may be caused by hose breaks, pinholes, cracks in fittings or measuring connections that failed to resist the load of pulsation, defective sealing elements, and mechanical damage by external influences. Sprays of easily inflammable petroleum oil will ignite in the presence of an ignition source whether the system has an operational pressure of 40 or 400 bar. Even the removal of the source of ignition will not help flame extinction. Fire-resistant fluids, however; may exhibit either fire-inhibiting or even self-extinguishing properties.

This symposium will address the vital question of proper assessment of fire resistance of industrial fluids. Basic principles in fire resistance characterization will be discussed. This will be followed by a discussion of standardization activities and current and recent test methodology development. There will be a comprehensive discussion on spray ignition tests and novel test methods and an assessment of these methods will be provided.

In specification development, it must be assured that potential hazards will not give rise to exaggerated safety requirements that will lead to technically unreliable applications. This would be intolerable not only for economic reasons but would also restrict many applications of fluid power technology. Operational safety and economics are imperative in fluid power technology! Hydraulic fluids represent only one element of the system and cannot be replaced indiscriminantly with no risk.

We are very fortunate that the experience gathered in the United States and Europe during the past 35 years in the development of fire-resistant hydraulic fluids and test methods to determine fire resistance can be presented here in one forum. Hopefully, as a result of this meeting, both national and international standards test methods for the determination of fire resistance for individual applications in the different industrial applications can be harmonized in the future.

Armand V. Brandao[1]

THE NEED FOR STANDARDIZATION OF FIRE RESISTANCE TESTING OF INDUSTRIAL FLUIDS

(First Keynote Address)

REFERENCE: Brandao, A. V., **"The Need for Standardization of Fire Resistance Testing of Industrial Fluids,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds, American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: This presentation will address the need for global standardization of fire resistance criteria to promote free trade and to maximize the purchasing power of users facing increasingly tight budgets. The current proliferation of standards, both from various jurisdictions and specific to different industries, increases the number of overlapping tests that producers must perform to bring a new fluid to market.

Relative fire resistance is but one of the properties that must be established for any new or reformulated fluid. However, there is little agreement on test methodology among various jurisdictions and industries. This is a result of the largely empirical nature of fire research until very recent times. While still embracing much empirically-derived technology, in the past several decades fire research has increasingly made use of a more scientific approach. Developments in combustion science have led to a better understanding of the underlying phenomena. These new insights are now available to facilitate the design of tests that are more universally applicable to a wide variety of potential fire scenarios.

KEYWORDS: Combustion, fire resistance, flammability tests, industrial fluids.

---

[1] Senior Engineer & Fuels Approvals Manager, Factory Mutual Research Corporation, Norwood MA 02062

INTRODUCTION

(Appropriate acknowledgments of the symposium organizers will be made.)

It is my great honor to address this gathering of experts in fire resistance and flammability. While my organization has established a presence in the industrial fluid marketplace through our work in flammability testing of hydraulic and transformer fluids, I personally am not a specialist in this industry. In the course of administering our fluid Approval programs I have had the good fortune to deal with many of you who are the experts and look forward to meeting more of you during this symposium.

As a representative of user and insurer interests, I would like to share with you my perspective on the opportunities available to us in this gathering.

PERSPECTIVES

There are two separate dynamics at work which suggest that this symposium may be more appropriate at this time than it would have been previously. One of these is economic, the other technical.

Economic Influences

I would like you to first consider some of the economic factors:

The emerging global marketplace argues strongly for universally recognized standards and evaluation technology for all goods and services. In the past decade we have seen the emergence of the European Union (or EU) from its earlier, more basic forms, the European Economic Community, and, still earlier, the Common Market. Today, Europe is progressing rapidly toward removal of all political and economic barriers to trade on the continent. The fragmentation of the former Soviet bloc represents yet another challenge and opportunity for the EU. These new free-market economies will not only be new users of EU goods and services, but stand poised to introduce new products to the marketplace, themselves. Rather than being third world nations, the former Soviet Union member nations come to the market with many specific, new technologies and highly educated citizens who will adapt to their new opportunities more quickly than their prior experiences would suggest.

In our own backyard, the North American Free Trade Act (or NAFTA) represents another attempt to deal with trade that is naturally restrained only by economic boundaries and not political ones. I serve on several committees which have made substantial progress over the last several years in harmonizing US national product standards with those of Canada. Mexico, while somewhat more recently entering this effort, is more and more being recognized as a necessary contributor to this process.

Moving still farther off of our own shores, the Pacific rim has grown steadily since World War II as a producer of high quality goods. In fact, the quality of these goods has been of such a level as to have reshaped the issues of quality and global competitiveness for the American and European economies. Fueled by the income from these efforts, the nations of the Pacific rim are becoming ever more affluent and are developing into growing, sophisticated markets for their own and other state-of-the-art goods and technology. More and more, they will come to represent market opportunities not unlike those in the West.

Despite these obvious developments, there exists a seemingly endless controversy over attempts to unfetter the global marketplace from artificial constraints. This will be ultimately futile. The General Agreement on Trade and Tariffs (GATT) will pass into history, not as bold new direction, but as a timid recognition of economic reality, which represented a relatively minor step in the journey toward a more efficient worldwide economy. One occasionally hears the admonition, "It's the money, stupid!" Actually, that is not so much an acknowledgment of the universality of greed as it is an acceptance of the reality of what can be called economic Darwinism. It's a matter of the survival of the most fit. If something works, it grows and prospers. If it doesn't, it gets bypassed and eventually withers away. For all the posturing of politicians, governments are no different from any other institution in free societies, including industry. If they cannot deliver the needed goods and services at acceptable costs, their former supporters will eagerly build bypasses around them to pursue emerging opportunities.

In this symposium, we have a unique opportunity to take another step to further the globalization of the marketplace for lubricants.

Technical Influences

However, turning from economics to technology, one of the harsh realities of human progress has been that it always takes a while for science to filter down through to useful technology. Regrettably, fire science has traditionally been somewhat of a backwater of technology. Although, in the 20 plus years that I have been involved in this area, I have seen encouraging progress. Looking back, two decades ago, we had somewhat cloistered scientists toiling away, attempting to further our understanding of the fundamental mechanisms of combustion and extinguishment. Simultaneously, we had practitioners conducting empirical tests which attempted to simulate specific scenarios on the largest practical scales. Over the years, these two efforts continued, mostly in parallel, with each looking in on the other from time to time and, perhaps, gaining incidental insights, but not actually doing a good job of coordinating their efforts. More recently, two growing influences have resulted in increasing convergence of this work:

Firstly, engineers have acquired increasingly more scientific backgrounds and have had ever more precise and sophisticated instrumentation available to them at lower relative costs. Secondly, researchers everywhere have been under increasing pressure to demonstrate the economic necessity of their work. This has resulted in what might have been considered a forced alliance (or shotgun wedding) of the basic and applied research areas. However, as with most collaborations of reasonable individuals with common purposes, a synergy has become increasingly evident.

Today, fire research is more goal-driven. Tasks are arranged on the basis of short-range and long-range timetables for deliverable results. At this juncture, we have reached levels of application of the science of combustion to the technology of testing that allow us to move from incident simulations to more fundamental tests and evaluations. Rather than attempting to simulate all specific incident scenarios, we can analyze the relevant underlying characteristics of materials and the various deployment and ignition configurations and attempt to design tests which will represent fundamental flammability characteristics. Such tests will yield results which allow the consistent flammability classification of lubricants, in all applications.

CONCLUSION

In a marketplace characterized by increasing rates of change, the ability of manufacturers to react to market demands is impeded by multiple, overlapping test requirements for their products. Seemingly, fluid formulations are now continuously modified in response to increasing performance demands of equipment manufacturers, the advent of new materials compatibility issues, and ever-tightening health and environmental restrictions. Each time a formulation is significantly changed, the fluid producer must conduct a battery of both internally and externally required tests to assure the fluid's continued acceptability to all potential users.

Unfortunately, even if it were possible to develop a single, universally predictive test of fire resistance, it would be of little value, unless all interested parties were willing to accept this test. Neither the development of improved test methodology nor its acceptance will be possible unless good channels of communication are established among all affected parties. This symposium offers participants a unique forum to enhance an international exchange of technology that should continue to the benefit of all. Maximum advantage should be taken from this opportunity.

When evaluations are based upon sound science and technology, acceptance across industries and jurisdictions is facilitated. While one can argue that one scenario does not adequately represent another, it is far more difficult to suggest that a lubricant will ignite and burn differently in one jurisdiction than another. In so far as we are able to share our ideas and technologies, we can learn from one another and better work toward a consensus on appropriate tests of fire resistance. This will benefit all concerned with these issues, regardless of whether they are users, manufacturers, insurers, or jurisdictional authorities.

Jeffrey S. Newman[1]

COMBUSTION FIRE CHEMISTRY OF INDUSTRIAL FLUIDS

REFERENCE: Newman, J. S., "**Combustion Fire Chemistry of Industrial Fluids,**" Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: Fires generate two types of fire products in an uncontrolled fashion: heat and chemical compounds. Fires involving industrial fluids vary in the production of heat and chemical compounds due to 1) the chemical structure of the fluid, such as an aliphatic versus an aromatic hydrocarbon, and 2) the geometry or configuration of the fluid fire, such as a spray fire versus a pool fire. This paper illustrates the impact of both chemical structure and configuration on the production of heat and chemical compounds from fires.

KEYWORDS: combustion, fire chemistry, combustion efficiency, carbon monoxide, particulates

INTRODUCTION

Fire is a combustion process in which heat is generated primarily through oxidation chemical reactions between fuel vapors and oxygen from ambient air. Heat generated in chemical reactions is defined as the chemical heat and the rate of generation of chemical heat is the chemical heat release rate [1]. The chemical heat release rate consists of two components - a convective component associated with the hot buoyant gases which comprise the fire plume and a radiative component due to the transfer of energy from the hot flames to surrounding much cooler surfaces. Chemical compounds generated by fires are distributed into substances associated with complete

---

[1] Manager, Factory Mutual Research Corporation Test Center, W. Glocester, RI 02814

combustion, such as carbon dioxide and water vapor, and substances resulting from incomplete combustion, such as carbon monoxide (CO), particulates, gaseous and liquid hydrocarbons. If the fuel is oxidized completely to carbon dioxide and water vapor, the combustion is defined as 100% efficient, or equivalently, the combustion efficiency is unity. However, if the fuel is not oxidized completely, as is typically the case, carbon monoxide, particulates and other compounds are also released as heat is produced.

The following discussion addresses the impact of an industrial fluid's chemical structure and the fluid potential fire scenario configuration on the combustion efficiency as demonstrated by the relative amounts of chemical, convective and radiative heats, and incomplete products of combustion, such as carbon monoxide and particulates.

CHEMICAL STRUCTURE EFFECTS ON HEAT AND CHEMICAL COMPOUND GENERATION

The chemical structure of an industrial fluid plays a strong role in the quantity and relative distribution of heat and chemical compounds resulting from a fire. This effect of chemical structure is shown in Figures 1 and 2, where the calculated carbon monoxide and particulate yields for various hydrocarbons are plotted versus molecular

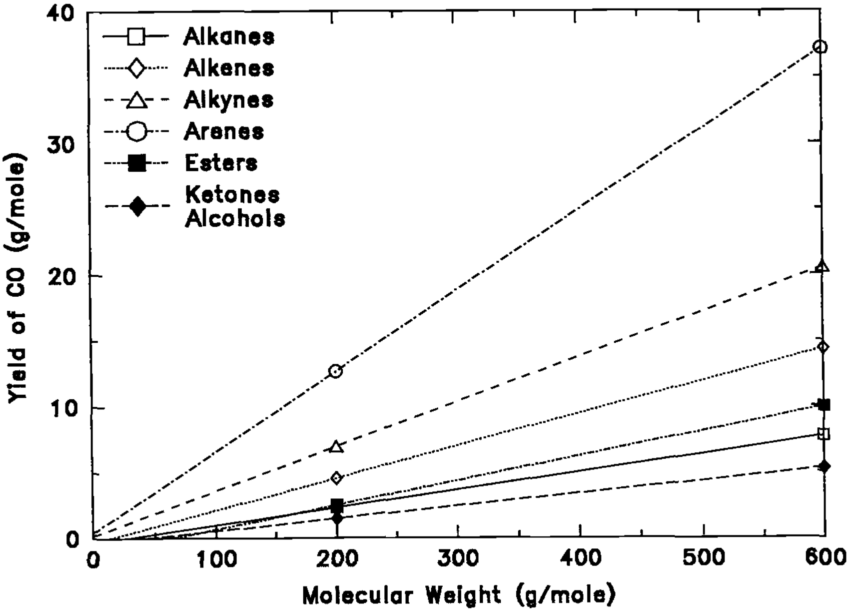


FIG. 1--Carbon monoxide yield versus molecular weight.

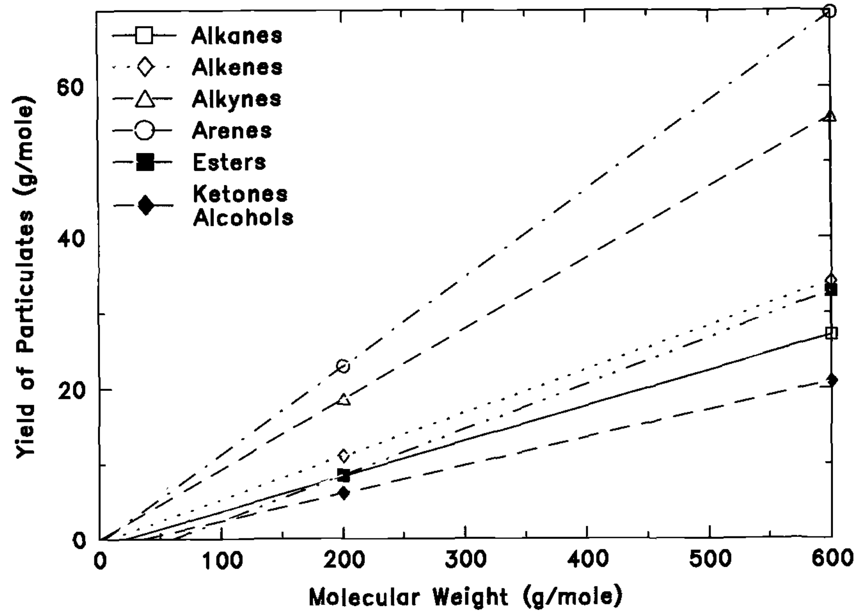


FIG. 2--Particulate yield versus molecular weight.

weight [2,3]. For reference, alkanes, alkenes and alkynes are aliphatic hydrocarbons. Alkanes have single bonds between C and H atoms, alkenes have double bonds between C and H atoms, and alkynes have triple bonds. Arenes are aromatic hydrocarbons with a benzene ring structure. Esters, ketones and alcohols all have H-C-O structures. Higher values of CO or particulate yield indicate less efficient combustion. The figures illustrate that the yields of CO and particulates are lowest for fuels with H-C-O structures, and increase with changes in chemical bonds from single to double to triple to benzene rings in the structure, i.e., increase with bond saturation.

Figure 3 charts combustion efficiency versus chemical structure of various compounds. In the figure, the combustion efficiency is defined as ratio of the chemical heat to the theoretical heat assuming complete conversion to carbon dioxide and water vapor. Similar trends are obtained as previously shown in Figures 1 and 2: increases in bond saturation result in lower combustion efficiencies, while H-C-O structures promote higher combustion efficiencies. Figures 4 and 5 give the convective and radiative fractions versus chemical structure, respectively. The convective fraction is associated with the sensible heat released in the combustion reactions. The radiative fraction is associated with the electromagnetic emission from the flame. (The sum of the convective and radiative fractions is equal to the combustion efficiency for a given material.) Higher values of convective fraction indicate more efficient combustion, while higher values of radiative fraction indicate lower combustin efficiency.

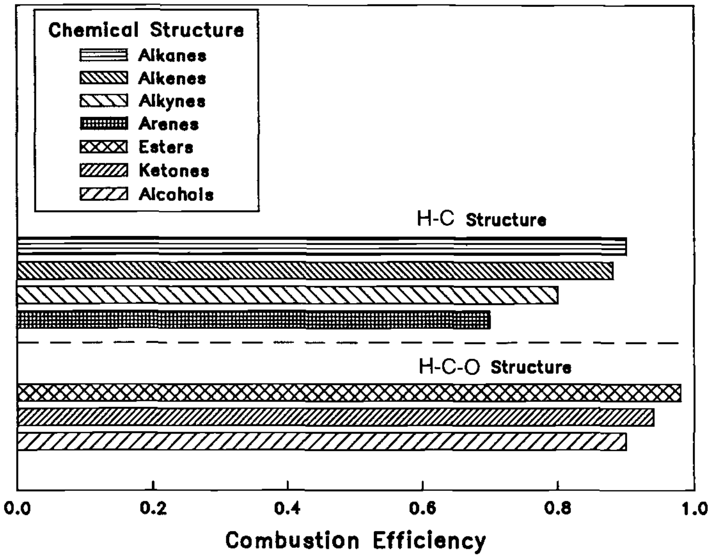


FIG. 3--Combustion efficiency for various chemical structures.

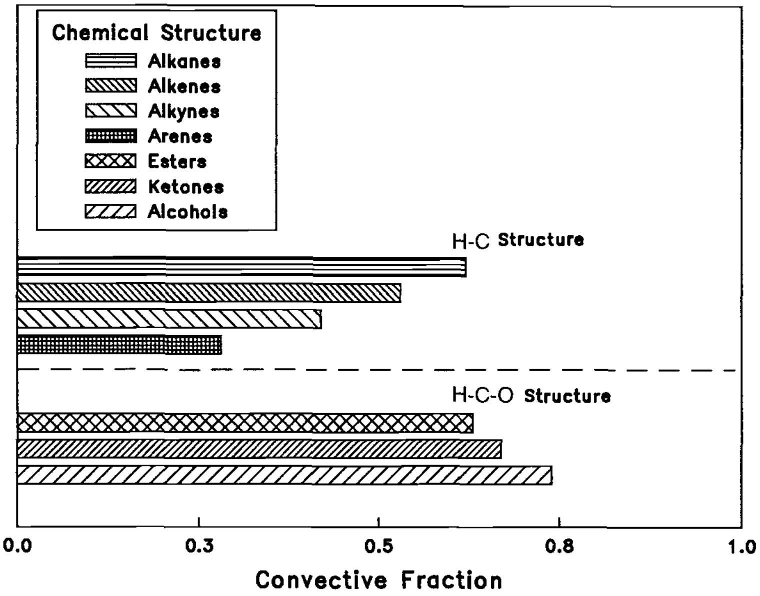


FIG. 4--Convective fraction for various chemical structures.

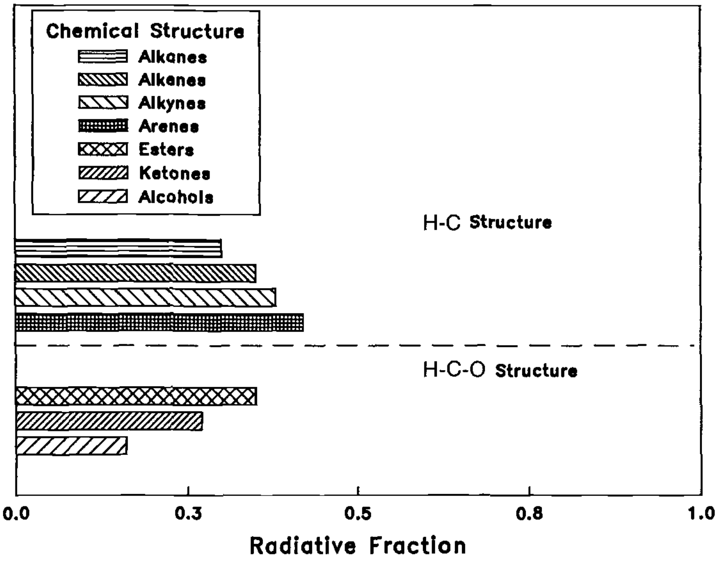


FIG. 5--Radiative fraction for various chemical structures.

Therefore, as expected, bond saturation promotes higher flame radiation and lower convection and H-C-O structures promote lower flame radiation. While not shown here, the introduction of N and S atoms also lower the efficiency of combustion, with S atoms having more effect than N atoms [3].

CONFIGURATION EFFECTS ON HEAT/CHEMICAL COMPOUND GENERATION

Fires involving industrial liquids vary in the production of heat and chemical compounds due to the strong effect of configuration. For example, a fire involving a hydraulic fluid during a high pressure rupture, could produce an intense spray fire generating large quantities of heat but with little smoke due to efficient combustion [4]. The same fluid in a pool fire scenario could produce much lower heat release rates but substantially higher levels of smoke and other incomplete products of combustion due to less efficient burning.

Configuration influences the efficiency of combustion primarily through ventilation effects [5,6]. Configurations that promote fire ventilation result in more efficient combustion, and correspondingly lower yields of CO and particulates. For example, Figure 6 plots the yield of CO in g of CO per g of fuel burned versus air-to-fuel stoichiometric fraction,ϕ, for a typical alkane [1]. In the figure, CO production is nearly independent of ϕ for values greater than approximately 2, while a strong dependence is observed for values less than 2 to about 0.5 (corresponding to flame extinction). Similar results are obtained for the combustion efficiency, which is shown in Figure 7. In region defined by $2.0< \phi <0.5$, the combustion is ventilation controlled,

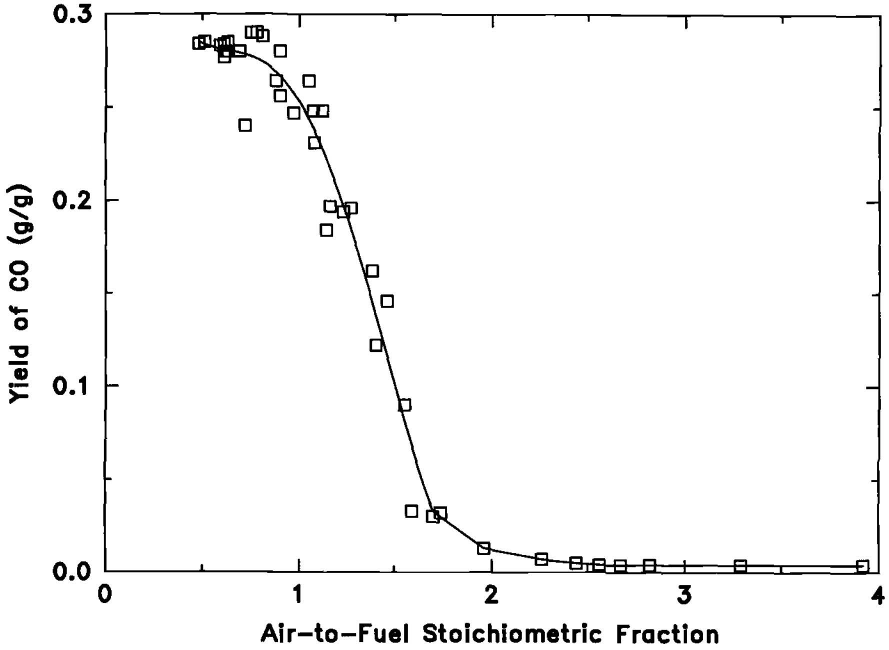


FIG. 6--Carbon monoxide versus air-to-fuel stoichiometric fraction.

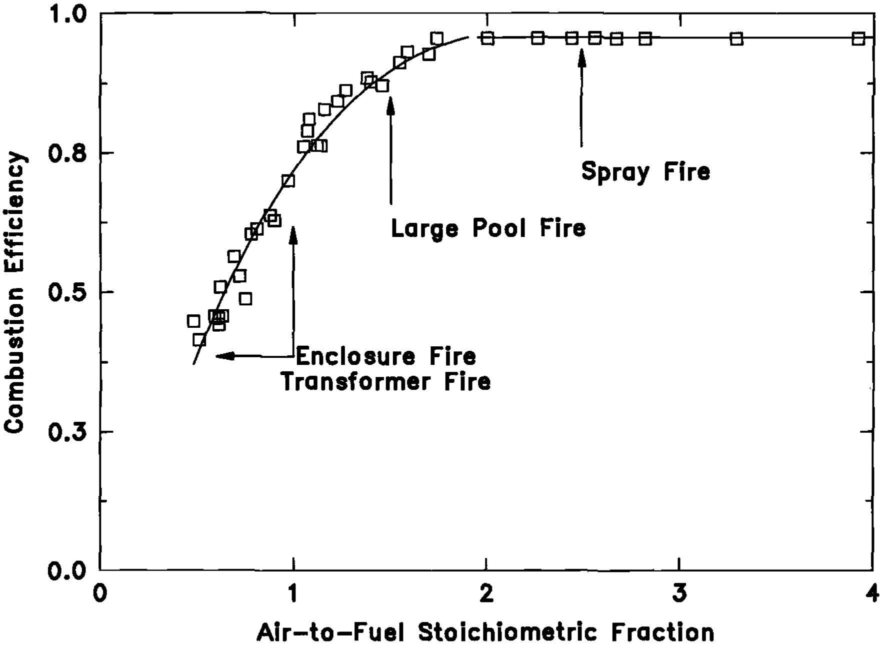


FIG. 7--Combustion efficiency versus air-to-fuel stoichiometric fraction.

with the combustion efficiency strongly influenced by the availability of ambient oxygen for combustion.

Three examples of configuration impact on combustion efficiency are indicated on Figure 7. An industrial liquid spray fire would have a high combustion efficiency associated with well-ventilated burning, and is indicated at a ϕ value of about 2.5 [4]. A large pool fire of the same fluid would typically exhibit 5-10% less efficient combustion than a spray fire [7], and is indicated in the figure by the arrow at $\phi = 1.5$. Finally, an enclosure fire, such as within a transformer, could have a range of combustion efficiencies down to about 0.4. At $\phi < 0.25$ flame extinction typically occurs [6,8], although limited non-flaming combustion may continue for values of $\phi \geq 0.1$.

Finally, the impact of fluid additives on combustion behavior can also be significant. Viscosity enhancers, for example, could affect the spray fire behavior of a lubricating fluid through narrowing of the spray angle and decreasing the fuel surface area. This would result in less ambient oxygen available for combustion and subsequently a lower combustion efficiency. Viscosity enhancers, thus, would have little impact in a spill fire pool configuration.

SUMMARY

1. The chemical structure of an industrial fluid plays a strong role in the quantity and relative distribution of heat and chemical compounds resulting from a fire. For example, the efficiency of combustion decreases and the production of carbon monoxide and particulates increase with an increase in the bond saturation and aromatic nature of a fluid.

2. Configuration and geometry affects the production of heat and chemical compounds in fires involving industrial fluids through the impact of fire ventilation. Production of carbon monoxide and particulates significantly increase due to less efficient combustion as ventilation is restricted, such as in enclosed transformer fires. Spray fires typically burn efficiently, with corresponding low levels of carbon monoxide and particulate production.

REFERENCES

[1] Tewarson, A., "Generation of Heat and Chemical Compounds in Fires," in SFPE Handbook of Fire Protection Engineering, P.J. DiNenno, Ed., National Fire Protection Association Press, Quincy, MA, 1988, pp 1-179 - 1-199.

[2] Tewarson, A., "Prediction of Fire Properties of Materials. Part 1. Aliphatic and Aromatic Hydrocarbons and Related Polymers," Report NBS-GCR-86-521, National Bureau of Standards, Gaithersburg, MD, 1986.

[3] Tewarson, A., "Smoke Point Height and Fire Properties of Materials," Report NTIS P889-41089, National Bureau of Standards, Gaithersburg, MD, 1988.

[4] Khan, M.M., "Characterization of Liquid Fuel Spray Fires," Proceedings of Heat and Mass Transfer in Fire and Combustion Systems ASME 1992, HTD-Vol.223, The American Society of Mechanical Engineers, New York, 1992.

[5] Tewarson, A., and Steciak, J., "Fire Ventilation," Combustion and Flame, Vol. 53, 1983, p 123.

[6] Tewarson, A., Jiang, F.H., and Morikawa, T., "Ventilation-Controlled Combustion of Polymers," Combustion and Flame, Vol. 95, 1993, p 151.

[7] Tewarson, A., and Newman, J.S., "Scale Effects on Fire Properties of Materials," Fire Safety Science, Proceedings of the First International Symposium, Hemisphere Publishing Corporation, New York, 1986, p 451.

[8] Beyler, C.L., "Major Species Production by Solid Fuels in a Two-Layer Compartment Fire Environment," Fire Safety Science, Proceedings of the First International Symposium, Hemisphere Publishing Corporation, New York, 1986, p 431.

Anthony Hamins,[1] Takashi Kashiwagi,[2] and Robert R. Buch[3]

CHARACTERISTICS OF POOL FIRE BURNING

REFERENCE: Hamins, A., Kashiwagi, T., and Buch, R., ''**Characteristics of Pool Fire Burning,**'' Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jurgen Reichel, Eds. American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: The structure and energetics of hydrocarbons burning in a pool fire configuration are reviewed. Examples of non-hydrocarbons are also presented. The character and structure of pool fires are discussed with special regard to the flame shape, flame pulsation frequency, flame height, and the detailed flame structure. An enthalpy balance about the flame considers enthalpy losses to the surroundings due to radiation, convection of sensible heat, and combustion efficiency considerations. The power radiated from a flame as a function of burner diameter is discussed. An enthalpy balance about the pool surface partitions the heat feedback into conduction, convection, and radiation. This enthalpy is part of a positive feedback loop which goes to vaporize the fuel. Differences between field and zone models are discussed.

KEYWORDS: burning rate, flame height, pool fire, radiative heat transfer

INTRODUCTION TO THE CHARACTER AND STRUCTURE OF POOL FIRES

Many common fire scenarios can be classified as pool fires. These include fires ranging in size from a cigarette lighter, where D is approximately 10^{-3} m, to a forest fire, where D can be as large as 10^5 m. A pool fire is defined as a buoyant diffusion flame in which the fuel is configured horizontally. Although the name implies that the fuel is a liquid, it may be a gas or a solid. The fuel bed may be of an arbitrary geometry, but for simplicity, most studies consider a circular configuration characterized by a single geometrical scale, the pool diameter (D). Beyond obvious differences in length scale, fire hazard can be characterized in terms of the combustion kinetics of a fuel such as resistance to suppression, flash point temperature, or lower flammability limits, or in terms of heat transfer during combustion, which can be characterized by the total heat release rate, the flame spread rate, or the power radiated to the surroundings. Fire hazard can be modified by ambient conditions such as the absence or presence of an enclosure, a hot surface, wind, currents, or ventilation. These

---

[1] Mechanical Engineer, Building and Fire Research Laboratory (BFRL), National Institute of Standards and Technology, Gaithersburg, MD 20899

[2] Group Leader and Research Scientist, Material Flammability Group, BFRL, National Institute of Standards and Technology, Gaithersburg, MD 20899

[3] Senior Research Specialist, Dow Corning Corp., Auburn, MI 48611

conditions play a role in governing both the detailed structure and the overall hazard of a fire. For a comprehensive review of pool fires including enclosure effects the reader is directed to the excellent review on the topic by Hall [1] and Blinov and Khudyakov [2]. This paper focusses on the structure and character of a pool fire burning in a quiescent environment with an emphasis on mass vaporization and heat release rates. Recent aspects of research in this field are summarized.

Flame Character and shape

When the mass burning rate of a flame exceeds a certain value, the flow field ceases to be laminar. As the mass burning rate continues to increase, the flow field changes from buoyancy to momentum dominated. Accidental liquid spills which result in a pool fire are almost always buoyancy dominated and are typically turbulent.

It is commonly accepted that the larger the fuel supply rate, the larger the heat release rate, and the larger the flame height. Historically, the modeling of pool fires has been based on the assumption that flame dynamics are similar regardless of fire size or fuel type. Pool fire Froude modeling suggests that the ratio of inertia to buoyant forces are the key in simulating the fluid dynamic aspects of pool fires and that chemistry plays a secondary role. Froude modeling has been a common thread used to develop simple models for flame height, pulsation frequency, and mass burning rates in pool fires.

The gross structure of a turbulent buoyant fire can be described in terms of three regions; a fuel rich core known as the persistent zone, an intermittent region with a time varying visible flame tip, and a downstream plume region [3]. The fuel rich core and the plume regions can be thought of as approximately non-reacting, whereas the majority of the heat release occurs in the intermittent region. The fuel rich core is the region just above the fuel surface where little oxygen has penetrated [4]. This region, nominally 20% of the average flame height, is relatively cool and rich in fuel and pyrolysis intermediates [5]. Large scale vortices roll into the fire, entrain air, and define the boundaries of the fuel rich core. Above the fuel rich core is the intermittent region where air is convected radially into the fire. Heat is released as the pyrolysis intermediates react with the entrained air, yielding combustion intermediates, such as carbon monoxide (CO) and soot particles, and combustion products such as water vapor and carbon dioxide. In the fire plume, the rate of chemical reactions decrease exponentially as the temperature drops and more cold air is entrained. Some combustion intermediates like soot or CO may escape the intermittent region into the plume, where temperatures are often too low to completely oxidize these species.

The structure and shape of flames is important in understanding the near field distribution of emitted radiation [6,7]. In general, flame shapes change with time through a pulsation cycle. Often, the time-averaged shape of turbulent fires is taken as approximately either cylindrical or cone-like with the bottom taken as the pool diameter and the top given by the visible flame height. Empirical results by Orloff and de Ris [6,7] have shown that a simple relation adequately describes the time-averaged flame shape over a range of moderate pool diameters (0.1 to 0.7 m), fuel types, and fuel flow rates. Their expression generates a hyperbolic-like curve which replicates the "necking-in" of the flame edge near the pool base which is due to lateral entrainment, and the downstream cresting at the visual flame tip. The lateral extent of the flame boundary at the necking-in region is related to the Froude number. For liquid pool fires, the smaller the Froude number, the more organized the flame structure and the larger the time varying lateral change in the amplitude of the flame boundary at the necking-in region.

The Froude number (Fr) is defined as the ratio of inertial to buoyant forces:

$$Fr = V^2/(L \cdot g) \qquad (1)$$

where g (9.8 m/s^2) is the gravitational acceleration, V is a characteristic velocity, often taken as the (gas phase) fuel velocity at the burner exit and L is a characteristic length scale, often taken as the pool diameter. For Fr >> 1, the flow field is momentum dominated, whereas for Fr << 1, the flow field is buoyancy dominated.

Pulsation Frequency

A large number of experimental, theoretical and scaling studies have investigated the coherent vortical structures which are shed by flames. This phenomenon has been documented for a wide range of burner diameters, heat release rates, Reynolds numbers and fuel types [8-28]. The vortical structures and their shedding frequency influence the rate of air entrainment into a fire [8]. The pulsing nature of the flow field propagates downstream leading to the time varying flame length which is observed in turbulent fires.

Chen et al. [29] employed flow visualization in buoyant diffusion flames to study the large torroidal vortices which give rise to the flame bulges which are seen as flame pulsations. Experimental studies of the pulsation frequency have utilized various measurement techniques including acoustic detection, hot wire anemometry, fast photography, video, photoelectronic devices, and local temperature and velocity measurements. Typically, these measurements have been correlated with physical dimensions such as the burner surface area [13] or diameter [27].

Buckmaster and Peters [30] suggested that flame pulsations were due to a modified Kelvin-Helmholtz instability. Bejan [31] based his analysis on the buckling theory of inviscid streams and predicted a vortex shedding frequency in qualitative agreement with experimental results. Hertzberg et al. [32] used an order of magnitude analysis to relate the pulsation frequency to the flame speed of a near limit fuel-air mixture propagating from the fire edge towards the axis of the burner.

Emori and Saito [33] emphasized the importance of the Strouhal and Froude numbers in a dimensional analysis of the pulsation frequency of pool fires. The Strouhal number (S) is a non-dimensional frequency defined as:

$$S = f \cdot L/V \qquad (2)$$

where L is a characteristic length (often taken as the burner diameter) and V is a characteristic velocity (often taken as the velocity of the fuel at the burner duct).

Putnam [34] suggested that an empirical dependence exists between S and Fr, although a quantitative analysis of this relationship was not provided. The Strouhal number plotted as a function of the inverse Froude number shown in Fig. 1 correlates the pulsation measurements taken from the literature for flames burning gaseous, liquid and solid fuels over 14 orders of magnitude in Froude number and covering a range of diameters from 0.007 to 50 m [28]. A power law fit to the data yields: $S \propto Fr^{-0.57}$. A power law fit with $S \propto Fr^{-1/2}$, would be equivalent to the expression: $f \propto D^{-1/2}$.

A buoyancy induced instability has also been observed in isothermal helium plumes as indicated in Fig. 1 [28]. The Strouhal number of the non-reacting flow is well correlated by the inverse Froude number, but yields a different power law exponent than the reacting flow case. This is not surprising considering that the local density gradients in the reacting and non-reacting structures are quite different. Although numerical simulations of the pulsation phenomena in buoyant plumes has been accomplished [35], the pulsing nature of buoyant fires remains to be modeled from detailed consideration of the conservation equations.

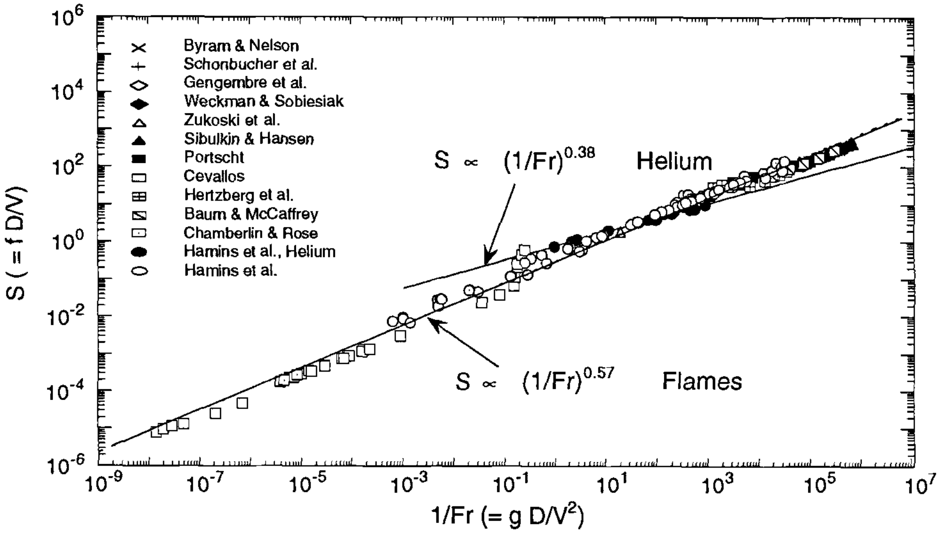


Figure 1 The Strouhal number as a function of the inverse Froude number for flames burning liquid, solid, and gaseous fuels and for a helium plume.

Flame Height

The shape and height of a fire have important implications in terms of fire hazard. In an enclosure, direct convective heat transfer to a ceiling may have dramatic consequences in terms of time to flashover. Flame height is also a key parameter in radiative heat transfer calculations to targets external to the fire and is related to possible ignition of a secondary object. In global burning rate models, the flame height impacts the calculated radiative feedback rate to the fuel surface and thereby influences predictions of fire growth and spread. In zone fire models, the calculation of flame height impacts estimates of radiative flame emission, the occurrence of reignition in upper layer gases in an enclosure, and estimates of the thermal insult on structural members [36]. McCaffrey [37] reviewed the large number of studies that have investigated flame heights, covering a wide range of burner diameters and different fuels. A common definition for flame height (or boundary) is that of the visible edge of flame luminescence. For turbulent diffusion flames, early research often relied on visual observation to estimate an average flame height. Zukoski et al. [17] used the 50% visible intermittency height to define a characteristic flame height (Z_f), which is defined as the location where the flame resides above and below this threshold 50% of the time.

The flame height correlations of Zukoski et al. [17] and Heskestad [38] are commonly used in the fire literature. Heskestad's algorithm relates flame height to a power law in terms of $N(\dot{Q})$, a non-dimensional heat release rate:

$$Z_f/D = -1.02 + 15.6 \cdot N(\dot{Q})^{0.2} \qquad (3)$$

TABLE 1--Thermochemical and combustion properties of several fluids.

Fuel	χ_s	T_b, K	H_c, MJ/kg	l_s, cm	r	χ_r
Methane	...	112	50.0	...[a]	12.9	0.21[b]
Propane	...	231	46.4	16	15.7	0.24[b]
Acetylene	...	...	48.2	1.9	13.3	0.28[b]
Methanol	0.063	338	20.0	...[a]	6.9	0.22
Ethanol	0.037	351	26.8	23	9.4	0.18
Acetone	0.020	329	28.6	21	9.9	0.27
Heptane	0.011	371	44.6	12	15.2	0.33
Toluene	0.013	383	40.5	0.6	13.5	0.34
PDMS[c] (D4)	0.017	449	24.8	0[d]	7.5	0.37
PDMS[c] (MD_2M)	0.016	467	28.8	0[d]	8.9	0.37
PDMS[c] ($MD_{15}M$)	0.13	≈648[e]	24.8	0[d]	7.5	0.31

[a] The smoke point has not been accurately measured, but is expected to be extremely large.

[b] χ_r is listed for large fuel flow rates, see Figs. 7 and 8 for χ_r as a function of mass flux in the 0.38 m burner.

[c] PDMS (polydimethylsiloxane) with $M=(CH_3)_3SiO$ and $D=(CH_3)_2SiO$.

[d] SiO_2, an oxidized particle, is a stable product that escapes the flame tip for all combustion conditions.

[e] Estimated temperature for thermal degradation (reversion) to volatile cyclics (D_3, D_4, ..., D_n).

where D is the pool diameter and $N(\dot{Q})$ is defined as:

$$N(\dot{Q}) = [c_p \cdot T_o/(H_c/r)]^3 \cdot (\dot{Q}_D{}^*)^2 \qquad (4)$$

r is the stoichiometric (mass based) ratio of air to fuel, c_p is the heat capacity of air at ambient temperature, T_o, and H_c is the heat of combustion for a particular fuel. $\dot{Q}_D{}^*$ is defined as:

$$\dot{Q}_D{}^* = \dot{Q}/(\rho_o \cdot c_p \cdot T_o \cdot (g \cdot D^5)^{0.5}) \qquad (5)$$

where ρ_o is the ambient air density and g is the gravitational acceleration. The parameter $N(\dot{Q})$ is proportional to the Froude number defined in Eq. 1 and is related to the fire heat release rate ($\dot{Q}$). The values of r and H_c can vary by a factor of two for different fuels as seen in Table 1.

Hasemi and Nishihata [39] studied small $\dot{Q}_D{}^*$ flames, where small $\dot{Q}_D{}^*$ was defined as $\dot{Q}_D{}^* < 0.1$, $N(\dot{Q}) < 10^{-5}$, or $Z_f/D < 0.5$. Intermediate and large flames are characterized by ($\dot{Q}_D{}^* > 0.1$). Hasemi and Nishihata [39] found that:

$$\text{for small flames} \qquad Z_f/D \propto (\dot{Q}_D{}^*)^2 \qquad (6a)$$

$$\text{for intermediate flames} \qquad Z_f/D \propto (\dot{Q}_D{}^*)^{(2/3)} \qquad (6b)$$

Zukoski et al. [17] correlated flame height to a power law in terms of $\dot{Q}_D{}^*$:

$$Z_f/D = 3.3 \cdot (\dot{Q}_D{}^*)^{(2/3)} \text{ for } \dot{Q}_D{}^* < 1 \qquad (7a)$$

$$Z_f/D = 3.3\cdot(\dot{Q}_D^*)^{(2/5)} \text{ for } \dot{Q}_D^* \geq 1 \qquad (7b)$$

Zukoski et al.'s [17] algorithm can be related to the Heskestad [38] expression through $\dot{Q}_D^*$. Heskestad's and Zukoski's correlations given in Eqs. 3 and 7 relate the normalized flame height (Z_f/D) to the total fire heat release ($\dot{Q}$).

Figure 2 shows our measurements [40] of the normalized flame height as a function of $N(\dot{Q})$ in gaseous pool fires burning acetylene, propane, and methane in 0.10, 0.38, and 1.0 m water-cooled sintered-metal and sand-filled burners. Like Zukoski et al. [17], the 50% intermittency visible flame height was used to define the characteristic flame height. The bars on some data points represent minimum and maximum observed non-dimensional flame heights which varied from approximately 0.7 to 3 times the average flame height. Measurement uncertainty is estimated to be approximately 10%, which is smaller than the symbol size representing the data in Fig. 2 [40]. Also shown are the correlations of Zukoski (for CH_4, C_3H_8, and C_2H_2) and Heskestad. The correlations of Heskestad and Zukoski behave very similarly for $N(\dot{Q}) > 4\cdot10^{-5}$. For $N(\dot{Q}) < 4\cdot10^{-5}$, the predictions are significantly different. Heskestad's [38] correlation appears to adequately represent the data in Fig. 2 except for the high C_2H_2 mass flows, where the flames are smoky and the combustion efficiency is small.

In the original development of a flame height model based on the Froude number, Heskestad [41] proposes that the non-dimensional flame height should be written in terms of N and the sensible heat loss from the flame ($\dot{Q}_c$) as:

$$Z_f/D = f(N/\dot{Q}_c) \qquad (8)$$

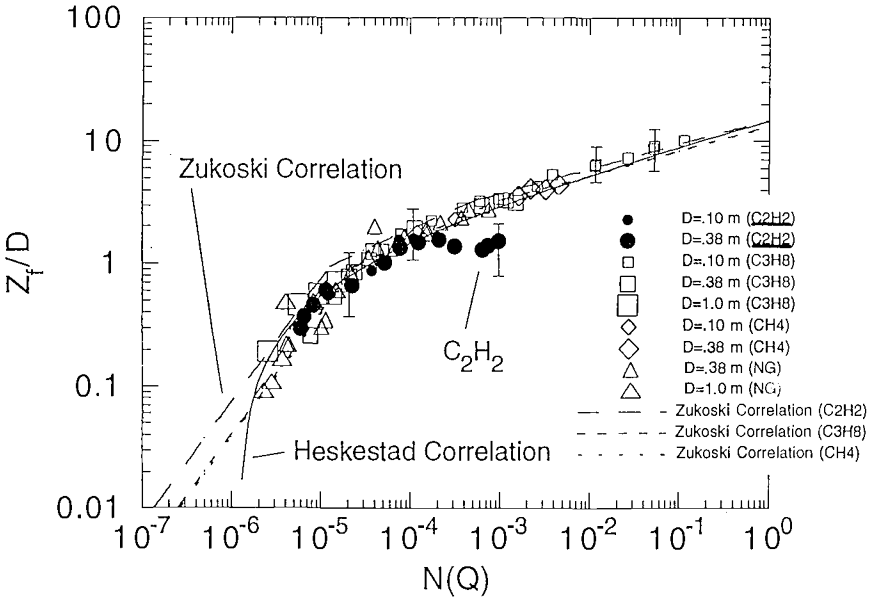


Figure 2 Measurements of the normalized flame height as a function of $N(\dot{Q})$. The flame height correlations of Heskestad [37] and Zukoski [17] are also shown.

where $N=N(\dot{Q}_c)$. Physically, $\dot{Q}_c$ is the flame enthalpy convected away by the plume to the surroundings. It is discussed in detail in Section 2.

Unfortunately, the fuels used to develop the flame height algorithms [17,38,39] relied almost exclusively on non-smoky fuels, where the non-dimensional parameter χ_c ($=\dot{Q}_c/\dot{Q}$) is typically greater than 0.7. Common fuels are often smoky and thus, it is of interest to test the flame height correlation for a fuel like acetylene, which has a high sooting tendency and which may have χ_c values much smaller than 0.7 [42]. An attempt to correlate the non-dimensional flame height according to Eq. 8 also failed to collapse the high mass flow acetylene results. This may be because the physics controlling the length scales in very sooty fires may be different than in non-smoky fires [43].

A fit of the same normalized flame height data used in Fig. 2 as a function of $\dot{Q}_D{}^*(\dot{Q}_c)$ fares much better as shown in Fig. 3. The correlation by Zukoski for $\dot{Q}_D{}^*(\dot{Q})$ is also shown, but as expected it does not correlate the data. These results imply that non-smoky fuels are reasonably predicted by the literature flame height correlations. For smoky fuels, however, the literature correlations do not do a good job of predicting average flame heights. A better fit is obtained when $\dot{Q}_c$, the sensible heat loss from a flame is considered. However, in most common fire scenarios, measurement of $\dot{Q}_c$ is impractical.

The Detailed Structure of Pool Flames

The turbulent nature of a fire plays an important role in mediating flame radiation. Local radiative emission is governed by the time-

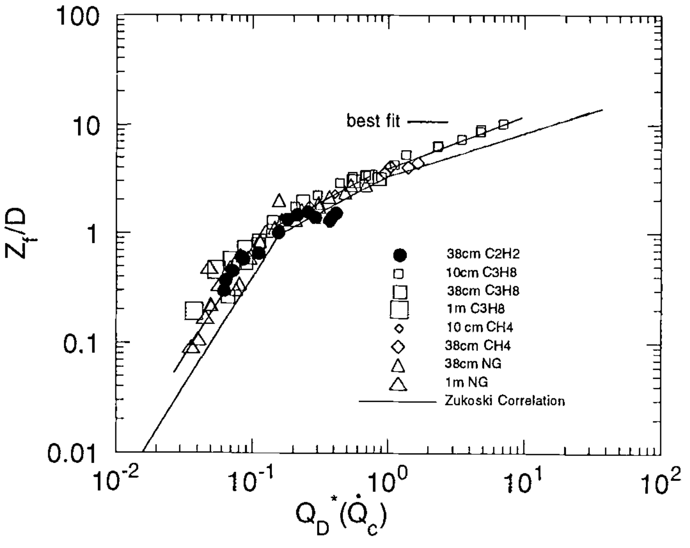


Figure 3 The measured flame height as a function of $\dot{Q}_D{}^*(\dot{Q}_c)$. Zukoski's correlation for $\dot{Q}_D{}^*(\dot{Q})$ is also shown.

varying correlated distributions of temperature and soot volume fraction. Because of the highly non-linear dependence of Plank's function, small uncertainties in flame temperature can propagate large errors in the calculation of radiative emission from a flame. In addition to particle radiation, emission by water and carbon dioxide must also be considered. Thus, it is of interest to understand the temporal and spatial structure of a turbulent fire. The structure of a steady laminar diffusion flame is defined by the scalar distributions of temperature and chemical species, including both soot particles and stable and unstable reactive radical gas phase species, and by the vector velocity field.

A complete set of flame structure information can be used to make calculations of radiative flame emission and feedback to the fuel surface, as well as estimates of the key chemical heat release pathways [44,45]. The structure of an unsteady turbulent fire is complicated by the time varying distributions of these quantities. The number of investigations on the detailed structure of buoyant turbulent pool fires is much, much smaller than in laminar flames. Enough information does exist in pool fires, however, to qualitatively understand trends in the mean temperature, velocity, and stable species concentrations [4,9,14,16,46-49].

McCaffrey [50] represented the mean temperatures and velocities as functions of the heat release. The mean centerline temperature rapidly increases from the fuel surface to a peak value of nearly 1200 K in a distance of approximately one pool diameter for buoyant 0.3 m propane pool fires [9]. Above the temperature maximum, the mean centerline temperature slowly decreases due to cooling by entrained air and a halt to the chemical reactions. In the intermittent zone, the mean temperature decreases, whereas in the persistent region, the temperature is essentially unchanging. In the intermittent region, McCaffrey [50] showed that the radial dependence of the mean axial temperature and velocity scaled like a gaussian function. The RMS temperature variation at a single location near the edge of a hydrocarbon fire is typically as large as 500 K, almost as large as the mean temperature itself [51].

The mean axial velocity profile also scales with the heat release [50]. At the pool surface, the gas phase fuel velocity is small for liquid fuels (≈0.1 m/s) and even smaller for burning solids. Gas velocity in a fire rapidly accelerates above the pool surface, driven by the volume expansion associated with chemical reaction. A few centimeters above the pool surface, vertical speeds on the order of 1 m/s are obtained for buoyant 0.3 m propane pool fires [9]. The gas velocity continues to increase until the heat release stops near the top of the visible flame, with vertical speeds reaching 3 to 4 m/s at 0.2 to 0.4 m above the fuel surface [9]. The rms velocity variation has not been as carefully characterized.

The average of the time varying species concentration field in a turbulent flame bears some resemblance to that of a laminar flame. In laminar non-premixed flames, it has been shown that the temperature and many of the major and minor species concentrations are related through simple state relationships, which is a function of the local equivalence ratio [51,52]. Soot volume fraction does not correlate in this same manner. On the flame axis, the concentration of fuel decreases rapidly and the concentration of oxygen increases. In a turbulent flame, the time-averaged species concentration and temperatures are smoothed out. In most flame regions, their values do not obtain peak values as large as in laminar flames [4,9,14,16,46,49]. The concentration of intermediate species such as carbon monoxide, molecular hydrogen and the soot volume fraction do increase with distance above the fuel surface [9].

ENTHALPY BALANCE IN THE FLAME

There are wide differences in the radiative emission characteristics of fires depending on the fuel composition. Flames burning methyl alcohol, for example, do not contain soot particles and appear blue in color due to non-equilibrium thermal processes. Flames burning H_2 are not visible at all. In contrast, hydrocarbon fires are extremely luminous due to significant concentrations of soot particles which emit blackbody radiation. Gas species such as carbon dioxide, water, and to a lesser extent carbon monoxide and hydrocarbon intermediates, emit infrared radiation in hydrocarbon and non-hydrocarbon fires, but the visible radiation intensity emitted by soot typically far exceeds that of gaseous emission. For some fuels, as the fire source becomes large, the rate of soot production exceeds the rate of soot oxidation and carbonaceous soot particles are convected through the fire to the surroundings. If the soot yield is very high, then flame radiation will be blocked and the fractional radiative emission will decrease.

Beyond spectral differences, radiated power differs with fuel type even for the same values of heat release, $\dot{Q}$. This implies that the simple assumptions of Froude modeling must be modified to account for differences associated with chemical influences on the structure of a fire.

The energy radiated from a flame is a key parameter in fire safety considerations. The magnitude of the radiative transfer to targets external to the flame affects the hazard posed by a particular fire and influences fire spread rates. Radiative transfer from the flame to the fuel surface is the dominant heat feedback mechanism in large fires, controlling the fuel mass evaporation rate.

An overall enthalpy balance about a diffusion flame shows that the actual heat release from chemical reactions ($\dot{Q}_a$) is equal to the sum of the energy convected from the buoyant plume to the surroundings ($\dot{Q}_c$), enthalpy feedback to the fuel surface ($\dot{Q}_s$), and energy radiated to the surroundings by high temperature soot particles and gas species ($\dot{Q}_r$):

$$\dot{Q}_a = \chi_a \cdot \dot{Q} = \dot{Q}_r + \dot{Q}_c + \dot{Q}_s \qquad (9)$$

where the actual heat release ($\dot{Q}_a$) is equal to the idealized heat release ($\dot{Q}$) modified by the combustion efficiency (χ_a). The idealized heat release ($\dot{Q}$) is defined as:

$$\dot{Q} = \dot{m} \cdot H_c \qquad (10)$$

where $\dot{m}$ is the mass vaporization rate (kg/s) and H_c is the heat of combustion (MJ/kg). Dividing through by $\dot{Q}$, Eq. 9 can be rewritten as:

$$\chi_a = \chi_r + \chi_c + \chi_s \qquad (11)$$

where χ_s is defined as: $$\chi_s = \dot{Q}_s/\dot{Q} \qquad (12)$$

and represents the heat feedback to the fuel surface via radiation, convection and conduction. The fractional amount of total combustion enthalpy lost as sensible heat is defined as the convective heat loss fraction (χ_c):

$$\chi_c = \dot{Q}_c/\dot{Q} \qquad (13)$$

The fractional amount of total combustion enthalpy emitted from a flame is defined as the radiative heat loss fraction (χ_r):

$$\chi_r = \dot{Q}_r/\dot{Q} \qquad (14)$$

Radiative Emission

Figure 4 is a schematic drawing of the technique used to determine the

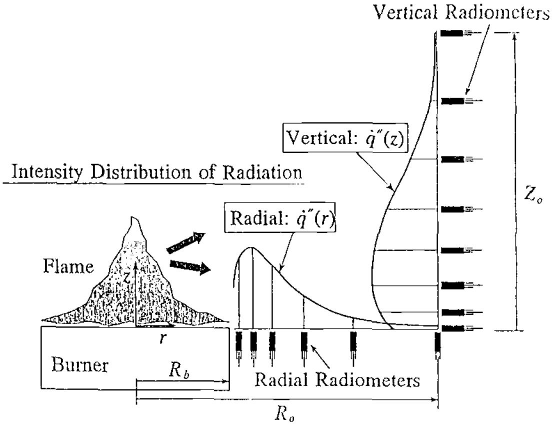


Figure 4 Schematic drawing of the methodlology to measure the radiative flux distribution over a surface surrounding the flame.

radiative flux distribution over a surface surrounding the flame. The radiated power ($\dot{Q}_r$) is determined by integrating the measured spatial distribution of radiant flux. At the same time, $\dot{Q}$ can be determined by monitoring the burning rate ($\dot{m}$). Figure 4 is a schematic of the location and orientation used to measure the radiated power from a flame. Typical profiles of the near field time-averaged radiative flux as a function of location in the radial and vertical directions are also shown. The radiative flux drops off very quickly in the radial direction, whereas in the vertical direction, the flux peaks at a vertical location equal to approximately 50% of the characteristic flame height. The vertical and radial flux distributions are numerically

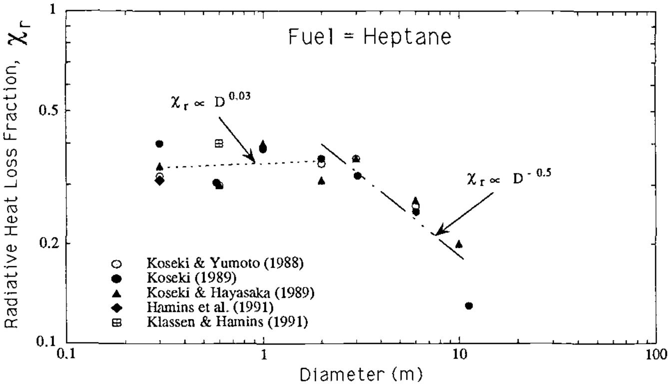


Figure 5 Measurement of χ_r as a function of pool diameter for heptane fires.

integrated to obtain the total radiant power output of the flame using the following expression:

$$\dot{Q}_r = 2\pi(\int r\cdot q''(r)\cdot dr + R_o\int z\cdot q''(z)\cdot dz) \qquad (15)$$

where the symbols for the r axis, z axis, and R_o are defined in Fig. 4. This method has been used by a number of investigators. Jeng and Faeth [54] used this technique for methane jet flames. Subsequently, Gore [55] applied this technique to jet diffusion flames burning a variety of fuels. Hamins et al. [56] have determined χ_r from detailed radiant flux measurements for a number of different fuels and pool diameters.

Figure 5 shows measurements from several authors of χ_r as a function of pool diameter for fires burning heptane [56-60]. Two distinct regimes are delineated in the figure. For $0.1 \text{ m} < D < 2 \text{ m}$, χ_r is relatively constant, whereas for $D > 2$ m, $\chi_r \propto D^{-½}$. Data for kerosene shows very similar dependencies [61].

Since measurements of the distribution of the radiant flux over a surface bounding the source is tedious and at times impractical, many measurements of radiative heat loss fraction reported in the literature rely on single point radiant flux data and the assumption of isotropy. For a spherical source, the total radiative power output $\dot{Q}_r$ (kW) is the product of the flux, $q''(r)$, and the spherical surface area ($4\pi r^2$):

$$\dot{Q}_r = 4\pi r^2\cdot q''(r) \qquad (16)$$

where R is the sphere radius. The incident thermal radiation flux (q'') is proportional to the inverse square of the distance from the source. McCaffrey [62] used single location measurements and the assumption of radiative isotropy to evaluate χ_r for medium sized pool fires. Modak [63] and Bouhafid et al. [3] measured radiative flux at various distances from pool fires. Modak [63] concludes that the assumption of an equivalent isotropic emitter improves with distance from the fire and is approximately valid for distances from the pool center equal to ten diameters.

Figure 6 shows our measurements of the power radiated to the surroundings ($\dot{Q}_r$) as a function of diameter for burning pools of a number of hydrocarbon and polydimethylsiloxanes (siloxane) fluids (Buch et al., 1995). $\dot{Q}_r$ is related to χ_r through Eq. 14 and to $\dot{m}$ through Eq. 10, yielding:

$$\dot{Q}_r = \dot{m}\cdot H_c\cdot \chi_r \qquad (17)$$

As shown in Fig. 5 for heptane, $\chi_r \approx$ constant for $D < 2$ m, leading to the result that the radiated power is proportional to the burning rate (i.e., $\dot{Q}_r \propto \dot{m}$ for $D < 2$ m). Figure 6 shows that for the same pool diameter, $\dot{Q}_r$ differs by an order of magnitude between fuels and is largest for the hydrocarbons (heptane and toluene) and oligomeric short chain siloxanes (MM, MDM, MD2M, and D4) and is more than an order of magnitude smaller for alcohols or polymeric siloxanes ($MD_{15}M$ and $MD_{58}M$) [64]. The notation describing the chemical structure of the siloxanes is explained in Table 1.

For $D > 2$ m, the mass vaporization flux ($\dot{m}''$) is approximately constant [65], and therefore, $\dot{m} \propto D^2$. For heptane and kerosene, $\chi_r \propto D^{-½}$ (see Fig. 5). This leads to an expression that can be expected for typical liquid hydrocarbons (i.e., $\dot{Q}_r \propto D^{1.5}$). Mudan and Croce [66] show measurements of the emissive power for liquified natural gas (LNG) which suggest that $\dot{Q}_r \propto D^2$ for $D >> 2$. This implies that $\chi_r \approx$ constant for $D >> 2$ m for LNG, quite different from the results seen in Fig. 5 for a larger hydrocarbon like heptane, which has a higher sooting tendency.

Table 1 lists χ_r for a number of fluids burning in a 0.3 m diameter pool. Table 1 shows that the fluid type has a significant influence on χ_r, which is smallest for the non-luminous methanol fires.

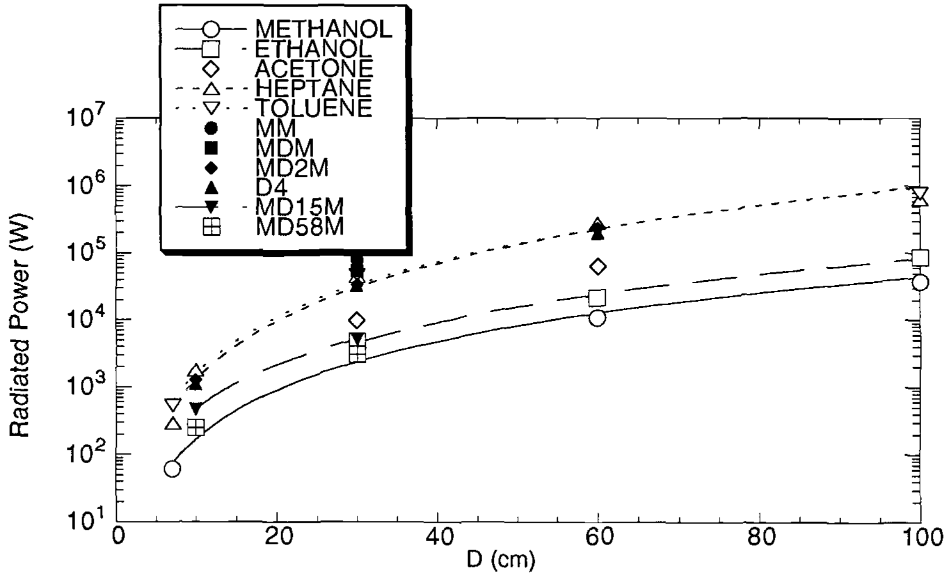


Figure 6 Measurement of $\dot{Q}_r$ as a function of pool diameter for fires burning a number of liquid fuels.

As $\dot{Q}_r$ increases, $\dot{Q}_s$, the heat feedback rate to the pool surface can also be expected to increase. Other factors, however, such as radiation blockage by fuel vapor, pyrolysis intermediates, and soot particles, play an important role in mediating radiative heat feedback [67,68]. Thus, the modeling of $\dot{Q}_s$ requires a detailed understanding of flame structure, and cannot be predicted from global flame energetics alone. Detailed measurements of $\dot{Q}_s$ on the pool surface could also differentiate the relative importance of radiative and convective transfer in intermediate sized pool fires. For large burner diameters (D >2 m), radiative transfer is expected to dominate.

For a hydrocarbon fire, the ratio ($\dot{Q}_c/\dot{Q}=\chi_c$) typically takes on values much less than unity [42], depending on a number of factors including, most importantly, the fuel type and fire size which controls χ_a and χ_r. Experimentally, the sensible enthalpy loss from a fire ($\dot{Q}_c$) can be estimated from the heat carried by the combustion products [69]. In an exhaust duct, the sensible enthalpy loss from the fire can be expressed as [40]:

$$\dot{Q}_c = V_a \cdot A \cdot \rho \cdot c_p \cdot \Delta T \qquad (18)$$

where V_a is the velocity of the exhaust at the location of the thermocouple array, A is the duct area, ρ is the gas density, c_p is the heat capacity of the exhaust gases, and ΔT is the temperature difference between ambient and the average exhaust temperature, measured by thermocouples.

Measurements of $\dot{Q}_c$, $\dot{Q}_r$, $\dot{Q}_s$, and $\dot{m}$ for a particular fuel allow determination of χ_a from Eqs. 9 and 10. Experimentally, enthalpy losses to a water cooled burner ($\dot{Q}_s$) can be determined by monitoring the volumetric flow of cooling water and the temperature increase of the water [40]. Alternatively, χ_a can also be determined by oxygen depletion calorimetry [42]. Tewarson [42] related the smoke point height (l_s) to global combustion properties such as χ_r, χ_a, and χ_c from calorimetry and radiative flux measurements made on a large number of solid, liquid, and gaseous fuels burning in small diameter pools. Table 1 lists the smoke point height (l_s) for several fuels. l_s is defined as the critical flame length at which soot escapes from the flame tip [70]. Typical hydrocarbons are characterized by l_s values ranging from 0.5 to 20 cm. Small values of l_s, are associated with hydrocarbons with a higher tendency to soot. Methanol flames contain near-zero concentrations of soot and thus are characterized by infinite smoke point heights. Although l_s is helpful in ranking the combustion efficiency of various organic fuels, combustion efficiency is also a function of the fuel flux. This is seen in Fig. 7, where the measured values of χ_r, χ_s, and χ_c and the calculated values of χ_a are presented as a function of the mass burning flux of acetylene in a 0.38 m diameter water-cooled sintered-metal burner. The enthalpy feedback to the burner (χ_s defined in Eq. 12) is relatively small except for small fuel fluxes. The enthalpy feedback decreased with increased fuel flux, consistent with thin film models of convective transfer [6,7]. As the acetylene mass vaporization flux ($\dot{m}''$) increased, χ_r increased and χ_c decreased. For very small acetylene mass fluxes, the flames were non-smoking and χ_a was determined to be close to unity. This is because hydrocarbon fuels like acetylene with a high tendency to soot, typically yield smoke only for moderate and high mass fluxes. As the acetylene mass flux increased, Fig. 7 shows that the fires produced copious quantities of soot and χ_a decreased, obtaining values as low as 0.6. For small mass fluxes, χ_c took on values nearly 0.4.

Similar measurements for methane (and natural gas composed of ≈96%

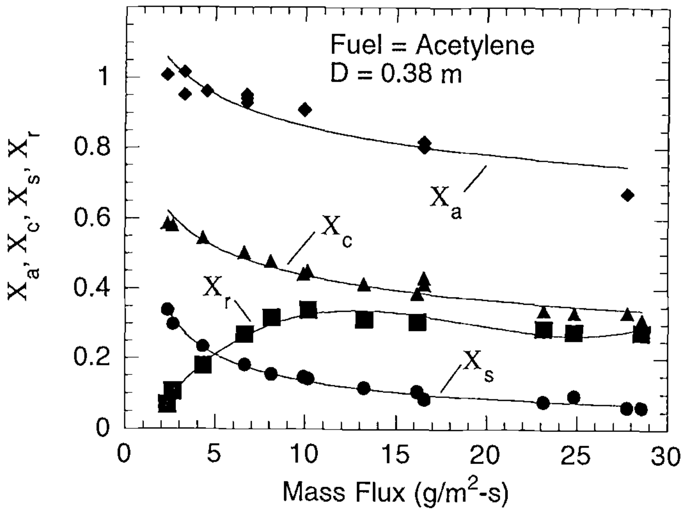


Figure 7 Measurements of χ_r, χ_s, and χ_c as a function of the mass burning flux of acetylene in a 0.38 m burner. The calculated value of χ_a is also shown.

methane) are shown in Fig. 8. Because these fires were not observed to produce smoke, it was assumed that $\chi_a \approx 1$. A comparison of Figs. 7 and 8 shows that for the same mass flux, the χ_r values for natural gas and methane were smaller and the χ_c values were generally larger than in the acetylene flames.

ENTHALPY BALANCE AT THE FUEL SURFACE

The heat feedback rate, $\dot{Q}_s$ (kW), from the flame to the pool surface can be partitioned into the three major heat transfer mechanisms: conduction [71], convection [72-74] and radiation [75-79]. A large number of studies have investigated each of these mechanisms in an effort to accurately model mass vaporization rates in burning pools. The relative contributions of each of these are related to geometrical parameters such as the pool diameter, burner material, and lip height, but more fundamentally to the structure of the flame itself, including the flame shape and the spatial distribution of temperature, species concentration and soot volume fraction.

Hottel [75] represented heat transfer to the pool surface in terms of global flame properties:

$$\dot{Q}_{s,cond} = k'\pi D(T_f - T_s) \tag{19}$$
$$\dot{Q}_{s,conv} = hA_s(T_f - T_s) \tag{20}$$
$$\dot{Q}_{s,rad} = \sigma V A_s(T_f^4 - T_s^4)(1 - \exp(-\Gamma \cdot D)) \tag{21}$$

where $\dot{Q}_{s,cond}$, $\dot{Q}_{s,conv}$, and $\dot{Q}_{s,rad}$ are respectively conduction, convection and absorbed radiation heat transfer to the pool surface, k′ (kW/m·K) is a conduction coefficient, D (m) is the pool diameter, A_s (m^2) is the pool surface area, T_f (K) is the flame temperature, T_s (K) is the pool surface temperature, h (kW/m^2·K) is a convective heat transfer coefficient, σ is the Stefan-Boltzmann constant, V is a dimensionless flame-pool surface radiative configuration factor, and Γ (m^{-1}) is a radiative extinction coefficient.

Hottel [75] noted that when D is small (D<<1), conduction dominates the heat feedback because convection and radiation are proportional to D^2 and conduction is proportional to D. When D is large, the importance of conduction diminishes and radiation eventually dominates convection. This is because $\Gamma \cdot D$ in Eq. 21 becomes large and radiation is proportional to T_f^4. Burgess and Hertzberg [76], using Hottel's [75] bulk properties formulation for pool burning and Blinov and Khudyakov's [80] burning rate data, determined that radiative transfer becomes dominant over convection for pool diameters from 0.1 to 0.5 m depending on fuel type. Below these sizes, convection was found to be important.

A schematic diagram of the enthalpy balance in a liquid pool fire is shown in Fig. 9 for a quasi-steady state system [81]. Such a system is achieved by adding fuel from a reservoir into the pool bottom at a rate that matches the fuel burning rate, such that the fuel level remains constant. The gradual growth of the thermal layer inside the liquid pool ($\dot{Q}_{corr}$) must also be considered. A short time after ignition, the mass vaporization rate ($\dot{m}$) in such a system is nearly constant, but the bulk temperature throughout the pool continues to gradually increase [81], which represents a flame enthalpy loss mechanism ($\dot{Q}_{corr}$). The enthalpy balance for a control volume about the liquid pool can be represented as:

$$\dot{Q}_s = \dot{Q}_{s,cond} + \dot{Q}_{s,conv} + \dot{Q}_{s,rad} - \dot{Q}_{reflect} \tag{22}$$

$$\dot{Q}_s = \dot{m} \cdot H_g + \dot{Q}_{rerad} + \dot{Q}_{loss} + \dot{Q}_{corr} \tag{23}$$

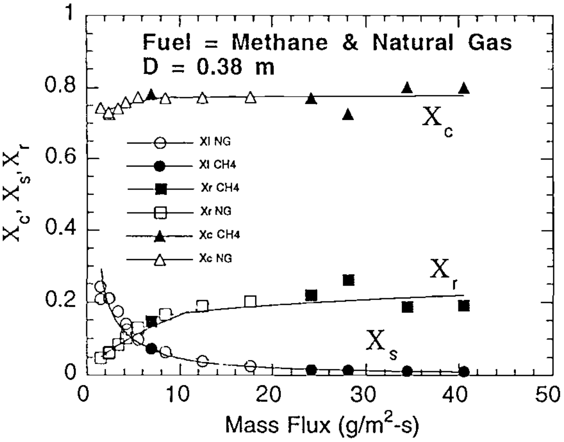


Figure 8 Measurements of χ_r and χ_s as a function of the mass burning flux of methane and natural gas in a 0.38 m burner. The calculated values of χ_c are also shown.

The net rate of heat feedback to the pool surface, $\dot{Q}_s$ (kW), is determined by the sum of the rates of convective ($\dot{Q}_{s,conv}$), conductive ($\dot{Q}_{s,cond}$) and radiative ($\dot{Q}_{s,rad}$) feedback. The rate of absorbed radiative enthalpy is equal to the incident ($\dot{Q}_{s,rad}$) minus the reflected rate of radiative enthalpy ($\dot{Q}_{reflect}$). The amount of surface reflection ($\dot{Q}_{reflect}$) depends on the angle of incident radiation and the refractive index of the fuel [81], where H_g (kJ/kg), for a steadily burning fire, is an effective heat of gasification defined as:

$$H_g = H_v + \int C_p \cdot dT \tag{24}$$

H_v (kJ/kg) is the latent heat of vaporization at the pool surface temperature, C_p (kJ/kg·K) is the specific heat of the liquid fuel and the limits of integration are from ambient temperature (T_o) to the pool surface temperature (T_s). These terms are balanced primarily by the product: ($\dot{m} \cdot H_g$).

The width of the arrows in Fig. 9 symbolize the approximate importance of each of the key terms in the enthalpy balance occurring in a 0.30 m heptane pool fire. A detailed heat balance must consider other thermal sources and sinks. These include heat gain due to conduction through the metal burner walls, heat losses due to radiation from the fuel surface to the surroundings ($\dot{Q}_{rerad}$), losses from the bottom and sides of the burner ($\dot{Q}_{loss}$). The loss terms ($\dot{Q}_{rerad}$ and $\dot{Q}_{loss}$) act to diminish the fraction of enthalpy available for fuel vaporization, but are typically small when compared to the term ($\dot{m} \cdot H_g$) for liquid fuels. The combustion of a solid material can have a high surface temperature, leading to large values of $\dot{Q}_{rerad}$. Another possible contribution to the overall heat balance is from water condensation ($\dot{Q}_{water}$) on the fuel surface. Condensation of gas-phase water molecules, diffusing from the flame towards the relatively cool fuel surface, can impact the fuel burning rate measurement and increase the enthalpy of the pool. The impact of this process may be non-trivial for fuels with pool surface temperatures significantly less than the water boiling point (T_s<<373K).

Experimental characterization of the local heat transfer to the pool surface is essential for the development and validation of detailed models which predict the burning rates of liquid hydrocarbons and solid

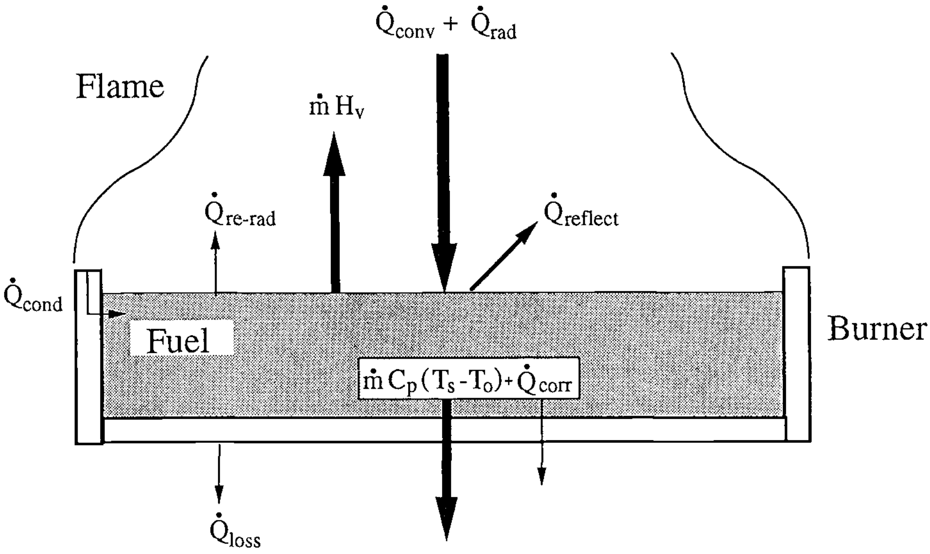


Figure 9 Schematic drawing of the enthaply balance for a pool fire burning a liquid fuel.

polymers. Yet, only a limited number of experiments have measured local heat transfer to the fuel surface.

Previous measurements of the local radiative or net heat flux at the surface of pool fires are listed in Table 2. Measurements have been conducted on pools varying in diameter (D) from approximately 0.01 to 3 m for a number of different liquid fuels and for solids including polymethylmethacrylate (PMMA). Studies of local mass vaporization rates have been conducted using ring pool burners [2,81,82] and insulated fuel wells [83] where local measurement of $\dot{m}$ in conjunction with Eq. 23 allows estimate of the local heat flux.

In their extensive investigation of pool fires, Blinov and Khudyakov [2] measured the burning rate of numerous hydrocarbon fuels in different sized concentric ring burners including a 0.80 m four-ring burner and a 0.30 m four-ring burner. Fuels tested included benzene, gasoline, kerosene and diesel oil. For all fuels, the burning rates were highest in the center ring, decreased away from the center and increased in the outer ring. These results were qualitatively different from the measurements reported by Akita and Yumoto [82] for methanol. Hamins et al. [81] measured burning rates in a 0.30 m four-ring burner and found that the mass vaporization flux ($\dot{m}''$) was nearly constant (within 20%) as a function of ring location on the pool surface for both luminous and non-luminous fuels.

In a series of square pool fires burning polymethylmethacrylate (PMMA), Modak and Croce [84] measured a monotonic decrease in burning rate from pool center to pool edge. For a PMMA square (0.31 m x 0.31 m), the local burning rate at the pool edge was approximately half the burning rate at the pool center.

TABLE 2--Heat feedback measurements in pool fires.

Reference	Fuel	D, m	$\dot{Q}''_{rad}$	$\dot{Q}''_{net}$	Steady State?	Comments
Blinov & Khudyakov (1961)	benzene gasoline kerosene oil	0.03-.8		X	yes	ring burner
Corlett & Fu (1966)	methanol acetone	0.006-0.3	X		yes	insulated fuel well
Akita & Yumoto (1965)	methanol	0.1-0.3	X		yes	ring burner
Yumoto (1971)	gasoline hexane	0.6-3	X	X	yes	pool center
Modak & Croce (1977)	PMMA	0.2		X	no	recession rate
Alger et al. (1979)	methanol JP-5	3	X		no	Gardon gauges
Shinotake et al. (1985)	heptane	0.3-1.0	x	x	no	dual Gardon gauges
Hamins et al. (1994)	methanol heptane toluene MMA	0.3	X	X	yes	ring burner/ radio-meter

Local radiative heat fluxes have been measured using dual Gardon gauges [85,86], aspirated radiometers [87] or a windowless, nitrogen purged, water-cooled narrow view-angle detector [81]. Yumoto [85] measured heat feedback to intermediate-sized (0.6 m $< D < 3.0$ m) gasoline and hexane pool fires using dual Gardon gauges with different emissivities, but measurements were made at the pool center only. Alger et al. [87] measured the radiative feedback to large scale (3 m) methyl alcohol pool fires using Gardon and transpiration radiometers at several pool locations. They found that the radiation decreased from the pool center towards the pool edge by almost a factor of two, consistent with the results of Modak and Croce [84]. Shinotake et al. [86] determined convective and radiative heat feedback near the center of intermediate sized pools burning heptane by use of dual Gardon gauges with different surface emissivities. Their results showed that nearly 65% of the heat feedback near the pool center was due to radiation in a 0.3 m heptane fire. In those experiments, however, a thin fuel layer was floated over water, and the fuel was not maintained at a constant level. Corlett and Fu [83] estimated the local radiative heat transfer at several locations on the surface of methyl alcohol and acetone pool fires (0.05m$< D <0.225$m) using a small insulated well filled with fuel, but only a few measurements near the pool center were conducted.

Hamins et al. [81] characterized systematically the heat feedback rate to the surface of 0.30 m pool fires. The radial variation of both the mass vaporization rate and the incident radiative heat flux were measured. Figure 10 shows the absorbed radiative heat flux ($\dot{Q}_{r,abs}''$) normalized by the local net heat flux ($\dot{Q}''$) as a function of location on the surface of 0.30 m pool fires burning toluene, heptane and methyl alcohol. The absorbed radiative flux is the difference between the incident and reflected fluxes. The percentage of absorbed radiative heat feedback integrated over the pool surface was largest for toluene, followed by heptane and methanol as indicated in the figure. In Fig. 10, the difference from a value of 1.0 can be attributed to convection (see Eq. 20). Radiation was found to play an important, if not dominant role, in the heat feedback to 0.30 m pool fires for both luminous and non-luminous flames.

These results imply that the burning rate of luminous pool fires (0.3 m < D < 1 m) may be adequately modeled by a detailed analysis of the local radiative heat transfer at the pool center or any other location on the fuel surface. In such models, neglecting convective heat transfer would introduce some small error (<20%) in the prediction of the fuel burning rate. This error would diminish for large diameter pools (D>1 m), as radiative heat transfer becomes relatively more important.

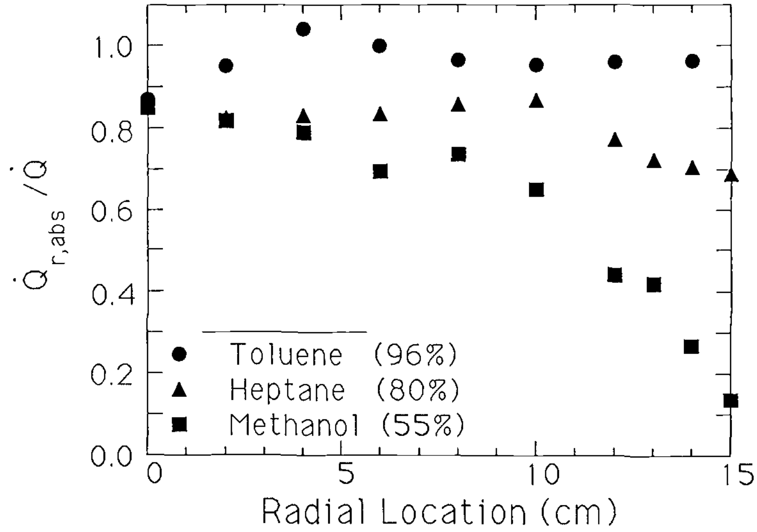


Figure 10 The normalized absorbed radiative heat flux as a function of location on the surface of 0.30 m pool fires. Numbers in parenthesis indicate the percentage of heat feedback due to radiation.

Mass Vaporization Rate

The heat flux to the surface of a pool fire and the mass flux vaporizing from the pool are coupled in a positive feedback loop. The rate of fuel evaporation depends on the rate of heat feedback from the flame to the fuel surface and the mass vaporization rate controls the total heat release rate and thereby the rate of heat feedback.

The steady mass vaporization rate is related to the ratio of heat transferred to the fuel surface ($\dot{Q}_s$) divided by the heat needed to gasify the fuel (H_g). From Eq. 23 with $\dot{Q}_{rerad}$, $\dot{Q}_{loss}$, and $\dot{Q}_{corr}$ considered small compared to the enthalpy of gasification term ($\dot{m}\cdot H_g$):

$$\dot{m} \approx \dot{Q}_s/H_g \tag{25}$$

Equation 25 assumes that heat losses to the burner, re-radiation by the fuel surface and other enthalpy loss terms are small. For a burning liquid pool in steady state, the surface temperature has been measured to be near the fuel boiling point [88]. For a solid fuel, the surface temperature is related to condensed phase degradation kinetics and is often called the pyrolysis temperature [89]. The total mass evaporation rate ($\dot{m}$) is determined by integrating over the pool surface:

$$\dot{m} = 2\pi\cdot\int \dot{m}''(r)\cdot r\cdot dr \tag{26}$$

where $\dot{m}''(r)$ ($kg/m^2\cdot s$) is the local mass vaporization rate of fuel. The average mass vaporization flux $\dot{m}''$ is related to the fuel burning rate (v), which is defined as:

$$v = \dot{m}''/\rho_c \tag{27}$$

and has units of length per unit time, where ρ_c is the density of the condensed phase fuel.

Using Eqs. 10 and 25, Eq. 12 can be expressed as the ratio of the heat of gasification, H_g (kJ/kg) to the ideal heat of combustion, H_c (kJ/kg):

$$\chi_s = H_g/H_c = \dot{Q}_s/\dot{Q} = 1/B \tag{28}$$

χ_s in Eq. 28 is the reciprocal of the diffusive transfer number, the B number, as cited in the literature [76,90]. The value of χ_s is independent of the mass vaporization rate and depends mainly on intrinsic properties of the fuel. Table 1 shows that χ_s can vary by a factor of five or more among some common liquid fuels.

Compiling data for a very large number of fuels, Babrauskas [65] showed that the mass vaporization flux ($\dot{m}''$) obtains an asymptotic limit for large burner diameters. The pool diameter for which the limit was obtained, differed from fuel to fuel, but was typically on the order of

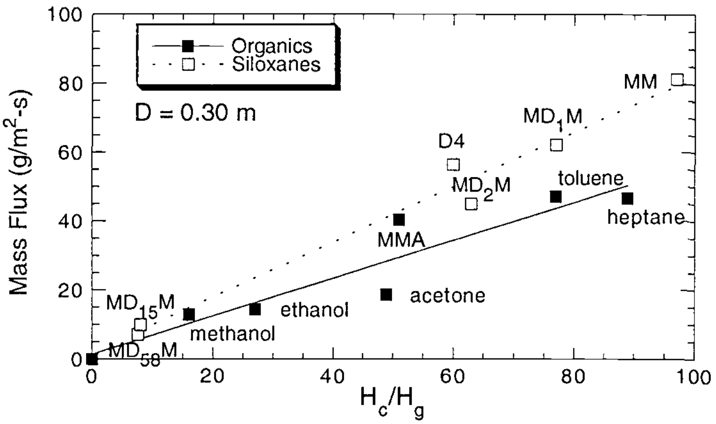


Figure 11 The measured fuel mass flux as a function of the fuel B number for a number of hydrocarbons and siloxanes burning in a 0.3 m burner.

a few meters for hydrocarbon fuels. Burgess and Hertzburg [76] showed that a plot of $\dot{m}''$ for hydrocarbons for large pool diameters was well correlated by the B number (χ_s^{-1}). It is of interest to consider the B number correlation in terms of (1) intermediate sized pool fires and (2) non-hydrocarbon fuels. Polydimethylsiloxanes (PDMS or siloxanes) are industrial fluids used in a wide range of applications. A combustion product of these fluids is SiO_2 particles which significantly impacts the radiation characteristics of the fires. Figure 11 shows the measured mass flux as a function of fuel B number ($= \chi_s^{-1}$) for a number of hydrocarbons and siloxanes burning in a 0.3 m pool [64]. Both, the siloxanes and the hydrocarbons are fairly well correlated by the B number. Figure 11 shows that the smaller oligomeric siloxane chains (MM, MD_1M, MD_2M and D4) burn much faster than the larger polymeric siloxanes ($MD_{15}M$ and $MD_{58}M$). In an analogous fashion, the hydrocarbons (heptane and toluene) burn faster than the alcohols. Plots similar to Fig. 11 can be constructed for burning hydrocarbons in a series of pool diameters. Figure 12 is a plot of the ratio of the fuel mass flux to the fuel B number ($\dot{m}''/B$) as a function of pool diameter for hydrocarbon fuels. A similar correlation could be developed for the siloxane fluids and plotted in Fig. 12. These results can be used to estimate the mass vaporization rate of typical hydrocarbon fuels for any burner diameter, assuming quiescent, freely burning conditions and that the fuel B number is known. Not surprisingly, the shape of the function in Fig. 12 is highly similar to the shape of a plot of the mass flux as a function of pool diameter for a fuel like toluene. Indeed, Fig. 12 is based on mass flux measurements for toluene and a number of other fuels. In addition, the correlation is limited to hydrocarbon fuels and will not predict mass evaporation rates for fuels with little tendency to form soot, such as the alcohols, methanol and ethanol. For these fuels $\dot{m}'' \approx$ constant, independent of pool diameter.

Vaporization Rate Models

Because of the complexities associated with heat and mass transfer, and gas phase kinetics in a turbulent fire, it is not currently possible to predict fuel vaporization rates from detailed solution of the conservation equations without resorting to empirical shortcuts. Thus, semi-empirical models of varying complexity have been developed, exploiting our knowledge of fluid dynamics, chemistry, and heat transfer in reacting systems. In general, the current models can be divided into global models and field models. Both types contain a large number of interacting submodels.

Global models often assign one or several zones of constant properties such as temperature or species concentrations. Transport is ignored. A mean beam length radiation submodel is often used to predict radiative transfer to the fuel surface [6,7,75]. The mean beam length is related to the flame shape. For small Froude numbers with a cylindrical flame shape, the mean beam length is related to the pool diameter and the flame height. Hayasaka and Koseki [91] used a mean beam length model with global flame properties and compared their predictions with measured burning rates for pools up to 10 m in diameter. Their model, however, has not been tested on fuels other than kerosene. Modak and Croce [84] calculated the radiative heat flux from the flame to a surface element on a burning pool (0.18 m) of PMMA in terms of an empirical time-averaged flame shape, an effective radiation temperature, and a mean gray-body absorption-emission coefficient. These parameters were all independently measured whereas convection was assumed to be negligible. Orloff and de Ris [6,7] represented the fire as a time averaged volume of constant property gases. Their measured radiative heat loss fraction (χ_r) was used to estimate a global absorption-emission coefficient. Measured flame shapes were used to calculate a mean beam length and convective heat feedback was estimated from experiments on a water cooled gas burner. The flame temperature was taken as a constant for all fuel types. Model predictions were compared to measurements for pools burning liquid methanol and solid thermoplastics. Unfortunately, the efficacy of this particular approach depends on knowledge of χ_r which varies significantly as a function of pool diameter and mass flow rate, as seen in Figs. 5, 7, and 8. Global models are also sensitive to total heat release, which depends on the combustion efficiency, χ_a, through Eq. 9. In addition, χ_a varies significantly as a function of pool diameter and mass flow (see Fig. 7). The global model of Orloff and de Ris [6,7] provides burning rate predictions to within a factor of 2 to 3 from experimental results, which may be the best that can be expected using a global approach. It remains unlikely that global models will be able to accurately predict mass vaporization rates for a variety of fuels, over a wide range of pool diameters.

Field models are much more detailed than global models [92]. Rather than one or several zones, these models endeavor to spatially resolve details of the fire structure. Combustion field models are related to the subject known as Computational Fluid Dynamics which is widely used in aerodynamic design. These models typically utilize the k-ε strategy for modeling turbulent transport, which treats turbulence by "time-averaging". This smears-out the transient large scale cyclical structures in the flame which were described in Section 1 [93]. A number of key parameters necessary for accurate k-ε modeling have not been empirically determined for general use and particularly for use in pool fires [94,95]. These parameters, such as the initial turbulence intensity, have a strong impact on the calculated temperature and velocity fields [46].

The key to prediction of mass vaporization rates is proper modeling of radiative transfer to the fuel surface, which is the dominant heat transfer mode for large diameter pool fires. This implies that the time varying distribution of temperature and soot volume fraction must be modeled with some accuracy, especially near the fuel surface. Field models incorporating realistic chemistry (e.g. including the intermediate species, carbon monoxide and molecular hydrogen) have reported physically reasonable calculated flame temperatures [93,96].

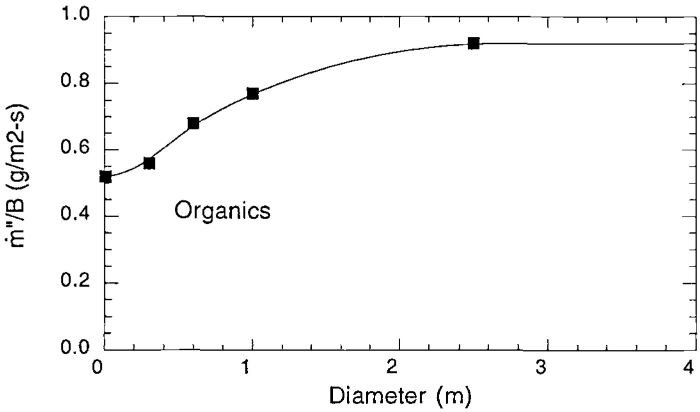


Figure 12 The ratio of the fuel mass flux to the fuel B number ($\dot{m}''/B$) as a function of pool diameter for hydrocarbon fires.

More difficult will be estimation of the soot volume fraction. Even for simple laminar flames, prediction of the soot volume fraction distribution from fundamental kinetics and reduced chemical models has been a challenging problem [97,98]. Only recently has some success been obtained for simple fuels [99].

Recent models using Lagrangian simulations of particle and thermal element trajectories in isothermal plumes [100] and jet flames [101], in conjunction with solutions of the energy and species conservation equations inside each of the reacting thermal elements [102] may provide a reasonable approach for predicting the soot and temperature distributions in pool fires. Simulations of radiative transfer could then determine radiative flux to targets internal or external to the fire [49,103]. Both zone and field models continue to be developed. It is hoped that within the near future these models will provide a basis for prediction of pool fire vaporization rates for varying scale and fuel type. However, much work remains to be completed.

ACKNOWLEDGEMENTS

The authors are very grateful to Professor Jay Gore, Michael Klassen, and Yudaya Sivathanu of Purdue University, Mun Choi and Ishwar Puri of the University of Illinois at Chicago, Katsu Konishi of the Saitama Institute of Technology, and Howard Baum, Paul Borthwick, Andrew Hubbard, Kevin McGrattan, Roy McLane, Holly Rushmeier and John Yang of NIST for technical assistance and many helpful discussions.

REFERENCES

[1] Hall, A.R., Oxidation and Combustion Reviews, **6**, 169 (1973).

[2] Blinov, V.I. and Khudyakov, G.N. (1961). Diffusion Burning of Liquids, Izdatel'stvo Akademii Nauk SSSR, Moscow. English Translation, U.S. Army Engineering Research and Development Laboratories, Information Resources Branch, Translation Analysis Section, Fort Belvoir, VI, No. T-1490a-c.

[3] Bouhafid, A., Vantelon, J.P., Souil, J.M., Bosseboeuf, G., and Rongere, F.X., Fire Safety Journal ,**15**, 367 (1989).

[4] Smith, D.A. and Cox, G., Combust. Flame, **91**, 226 (1992).

[5] Bouhafid, A., Vantelon, J.P., Joulain, P., and Fernandez-Pello, A.C., Twenty-Second Symp. (Int.) on Combust., p. 1291, The Combustion Institute, 1992.

[6] Orloff, L. and de Ris, J., Nineteenth Symp. (Int.) Combust., The Combustion Institute, Pittsburgh, PA, p. 885, 1982.

[7] Orloff, L. and de Ris, J., Froude modeling of pool fires. Factory Mutual Technical Report No. OHON 3.BU RC81-BT-9, Factory Mutual Research, Norwood, MA, 1983.

[8] Beyler, C.L., Ph.D. Dissertation, Harvard University, 1985.

[9] Gengembre, E., Cambray, P., Karmed, D., and Bellet, J.C., Combust. Sci. Tech., **41**, 55 (1984).

[10] Detriche, Ph., and Lanore, J.C., Fire Tech., **16**, 204 (1980).

[11] McCamy, C.S., Paper No. 2678, J. Res. Natl. Bureau of Standards, 293 (1956).

[12] Byram, G.M. and Nelson, R.M., Fire Tech., **6**, 102 (1970).

[13] Portscht, R., Combust. Sci. Tech., **10**, 73 (1975).

[14] McCaffrey, B.J., National Bureau of Standards Internal Report, NBSIR Number 79-1910, 1979.

[15] Baum, H.R. and McCaffrey, B.F., Fire Safety Science-Proceedings of the Second International Symposium. p. 129, 1989.

[16] Weckman, E.J. and Sobiesiak, A., Twenty-Second Symp. (Int.) Combust., The Combustion Institute, p. 1299, 1988.

[17] Zukoski, E.E., Cetegen, B.M. and Kubota, T., Twentieth Symp. (Int.) Combust., The Combustion Institute, p. 361, 1984.

[18] Schonbucher, A., Arnold, B., Banhardt, K., Bieller, V., Kasper, H., Kaufmann, M., Lucas, R., and Schiess, N., Twenty-First Symp. (Int.) on Combust., p. 83, The Combustion Institute, 1986.

[19] Beyler, C.L., Fire Safety J., **11**, 53 (1986).

[20] Sibulkin, M., and Hansen, A.G., Combust. Sci. Tech., **10**, 85 (1975).

[22] Hagglund, B., Fire Res. and Dev. News of Swedish Fire Protection Agency, FoU-Brand **1**, 18 (1977).

[23] Brotz, W., Schonbucher, A., Banhardt, V., and Schiess, N., Ber. Bunsenges. Phys. Chem., **87**, 997 (1983).

[24] Chamberlin, D.S., and Rose, A., The First Symp. (Int.) on Combust., p. 27, The Combustion Institute, 1965.

[25] Barr, J., Fourth Symp. (Int.) on Combust., p. 765, The Williams and Wilkins Co., 1953.

[26] Lamprecht, I., and Schaarschmidt, B., Nature, **240**, 445 (1972).

[27] Pagni, P.J., ASME Paper Number 89-WA/FE-5, p. 26, 1989.

[28] Hamins, A., Yang, J., and Kashiwagi, T., Twenty-Fourth Symp. (Int.) on Combust., p. 1695, The Combustion Institute, (1992).

[29] Chen, L.D., Seaba, J.P., Roquemore, W.M. and Goss, L.P., Twenty-Second Symp. (Int.) on Combust., p. 677, The Combustion Institute, 1988.

[30] Buckmaster, J. and Peters, N., Twenty-First Symp. (Int.) on Combust., p. 1829, The Combustion Institute, 1986.

[31] Bejan, A., J. Heat Transfer, **113**, 261 (1991).

[32] Hertzberg, M., Cashdollar, K., Litton , C., and Burgess, D., The Diffusion Flame in Free Convection, U.S. Bureau of Mines, Report Number 8263, 1978.

[33] Emori, R.I. and Saito, K., Combust. Sci. Tech., **31**, 217 (1983).

[34] Ghoniem, A.F., Personal Communication, Massachusetts Institute of Technology, 1994.

[35] Putnam, A.A., Nature, **192**, 1277 (1961).

[36] Deal, S., Technical Reference Guide for FPETool Version 3.2, National Institute of Standards and Technology report NISTIR 5486, 1994.

[37] McCaffrey, B.J., Flame Height, Chapter 1-18, SFPE Handbook of Fire Protection Engineering, (Ed: P.J. DiNenno), 1988.

[38] Heskestad, G., Fire Safety J. **5**, 103 (1983).

[39] Hasemi, Y., and Nishihata, M., Fire Sci. Tech., **7**, 27 (1987).

[40] Hamins, A., Borthwick, P., Konishi, K., and Kashiwagi, T., Flame Heights of Gaseous Pool Fires, in preparation, (1995).

[41] Heskestad, G., The Eightennth Symp. (Int.) on Combust., The Combustion Institute, p. 951-960, 1981.

[42] Tewarson, A., Smoke Point Height and Fire Properties of Materials, NIST-GCR-88-555, 1988.National Institute of Standards and Technology, available from National Technical Information Service, Springfield, VA 22161, USA.

[43] Delichatsios, M.A., Orloff, L., Delichatsios, M.M., Combust. Sci. Tech., **84**, 199 (1992).

[44] Grosshandler, W.L., RADCAL: A Narrow-Band Model for Radiation Calculations in a Combustion Environment, National Institute of Standards and Technology (NIST) Technical Note 1402, Government Printing Office, Washington, D.C., 1993.

[45] Lee, K.Y., Cha, D.J., Hamins, A., and Puri, I.K., "Heat Release Mechanisms in Inhibited Laminar Counterflow Flames", Combust. Flame, submitted, (1995).

[46] Crauford, N.L., Liew, S.K., and Moss, J.B., Combust. Flame **61**, 269 (1986).

[47] Walker, N.L. and Moss, J.B., Combust. Sci. Tech. **41**, 43 (1984).

[48] Vachon, M. and Champion, M., Combust. Flame **63**, 269 (1986).

[49] Choi, M., Hamins, A., Rushmeier, H., Kashiwagi, T., The Twenty-Fifth Symp. (Int.) on Combust., The Combustion Institute, p. 1471-1480, 1994.

[50] McCaffrey, B.J., Combust. Flame **52**, 149 (1983).

[51] Klassen, M., Sivathanu, Y.R., and Gore, J.P., Combust. Flame, **90**, 34 (1992).

[52] Bilger, R.W., Combust. Flame, **30**, 277 (1977).

[53] Sivathanu, Y. and Faeth, G.M., Combust. Flame, **8231**, 211 (1990).

[54] Jeng, S.M. and Faeth, G.M., ASME Journal of Heat Transfer, **106**, 886 (1984).

[55] Gore, J.P., Ph.D. dissertation, The Pennsylvania State University (1986).

[56] Hamins, A., Kashiwagi, T., Gore, J., and Klassen, M., Combust. Flame, **86**, 223 (1991).

[57] Klassen, M. and Hamins, A., Unpublished Results, (1991).

[58] Koseki, H., Fire Tech. **25**, 241 (1989).

[59] Koseki, H., and Hayasaka, H., Journal of Fire Science **7**, 237 (1989).

[60] Koseki, H., and Yumoto, T., Fire Tech. **24**, 33 (1988).

[61] Yang, J., Hamins, A., and Kashiwagi, T., Combust. Sci. Tech., **96**, 183, 1994.

[62] McCaffrey, B.J., Some measurements of the radiative power output of diffusion flames, Western States Section Meeting, The Combustion Institute, Paper # WSS/CI 81-15 (1981).

[63] Modak, A.T., Factory Mutual Research Corporation, Norwood Massachusetts, Technical Report Serial No. 22361-5, RC-B-67 (1976).

[64] Buch, R., Hamins, A., Borthwick, P., Konishi, K., and Kashiwagi, T., Pool Burning of Siloxane Fluids, in preparation, (1995).

[65] Babrauskas, V., Fire Tech, **19**, 251 (1983).

[66] Mudan, K.S. and Croce, P.A., Fire Hazard Calculations for Large Open Hydrocarbon Fires, Chapter 2-4, SFPE Handbook of Fire Protection Engineering, (Ed: P.J. DiNenno), 1988.

[67] Modak, A., Fire Safety J. **3**, 177 (1981).

[68] Lee, K.Y., Zhong, Z.Y., Tien, C.L., Twentieth Symp. (Int.) on Combust., p. 1629, The Combustion Institute, 1984.

[69] Kung and Stavriandus, Nineteenth Symp. (Int.) on Combust., p. 905, The Combustion Institute, 1982.

[70] American Society of Testing and Materials, D-1322, Standard Test Method for Smoke Points of Aviation Turbine Fuels, 1975, (Re-approved 1980).

[71] Nakakuki, A., Combust. Flame **96**, 311 (1994).

[72] Arpaci, V.S. and Selamet, A., Combust. Flame, **86**, 203 (1991).

[73] de Ris, J. and Orloff, L., Combust. Flame, **18**, 381 (1972).

[74] Corlett, R.C., Combust. Flame, **14**, 351 (1970).

[75] Hottel, H.C., Fire Research Abstracts Reviews, **1**, 41 (1959).

[76] Burgess, D. and Hertzberg, M., In Heat Transfer in Flames, (Eds.: N.H. Afgan and J.M. Beers), John Wiley & Sons, New York, NY, Chapter 27, 1974.

[77] Orloff, L., Eighteenth Symp. (Int.) Combust., The Combustion Institute, Pittsburgh, PA, p. 549, 1981.

[78] Mudan, K.S., Prog. Energy Combust. Sci., **10**, 59, (1984).

[79] de Ris, J., Seventeenth Symp. (Int.) on Combust., p. 1003, The Combustion Institute, (1979).

[80] Blinov, V.I. and Khudyakov, G.N., Dokl. Acac. Nauk SSSR **117**, 1094 (1957).

[81] Hamins, A., Klassen, M., Gore, J., Fischer, S., and Kashiwagi, T., Combust. Sci. Tech., **96**, 37 (1994).

[82] Akita, K. and Yumoto, T., Tenth Symposium (Int.) on Combust, p. 943, The Combustion Institute, 1965.

[83] Corlett, R.C. and Fu, T.M., Pyrodynamics, **4**, 253 (1966).

[84] Modak, A. and Croce, P.A., Combust. Flame **30**, 251 (1977).

[85] Yumoto, T., Combust. Flame **17**, 108 (1971).

[86] Shinotake, A., S. Koda and K. Akita, Combust. Sci. Tech., **43**, 85 (1985).

[87] Alger, R.S., Corlett, R.C., Gordon, A.S., and Williams, F.A., Fire Tech **15**, 142 (1979).

[88] Spalding, D.B., Fourth Symp. (Int.) on Combust., p. 1847, The Combustion Institute, 1952.

[89] Kanury, A.M., Introduction to Combustion Phenomena, Chapter 4, Gordon and Breach Science Publishers, Langhorne, PA, 1975.

[90] Spalding, D.B., Some Fundamentals of Combustion, Batterworth, London, England, 1955.

[91] Hayasaka, H., and Koseki, H., Estimation of thermal radiation from large pool fires. 11th Joint Meeting of the UJNR Panel on Fire Research and Safety, Berkeley, CA, 1989.

[92] Cox, G., In Fire Science in Technology, (Eds. F. Weichung and F. Zhuman), International Academic Publishers, Hefei, China, p. 50, 1992.

[93] Nicolette, V.F., Tieszen, S.R., Gritzo, L.A., Moya, J.L.,Cornell, G., Annual Conference on Fire Research, Gaithersburg, MD, October, 1994, National Institute of Standards and Technology internal report #NISTIR 5499, p.83, 1994.

[94] Bilger, R.W., Fire Safety Science-Proceedings of the Fourth International Symposium. p. 95, 1994.

[95] Adiga, K.C., Raemaker, D.E., Tatem, P.A., and Williams, F.W., Fire 6Safety J., **14**, 241 (1989).

[96] Holen, J., Brostrom, M., and Magnussen, B.F., Twenty-Third Symp. (Int.) on Combust., p. 1677, The Combustion Institute, 1990.

[97] Kent, J.H. and Honnery, D.R., Combust. Flame, **79**, 287 (1990).

[98] Kennedy, I. M. and Kollman, W., Combust. Flame, **81**, 73 (1990).

[99] Leung, K.M., Linstadt, R.P. and Jones, W.P., Combust. Flame, **87**, 289 (1991).

[100] Baum, H.R., Ezekoye, O.A., McGrattan, K.B., and Rehm, R.G., Theoret. Comput. Fluid Dynamics, **6**, 125 (1994).

[101] Jang, J.H., Sivathanu, Y.R., and Gore, J.P., Heat and Mass Transfer in Fire and Combusting Systems, **HTD-223**, 81 (1992).

[102] Zhang, Z, and Ezekoye, O.A., Computational Study of State Relationships for Acetylene-Air Diffusion Flames with Soot Radiation, to be presented at the National Heat Transfer Conference, Portland, OR, 1995.

[103] Klassen, M., Gore, J.P., Sivathanu, Y.R., Hamins, A., and Kashiwagi, T., Twenty-Fourth Symp. (Int.) on Combust., p. 1713, The Combustion Institute, 1992.

George E. Totten[1] and Glenn M. Webster[1]

FIRE RESISTANCE TESTING PROCEDURES: A REVIEW AND ANALYSIS

REFERENCE: Totten, G. E. and Webster, G. M., ''**Fire Resistance Testing Procedures: A Review and Analysis,**'' Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jurgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: Numerous tests have been developed to measure fire resistance of industrial fluids. However, few of these tests have been adopted as industry or national standards. Furthermore, little reference information is available illustrating how these tests correlate with specific fire-risk situations. This paper will provide an overview of the various tests that have been reported to quantify the relative fire-resistance of industrial fluids. This information will provide guidance in the future development of fire-resistance specifications for various types of industrial fluids.

KEYWORDS: fire resistance, flammability testing, hydraulic fluids, fire resistant hydraulic fluids, spray flammability, fire resistance specifications

INTRODUCTION

Considerable research has been performed to develop test methods that reproducibly simulate actual hydraulic fluid ignition hazards. Many factors must be taken into account when identifying a test procedure that will accurately model hydraulic fluid flammability: type of flame or source of ignition, amount of available energy in relation to the amount of fluid, and the physical state of the fluid [1]. There are many other factors that contribute to the flammability tendency of a hydraulic fluid, however, the selection of the appropriate test to model fire resistance is usually mandated by either the government (Mine Safety and Health Administration - MSHA), insurance industry (Factory Mutual Research Corporation), or labor unions.

Hydraulic fluid fires have been disasterous with respect to loss of buildings, equipment and, most of all, human lives. Many of these fire losses have been detailed in the literature [2 - 6].

A deficiency in available fire-resistance tests to model fire potential of various applications led to the formation of section N.06 of the ASTM D.02 subcommittee. The chairman of this study group made the following statement during a 1966 symposium on hydraulic fluids which was held to assess fire-safety testing methods available at that time.

---

[1] Union Carbide Corporation, 777 Old Saw Mill River Road, Tarrytown, NY, 10591

"A major problem confronting the industry today is the lack of test standardization and interpretation of test results to adequately measure fire resistance of fluids. Cooperative effort is recommended."[7] Although considerable test development work has subsequently been performed, completed national standards reflecting many of these developments still have not been published.

The objective of this paper is to review the test procedures currently used to evaluate the flammability properties of hydraulic fluids with respect to ignition sources being modeled.

DISCUSSION

A. Modes of Hydraulic Fluid Ignition

Hydraulic fluid ignition often occurs when a leak or break in the hydraulic system, usually operating at high pressures, results in a spray, stream, or mist of hydraulic fluid. The fluid may then ignite if it encounters a source of ignition such as an electrical spark, flame, or hot surface [8].

A hydraulic leak or spill may wet a hot surface or form a pool, which may then be ignited. During ignition, a distillation process occurs which separates the hydraulic fluid into several components. One or more of these volatile components may be easily ignited by a spark or flame.

Porous or wick-like material, such as pipe insulation or even coal during mining operations, may become soaked with hydraulic fluid and may slowly oxidize forming peroxide by-products, which may undergo subsequent spontaneous combustion [8].

Table 1 summarizes many fire hazard conditions that should be considered when selecting and installing a hydraulic system [1].

TABLE 1

Hydraulic Fluid Fire Conditions

Source of Ignition	Fluid Condition	Environment
Flame	Pool or Puddle	Air Temperature
Spark	Spray-Stream or Atomized	Air Current
Hot Metal Surface	Vaporized	Equipment Location
Electrical Contact	Wicking	–

Factors to consider when selecting a fire-resistant hydraulic fluid are [1]:

- Proximity of the fire hazard to the hydraulic equipment,
- Availability of fire-resistant fluids,
- Fluid properties, and
- Required equipment design changes.

It is important to note that all fire-resistant fluids fall into two basic categories: those that derive their fire resistance from the presence of water and those that demonstrate fire resistant qualities by their chemical composition or molecular structure [9].

B. Fluid Classification

The general designation for hydraulic fluids is "HF" [10]. Fire-resistant hydraulic fluids are further classified by composition according to ISO 6734/4 (Lubricants, industrial oils, and related products (Class L) - Classification - Part 4: Family H - Hydraulic systems) as shown in Table 2.

Table 2

ISO Classification of Fire-Resistant Hydraulic Fluids

Fluid Classification	Fluid Description
HFAE	oil-in-water emulsions, typically more than 80% water content
HFAS	chemical solutions in water, typically more than 80% water content
HFB	water-in-oil emulsions
HFC	water/polymer solutions, typically less than 80% water
HFDR	water free synthetic fluids consisting of phosphate esters
HFDS	water free synthetic fluids consisting of chlorinated hydrocarbon
HFDT	water free synthetic fluids consisting of mixtures of HFDR and HFDS
HFDN	water free synthetic fluids of other compositions than HFD-R or HRD-S or HFD-T

One of the most commonly used fluid flammability testing procedures employs a combination of hot-channel and spray-flammability tests that are specified by the Factory Mutual Research Corporation [11]. To pass the Factory Mutual spray flammability test, the resulting flaming fluid need only be self-extinguished within 5 s [11]. Factory Mutual Research Corporation has three classifications for fire-resistant hydraulic fluids are shown in Table 3.

TABLE 3

Factory Mutual Corporation Classification of Hydraulic Fluids

Group I	Water-Glycol fluids with additives
Group II	Synthetic fluids including phosphate-ester, polyol-ester, and halogenated hydrocarbon fluids
Group III	Water-in-oil and oil-in-water emulsions.

In reference to the above "HF" classification scheme, Group I fluids correspond to HFC, Group II fluids correspond to HFD(R,S,T,N), and Group III fluids correspond to HFAE, HFAS, and HFB.

C. Fire-Resistance Testing Strategies

One of the greatest concerns in fire-resistance testing is the selection of a procedure that adequately models the application of interest. Since each application has its own unique exposure, such as pool or spray, and ignition conditions, such as hot metal surface and open flame, multiple tests are typically conducted [2].

Two fundamental parameters should be considered when selecting a test to model the application:

(1.) ignition resistance, and
(2.) flame propagation [12].

These two parameters model fluid ignition and the propensity of the fluid to continue to burn once ignited. The experimental strategy is two fold. First, the test should provide information regarding resistance to ignition. Second, if ignited, flame propagation must be considered.

D. Fluid Flammability Tests

1. Fluid Volatility Characterization

This section will summarize testing procedures normally required to model flammability potential and describe experimental procedures to quantify fluid flammability properties.

a. Open-Cup Flash Point and Fire Point--The relative fire resistance of nonaqueous hydraulic fluids may be characterized by their flash and fire points. These procedures are described in ASTM D 92-90 (Standard Test Method for Flash and Fire Points by Cleveland Open Cup) [12,13,14]. The flash point and fire point are determined by passing a flame over the surface of the fluid at constant time intervals with uniform temperature rise. The flash point is the temperature where the vapors above the surface ignite. The fire point is the temperature where the fluid itself ignites and burns for at least 5 s. These results are dependent primarily on fluid chemistry and volatility.

Increasing flash points and fire points are indicative of increasing fire-resistance, particularly in applications where high-temperature fluid volatility is important such as required in many aircraft applications. This test is inappropriate for aqueous fire-resistant fluids since it is difficult to assess the proper heat-up times. This leads to non-reproducible data because of variable evaporation rates. It is also difficult to directly relate the flash and fire point data to specific end-use fire-risk potential.

b. Autoignition Temperature (AIT)--The AIT is determined according to ASTM D 2155-66 (Standard Test Method for Autoignition Temperature of Liquid Petroleum Products) where the fluid is injected via a syringe onto the surface of an Erlenmeyer flask heated in an oven as shown in Fig. 1 [12 - 18]. MacDonald has found that the AIT varies with the size of the Erlenmeyer flask [19]. The AIT measures the geometry-dependent spontaneous ignition temperature of a fluid in air. These measurements are difficult to relate to end-use applications [12].

Another combustion test is "the combustion indicator test". The combustion test, which will not be reviewed in detail here. The combustion test involves the determination of the compression ratio of the fluid in an engine where combustion occurs [20].

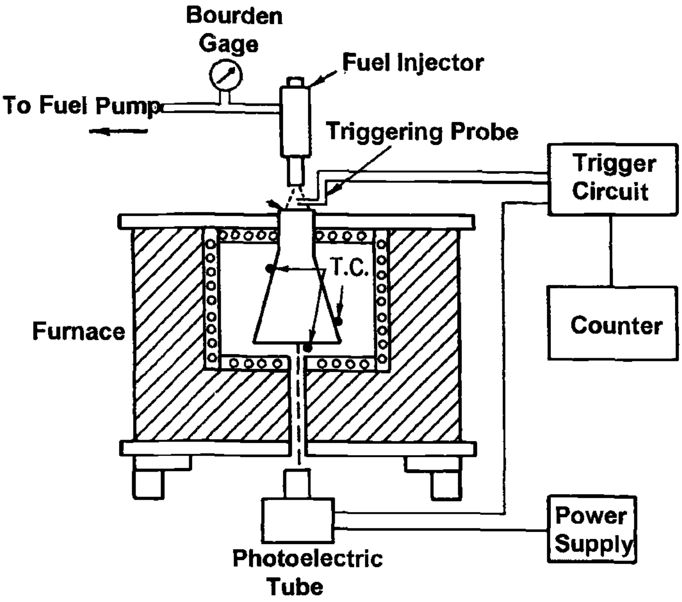


Figure 1 - Illustration of the Autoignition Apparatus

c. Gunfire Resistance-(MIL-H-83282 - Fire Resistant Hydraulic Fluid, Synthetic Hydrocarbon Base, Aircraft, Metric, NATO Code Number H-537) -- This is a specialized ignition test where the heat is provided by incendiary ammunition. This test is performed by firing a 50-caliber armor-piercing incendiary ammunition into aluminum cans partially filled with the fluid to be tested. Five shots are fired, and the number of ignitions and the severity of the fires are reported. Results of a gunfire resistance test reported by Snyder and Krawetz [14] are summarized in Table 4.

TABLE 4
Flammability Characteristics of Current and Developmental Aerospace Hydraulic Fluids

Fluid	Autogenous Ignition Temperature (°C)	Stream Hot-Manifold Ignition Temperature (°C)	Heat of Combustion (Kcal/Kg)	Horizontal Flame Propagation Rate (cm/s)	Gunfire Resistance Number of Fires 5 Shots
MIL-H-5606	232	388	10100	0.733	5
MIL-H-83282	354	322	9800	0.212	1
Phosphate Ester	524	760	7100	0.00[1]	0
Silicate Ester	400	371	8162	0.300	3
Silicone	409	477	5411	0.218	0
Chlorofluorocarbon	630	927	1328	0.00[2]	0
Fluoroalkyl Ether	669	927	989	0.00[2]	0

1. Sample self extinguished (would not stay lighted) on asbestos wire.
2. Sample could not be lighted on asbestos wire.

TABLE 5

Summary of Existing Spray Flammability Test Methods

Test Authority	Ignition Source	Fluid Temperature (°C)	Pressure and Source MPa (PSIG)	Fluid Spray Nozzle	Orifice Diameter	Rated Flow	Distance from ignition m (in)	Failure Criterion or Results Reported As
MSHA	1.Electric Spark 2.Propane Torch 3.Flaming Trough	65 ± 5	1.034 (150) (N_2 Cylinder)	900 Spray	0.635 (0.025)	3.28 gph	.45 (17.7)	Flame not to exceed 6 sec. at 18 in.
Naval Research	Electric Spark	Ambient 15.5 - 26.6	0.17 (25) (N_2 and O_2)	Poasche Model ML-8	--	158 gph	--	Spray Flammability Limit (Minimum $\%O_2$)
AFNOR	A Type REX No. 1 Charledave Torch size 750 tip	65 ± 5	7±0.3 (1015) (N_2 Cylinder)		1.6 to 0.4 with screen (0.063 to 0.016)	--	1.20 m (47.2)	1=no ignition 2=ignites but does not reach screen 3=ignites and reached screen
Factory Mutual	Rotating Propane Torch	40	6.9 (1000) (N_2 Cylinder)	800 Hollow Cone	--	1.50 gph	0.152 and 0.457 (6 and 18)	Flame not to exceed 5 sec. in 10 trials at 6 and 18 in.
NBS/CFR	Kerosene soaked cotton cheesecloth	65	1.034 (150) (N_2 Cylinder)	900 Spray Binks Model F-12-15	0.64 mm (0.025)	3.28 gph	.68 (26.7)	Rated by temperature rise - 204-296oC considered high heat potential
British Coal Board	oxy-acetylene torch with No. 10 nozzle	Water Containing - 65 All Others 85	6.89 (1000) (N_2 Cylinder)	800 Hollow Cone Monarch Manufacturing Type F80	--	2.5 gph	Varies	Length of spray and duration of flame
"New" Factory Mutual	15 kW, 0.14 m diameter propane-air ring burner	60	6.9, 5.2, 3.5, 1.7 (1000,754, 507, 246)	800 Hollow Cone	0.38 (0.015)	1.5 gph	Sprayed through ring burner	Spray Flammability Parameter
Buxton Ease of Stabilization	vertical propane flame	13 - 20	90 ml/min	Spraying Systems Co. twin fluid atomizer nozzle, type 1/4 JBC-12A	--	--	0.0425 (1.673)	Ignitability, Flame length, Smoke Emmisions

2. Calorimetric Procedures

a. Heat of Combustion--Snyder and Krawetz have illustrated the correlation of heat of combustion with the fire resistance of a fluid [14, 15]. The heat of combustion may be determined according to ASTM D 240 (Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimetry). Some illustrative examples for hydraulic fluids used in aerospace applications are shown in Table 4. As expected, fire resistance increases as the heat of combustion decreases. Marzani developed a "static bomb" - type reactor apparatus for evaluating the spontaneous ignition temperature for fluids at elevated pressures [21].

b. Heating Time--The fire resistance of a fluid is reflected by the time required to heat a given volume of fluid to 90°C from ambient temperature and comparing the heating time to a petroleum oil hydraulic fluid and distilled water [17]. The experiment is conducted by heating a given volume of fluid in an insulated, stirred, 2-liter stainless steel beaker equipped with a 56 watt immersion heater and a 76 mm immersion thermometer. Pollack, e.al. reported a heating time of 622 s for a hydrocarbon oil, 923 s for a water-in-oil emulsion and 1815 s for distilled water. These differences in heating times is related to the heat capacity of the fluid. In general, it is desirable to maximize the heating times.

c. Evaporation (Wick) Tests--In industries, such as the mining industry, it is of interest to evaluate the fire-risk potential associated with hydraulic fluid leakage on absorbent material, for example, coal, which would subsequently be exposed to an ignition source [12]. Tests used to model this risk are called "evaporation" or "wick" tests.

There are primarily two evaporation tests that are utilized. One test employs an asbestos tape used as the wick. In most test procedures, a ceramic fiber "tape" has replaced the asbestos [22-24]. The other type of test utilizes a pipe cleaner as the "wick"[12,25,26].

(1.) Asbestos (or Ceramic) Wick Test--The asbestos wick test is conducted by immersing one end of the asbestos (or ceramic) tape in the hydraulic fluid. After equilibration, one end of the wick is ignited and the persistence of the flame after the removal of the ignition source is recorded. This test is primarily a measure the relative ease of hydraulic fluid flammability after it saturates a porous substrate such as pipe insulation, coal, etc.

(2.) "Pipe Cleaner" Wick Test--The pipe cleaner wick test is conducted by soaking a pipe cleaner in the hydraulic fluid and then conditioning at 65°C (150°F) for 2 or 4 h in an oven. The conditioned pipe cleaner is then repeatedly passed through the flame of a bunsen burner until ignition occurs. The number of passes without ignition is recorded [16].

The water content of hydraulic fluids will affect the results of both of the wick tests described above. This is illustrated in Fig. 2 which shows the relationship between flame duration time versus the water content of a water-in-oil emulsion for the asbestos tape test [27].

d. Soaked Cube Flammability Test--The soaked cube flammability test models an exothermic reaction that might occur if a flammable fluid is absorbed into thermal insulation. The fluid is placed in a well that has been drilled into a 1 x 1 x 1 in. (25.4 x 25.4 x 25.4 mm) cube of asbestos-free calcium silicate insulation material (Johns-Manville-12 molded and block 2 in. (50.8 mm) pipe insulation) with a thermocouple mounted 1/8 in.(3.175 mm) below the bottom of the well. The cube is placed into a furnace and the temperature is increased until an exothermic reaction occurs [28]. An illustration of the test block appears in Fig. 3.

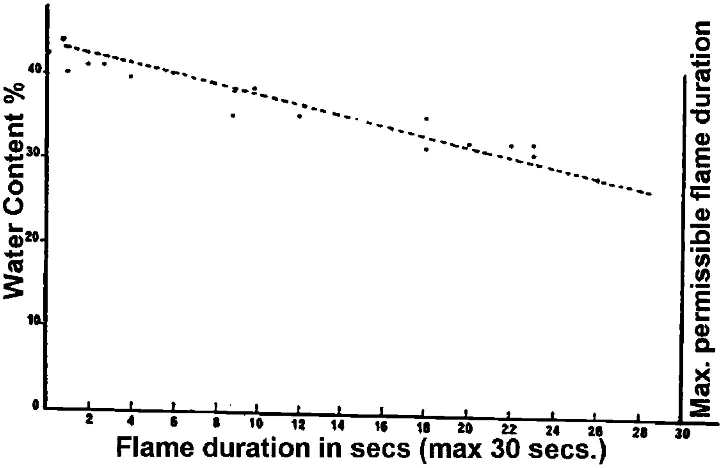


Figure. 2--Relationship between water content and flame duration

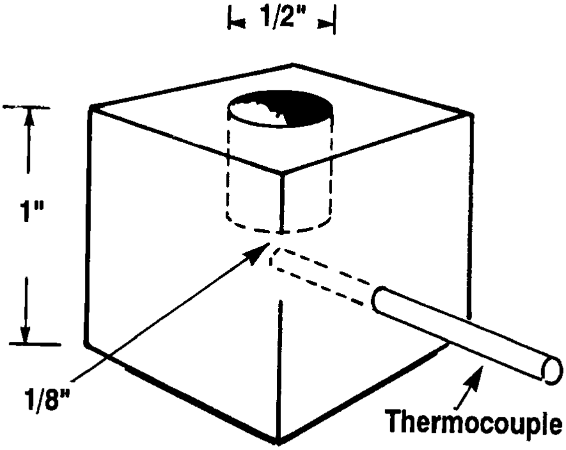


Figure 3--Illustration of the Soaked Cube Flammability Test

3. Flame Propagation

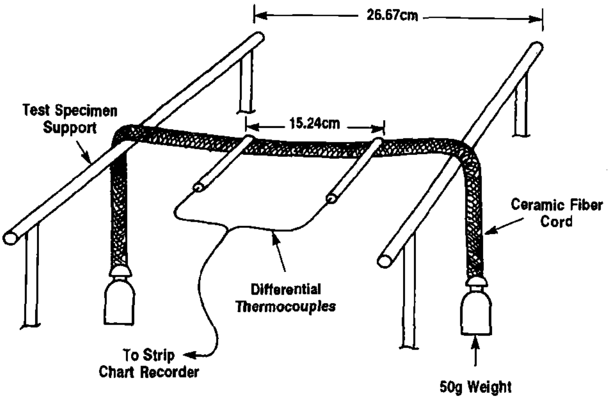
One of the greatest fire-risks of the use of petroleum-based hydraulic fluids upon ignition is flame propagation [1]. Fire-resistant fluids are more difficult to ignite, and they exhibit a reduced tendency for flame propagation. Therefore, it is not only important to measure the fire resistance but also flame propagation. Both properties are typically determined in the hot surface and the spray flammability tests to be discussed subsequently.

a. Linear Flame Propagation Test--Linear flame propagation measures the rate of flame travel on a ceramic fiber test sample presoaked with the hydraulic fluid (ASTM D 5306-92 - Standard Method for Linear Flame Propagation Rate of Lubricating Oils and Hydraulic Fluids). Linear flame propagation rates are determined by placing a 500 mm ceramic string into the fluid to be tested for 60 s. The fluid-saturated ceramic string is then placed on the test apparatus as shown in Fig. 4. Two differential thermocouples are attached to the string 15.24 com apart. One end of the string is ignited and the thermocouples are used to obtain the time required for the flame to propagate from one thermocouple position to the other. The linear flame propagation rate is reported in m/s and is calculated as follows:

$$\text{Linear Flame Propagation Rate} = \frac{dv}{p} \qquad (1)$$

where: d = distance between thermocouples in mm,
v = chart speed in mm/s, and
p = distance measured peak to peak between thermal effects.

Linear flame propagation rates are dependent on the relative flammability or ignitability of the fluid. This test method does not relate to the flammability properties of materials under actual fire-risk conditions. The linear flame propagation test is well suited for polyol esters and phosphate esters. This test is not utilized for volatile water-containing hydraulic fluids such as water-glycols, invert emulsions and high water content hydraulic fluids.



Thermocouple Junctions Are Held 2mm Above Ceramic Fiber Cord

Figure 4--Illustration of the Linear Flame Propagation Apparatus.

4. Hot Surface Ignition Tests

a. "Monsanto" Molten Metal Test -- Monsanto developed a test to evaluate the burning and flame propagation that may occur when a hydraulic fluid is sprayed on molten metal, either zinc at 800° F(427°(C) or aluminum at 1200°F (649°C) [12,29]. Fluid may be poured, sprayed or added dropwise to the molten metal. Burning rates and flame propagation to adjacent fluid wetted areas is determined. This test may be performed with, or without, an external ignition source. An illustration of the Monsanto molten metal test is illustrated in Fig. 5a. The European version of the molten metal test involves pouring of the the hydraulic fluid on to the molten metal as illustrated in Fig. 5b [30]. In either test, while visual differences between the various fire resistant hydraulic fluids were observed, the reproducibility of these tests was not adequate for quantification [30].

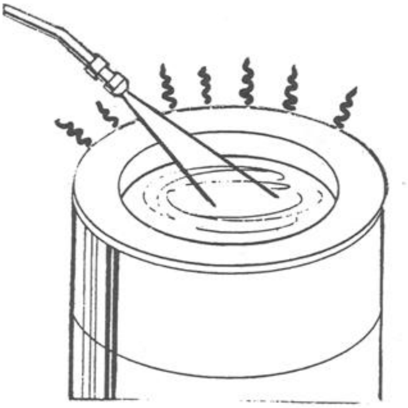


FIG. 5a--Illustration of the Monsanto Molten Metal Test

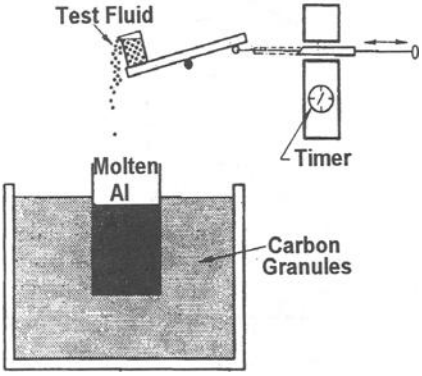


FIG. 5b--Illustration of the European Molten Metal Test

b. Hot Manifold Test -- In hydraulic systems, one of the primary concerns is the potential fire risk that may occur if a line ruptures near a heat source. One of the major tests used to model this situation is the hot manifold test [12,15,31,32]. The hot manifold test models the situation where hydraulic fluid may leak dropwise, or as a stream, directly on to a hot surface. In this test, 10 ml. of the hydraulic fluid is applied dropwise on to the surface of a heated stainless sttel manifold (tube) at 1300°F (704°C). Flashing or burning or burning of the fluid upon contact with the hot tube and flame propagation to the fluid residues that are collected in the bottom of the enclosure is observed. This test was originally of particular interest to the aviation industry [14].

c. Factory Mutual Hot Channel Ignition Test--When a hydraulic hose ruptures, it is more likely to form a spray, which may then contact a hot surface. This condition is modelled by a "hot channel ignition" test [33,34] shown in Fig. 6. Factory Mutual Corporation has developed a test method that has become an accepted for the determination of the response of a fluid to contact with a heated surface [33]. In this test the hydraulic fluid is sprayed onto a steel surface 7 in. (17.78 cm) wide, 27 in. (68.58 cm) long inclined at a 30° angle.

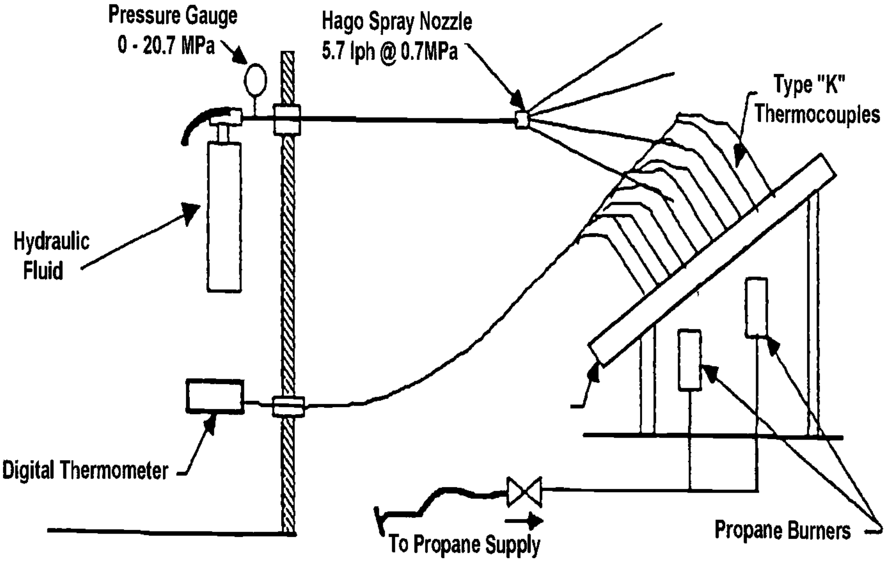
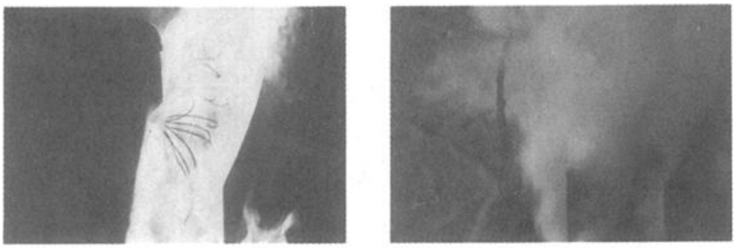


Figure 6--Illustration of the Factory Mutual Hot Channel Ignition Test

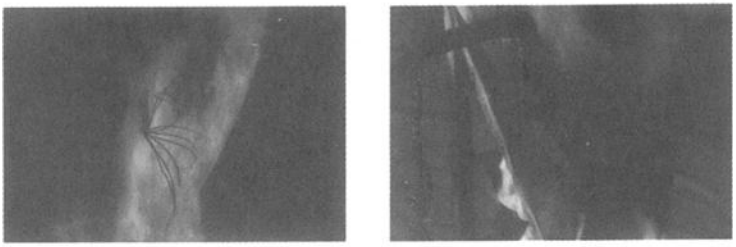
The test is conducted at a minimum temperature of 1300°F (704°C). This temperature is achieved by heating the metal with propane burners from below. The burners are turned off prior to spray application of the fluid onto the hot surface. The fluid is sprayed from a distance of 6 in.(15.24 cm) from the hot surface for 60 s. In order to be considered a "pass" in this test, the flame must not propagate and must not follow the spray source. Although this is an excellent end-use test, it is very difficult to adequately quantify and is reported on a pass/fail basis.

Recently, it was shown that although polyol esters, phosphate esters, and water-glycols all pass the Factory Mutual Hot Channel Ignition test, they all exhibit substantially different flammability properties, which are not indicated by the "pass" notation [35] This is illustrated in Fig. 7. Interestingly, the fire-resistant properties of these fluids were similar to those obtained by the molten metal test [30].



Conventional Hydraulic Oil

Phosphate Ester



Polyol Ester

High-Performance
Thickened Water-Glycol

Figure 7--Hot Channel testing of various hydraulic fluids.

One variant of these tests is to conduct them in a wind tunnel as described by Goodall and Ingle [32]. This work was conducted to model aerospace applications. The result showed that the risk of fire was dependent on the temperature of the critical volume of the fluid, the volume where spontaneous ignition of the fluid will occur, and not on the hot surface temperature.

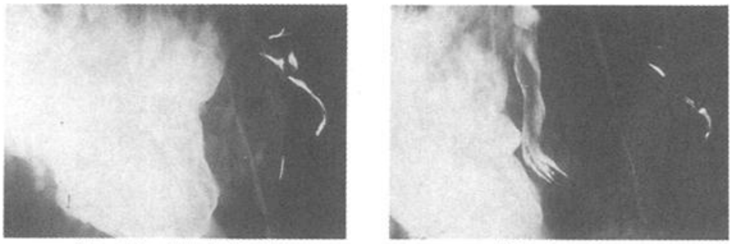
5. Spray Ignition Flammability Tests

Perhaps the most common test used to model the potential fire risk of a hydraulic line break is the spray flammability test. A variation of this test is incorporated in national standards in the United Kingdom, France, and Canada, and is also being incorporated into ISO Specificatioons [10,22,23,36]. Although this test has been accepted as a standard there are some deficiencies such as the pass/fail ranking , and the lack of repeatability when performed at different laboratories using similar test rigs. Although there is no national spray flammability test in the United States, there is a Factory Mutual Research Corporation insurance industry standard [33,34].

a. The ALCOA Low Pressure Spray Flammability Test-- ALCOA developed a relatively low-pressure spray flammability test which is described in ref. [37]. The low pressure spray source used is a Binks Thor No.7 paint spray gun (1.8 cm orifice and pressurized to 0.28 MPa with air) [12,37]. The hydraulic fluid is sprayed over an ignition source such as oil-soaked rags, and the flame characteristics of the flame is visually recorded [12]

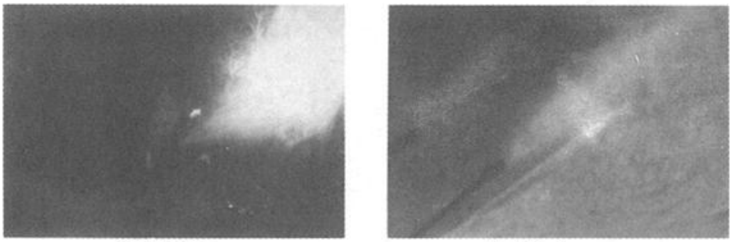
A number of high-pressure spray flammability tests are used throughout the world today. The most common tests are summarized in Table 5, which includes the source of ignition, fluid test temperature, spray pressure, nozzle description, pass/fail criteria, and references for the tests.

b. The Factory Mutual Spray Ignition Flammability Test--The most commonly encountered test in the United States is the Factory Mutual Spray Ignition Flammability Test [33]. Except for mineral oil hydraulic fluid, all of the fire-resistant hydraulic fluids shown in Fig. 8 exhibit very different flammability properties, although all are ratedas a "pass" in the current Factory Mutual Research Corporation spray flammability test [33]. Therefore, there has been an on going effort to identify a spray test that more adequately quantifies flammability risk.



Conventional Hydraulic Oil

Phosphate Ester



Polyol Ester

High-Performance Thickened Water-Glycol

Figure 8--Factory Mutual Spray Flammability testing of hydraulic fluids

E. New Test Development

Two groups have recently reported test procedures that provide this quantification. One group at Factory Mutual Research Corporation developed the "spray flammability parameter" test. The other group located at the University of Manchester in England developed the "stabilized flame release test". Both tests will be reviewed briefly here.

The Factory Mutual spray flammability parameter test is conducted by spraying the fluid vertically upward from an 80° hollow cone nozzle having an exit as shown in Fig. 9. A "spray flammability parameter" (SFP) is calculated and is related to the critical heat flux required for fluid ignition and the chemical heat release rate of the burning process. This is shown by Equation 2 [34,38,39].

$$SFP = \frac{4\,\dot{Q}_{ch}}{(\pi d_s \times \dot{q}''_{cr})} \qquad (2)$$

where $\dot{Q}_{ch}$ is the chemical heat release rate expressed in kW; $\dot{q}''_{cr}$ is the critical heat flux for ignition, below which ignition is not possible, expressed in kW/m^2; $\dot{q}''_{cr}$ and d_s is the equivalent diameter of the nozzle, expressed in meters (nozzle exit diameter multiplied by the square root of the ratio of the fluid density at the test temperature to the ambient air density (kg/m^3).

The $\dot{q}''_{cr}$ term may be related to the fire point temperature, T_{fire} (K) of the fluid as follows:

$$\dot{q}''_{cr} = \alpha\ \sigma\ T^4_{fire} \qquad (3)$$

where α is the fluid surface absorptivity, assumed to be unity, and σ is the Stefan-Boltzmann constant (5.67×10^{-11} kW/m^2 $\times$ K^4).

The successful use of the SFP to characterize and differentiate the potential fire-risk of various hydraulic fluids is shown in Fig. 10. This test is currently being developed into an ASTM test procedure.

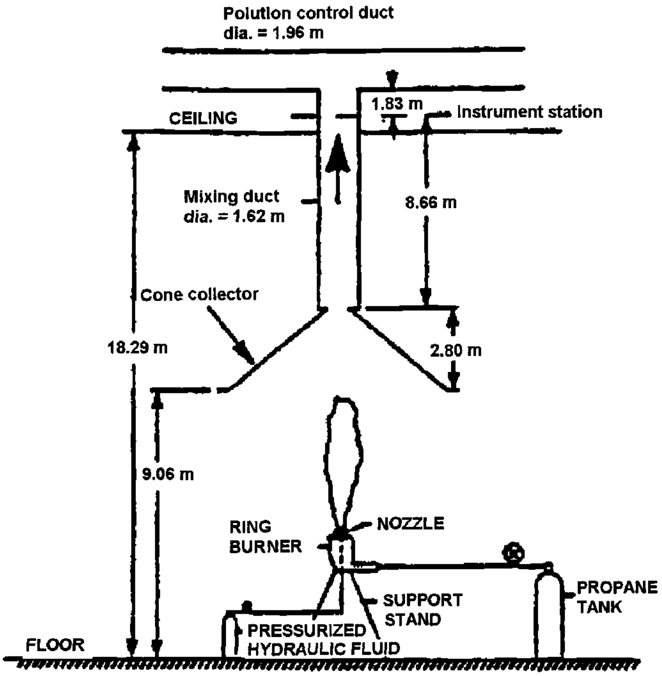
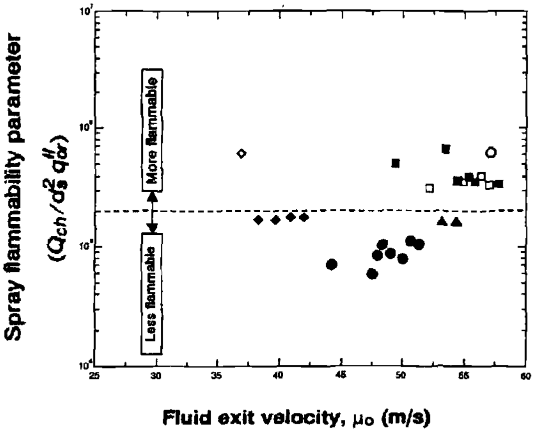


Figure 9--"New" Factory Mutual Spray Flammability Parameter Test



Spray flammability parameter as a function of fluid exit velocity at 8.9 MPa nozzle pressure:
Open symbols — fluids failed in FMRC approval tests
Solid symbols — fluids passed in FMRC approval test:
□ ■ organic/polyol esters;
◇ ◆ phosphate esters;
▲ water-in-oil emulsion;
● polyglycol-in-water;
○ mineral oil.

Figure 10--Use of "SFP" to characterize fluid flammability.

Recent work by Yule and Moodie has been performed using the twin fluid spray apparatus shown in Fig. 11 [40]. A horizontal combustion chamber is utilized. Fluids were ranked by exhaust temperature, flame length, and particulate emissions. The fundamental ranking parameters were the exhaust temperature and "ignitability" which was used to account for both ease of ignition and flame stabilization. Fig. 12 illustrates Yule and Moodie's correlation between heat of combustion and ignitability.

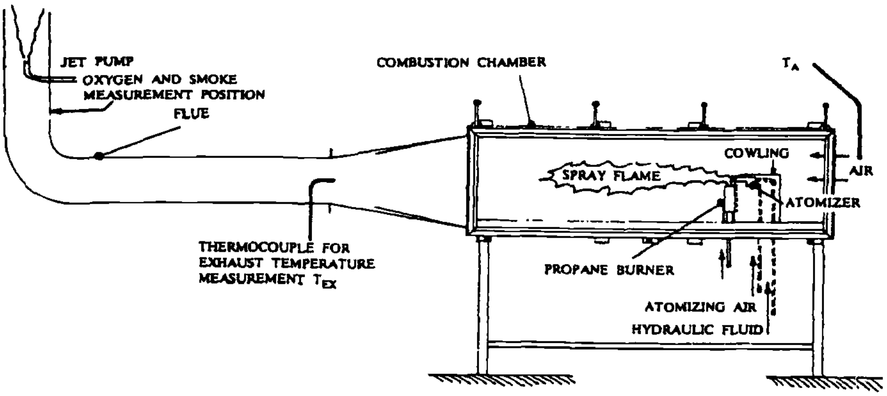


Figure 11--Illustration of the Buxton twin-fluid spray apparatus

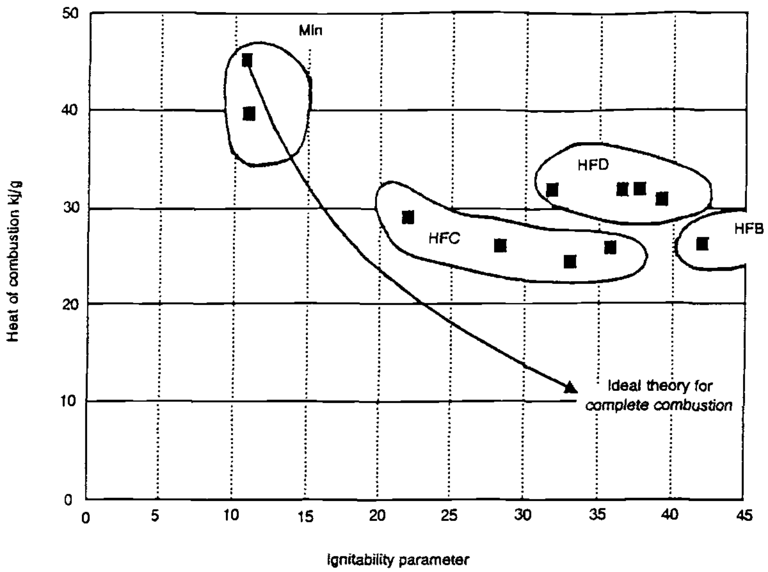


Figure 12--Correlation between ignitability parameter and heat of combustion.

Holmstedt and Persson reported a procedure which multiparametrically ranked the relative fire risk of a hydraulic fluid using heat release rates, heat of combustion, combustion efficiency, generation of carbon monoxide (CO), and smoke [41].

CONCLUSIONS

There are two areas of current activity. One area is the work being conducted by Factory Mutual Corporation on the development of an improved spray flammability test. This "spray flammability parameter" test (described above), although not yet a national standard, will become the predominating test used by hydraulic fluid users in most industries, except mining, in the United States. In Europe, however, it appears that the stabilized heat release test method, which utilizes the ignitability parameter, will dominate.

The second area of current work is the effort underway in Europe to develop ISO standards for testing fire-resistant hydraulic fluids. The status of this work is summarized in Ref. [42]. The optional fire-resistance test methods being recommended are:

- Autogenous Ignition Temperature
- High Pressure Spray
- Manifold Ignition test
- Evaporative Flammability
- Molten Metal or Salt
- Ignition on CFR motor
- Flame Propagation
- Soaked Lagging
- High-Pressure Spray With Screen
- Wick Test (Pipe Cleaner)

It is very difficult to model an industrial application with a single laboratory test. It is prudent to conduct a number of appropriate tests to select the hydraulic fluid that provides the lowest overall risk. This is the direction that the industry is now moving.

REFERENCES

1. R.E. Hatton & L.R. Stark, "Fire-Resistant Hydraulic Fluids - A Guide To Selection And Application"; Chem. Age India, v 28 n 9, Sept. 1977; pp 765-772.

2. J. Mathe, "Fire-Resistant Hydraulic Fluids for the Plastics Industry"; SPE Journal, pp 17-20, (1967).

3. J.M. Sullivan, "Wanted: Cheap, Safe, Enviro-Friendly Fluids", Lubricants World, pp 49-53, Sept. 1992.

4. D.F White, "The Unintentional Ignition of Hydraulic Fluids Inside High Pressure Pneumatic Systems"; A.S.N.E. Journal, pp 405-413, Aug. 1960.

5. S.P Polack, "Progress In Developing Fire-Resistant Hydraulic Fluids"; Iron and Steel Engineer, pp 87-92, Aug. 1958.

6. R. Davis, "Fire-Resistant Hydraulic Fluids"; Quarterly of the NFPA, pp 44-49, July 1959.

7. C.L. Early and R.E. Hatton, "Industrial and ASTM Fluid Fire-Test Programs" in Fire Resistance of Hydraulic Fluids; American Society for Testing and Materials, No. STP 406, Philadelphia, PA, 1966; pp 105-134.

8. J.P. Bai, "Fire Protection Gained From Synthetic Fluids"; The FRH Journal, 1984, Volume 4, No. 2, pp 139-145.

9. A.J. Harrison, "Fire-Resistant Hydraulic Fluids - Their Development and Use In The Mining Industry"; Potash Technology: Mining Processing, Maintenance, Transportation, Occupational Health and Safety, Environment, (Proc. 1st Int. Potash Tech. Conf.) pp 459-465, 1983.

10. Commission of the European Communities, Safety and Health Commission for the Mining and Extractive Industries, Working Party Rescue arrangements, Fires and Underground Combustion, Committee of Experts on Fire-resistant Fluids; Sixth Report on Specifications and Testing Conditions Relating to Fire-Resistant Hydraulic Fluids used for Power Transmission (Hydrostatic and Hydrokinetic) in Mines, Doc. 2786/8/81 E, Luxembourg, 1983.

11. "Approval Standard: Less Hazardous Hydraulic Fluid, Factory Mutual Research Corporation, Norwood, MA, 02062, February 7, 1975.

12. D.F. Smith, Hydraulics & Pneumatics, June, 77, (1970).

13. 5. C.E. Snyder and H. Schwenker, Materials on The Move, 6th National Sampe Tech. Conf. Series, 428,(1974).

14. C.E. Snyder and A.E. Krawetz, J. Soc. of Lubrication Engineers, December, 705, (1981).

15. L. Parts, "Assessment of Flammability of Aircraft Hydraulic Fluids", Technical Report, AFAPL-TR-79-2055, September 30, (1978).

16. J.J. Loftus, "An Assessment of Three Different Fire-Resistant Tests For Hydraulic Fluids", NBSIR 81-2395, October, (1981).

17. S.P. Pollack, A.F. Smith and H.F. Barthe, "Recent Developments in Fire-Resistant Hydraulic Fluids for Underground Use", IC Bureau of Mines Circular 8043, (1961).

18. "Determination of Ignition Temperature", DIN 51,794, January, 1978.

19. J.A. Macdonald, "Assessment of the Flammability of Aircraft Fluids", in Fire Resistance of Hydraulic Fluids, American Society of Testing and Materials, No. STP 406, Philadelphia, PA, 1966, pp 44-52.

20. "Military Specification - Hydraulic Fluid, Fire resistant, NonNeurotoxic", MIL-H-19457D, 28 April 1981.

21. J.A. Marzani, "An Apparatus for Studying the Fire Resistance of Hydraulic Fluids at Elevated Temperatures", in Fire Resistance of Hydraulic Fluids, American Society for Testing and Materials, No. STP406, Philadelphia,PA, 1966, pp 3-18.

22. "Fire resistant Fluids for Use in Machinery and Hydraulic Equipment", National Coal Board: London, NCB Specification No. 570/1981.

23. "Fire Resistant Hydraulic Fluids", Canadian National Standard, CAN/CSA- M423-M87.

24. "Wick Test", CETOP Provisional Recommendation RP-66H, 1974-05-31.

25. "Effect of Evaporation on Flammability", CETOP Provisional Recommendation RP-64H, 1974-05-31.

26. CFR Part 35 - "Fire Resistant Fluids" (US Mine Safety and Health Administration)

27. M.B. Myers, "Fire-Resistant Hydraulic Fluids - Their Application in British Mines"; Colliery Guardian, Oct. 1977.

28. Personal communication from Mr. R.J. Windgassen (Amoco Oil) to Mr. W.E.F. Lewis (Union Carbide Corporation) on July 16, 1986 concerning a new ASTM D.02N.06 working group for the development of "The Soaked Cube Flammability Test" chaired by J. Anzenberger (Stauffer Chemical Company).

29. C.H. Faulkner, Personal Communication, July 14, 1985.

30. F.D. Norvelle, "A Discussion of Fluid Flammability Tests - Part 2: Molten Metal Tests", pp 133-138, The FRH Journal, Volume 4, No. 2

31. "Manifold Ignition Test", CETOP Provisional Recommendation RP-65H, 1974-05-31.

32. D.G. Goodall and R. Ingle, "The Ignition of Flammable fluids by Hot Surfaces", in Fire resistance of Hydraulic Fluids, American Society of Testing and Materials, No. STP 406, Philadelphia,PA, 1966, pp 66-104.

33. "Approval Standard: Less Hazardous Hydraulic Fluid, Factory Mutual Research Corporation, Norwood, MA, 02062, February 7, 1975.

34. M.M. Khan, "Spray Flammability of Hydraulic Fluids and Development of a Test Method", Technical Report FMRC J.1. 0T0W3.RC, Factory Mutual Corporation, Norwood, MA, 02060, May 1991.

35. G.E. Totten, "Thickened Water-Glycol Hydraulic Fluids for Use at High Pressures", SAE Technical Paper Series, paper no. 921738, (1992).

36. "Hydraulic Transmission Fluids: Determination of the Ignitability of Fire-Resistant Fluids Under High Pressure with a Jet spray on a Screen", AFNOR NF E 48-618, November, 1973.

37. H.H. Rowand and L.B. Sargent, "A Simplified Spray-Flammability Test for Hydraulic Fluids", in Fire Resistant Hydraulic Fluids; American Society for Testing of Materials, No. STP 406, Philadelphia, PA, 1966, pp 28-43.

38. M.M. Khan and A. Tewarson, Fire Technology, November, 321, (1991).

39. M.M. Khan and A.V. Brandao, "Method of Testing the Spray Flammability of Hydraulic Fluids", SAE Technical Paper Series, Paper No. 921737 (1992).

40. A.J. Yule and K. Moodie, Fire Safety Journal, 18, 273, (1992).

41. G. Holmstedt and H. Persson, Fire Safety Science-Proceedings of the First International Symposium, October, 869, (1985).

42. "Schedule of Fire Resistant Tests for Fire Resistant Fluids", CETOP Provisional Recommendation RP 55 H, 1974-01-04.

JÜRGEN REICHEL[1]

STANDARDIZATION ACTIVITIES FOR TESTING OF FIRE RESISTANT FLUIDS

REFERENCE: Reichel, J., "**Standardization Activities for Testing of Fire Resistant Fluids,**" Fire Resistance of Industrial Fluids ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: The use of mineral oil as a hydraulic fluid in industrial plants, installations and equipment may create a problem, if exposure of the fluid to sources of iginition are possible. Many industrial processes require the use of hydraulic fluids that afford better fire safety than achievable with mineral oils. In proposals to the governments of the member states of the European Union (EU) fire-resistant fluids intended for use in underground mines must conform the "**Requirements and Tests Applicable to Fire-Resistant Hydraulic Fluids used for Power Transmission**" (7th Luxembourg Report, adopted by the Safety and Health Commission, March 3rd 1994). The immediate stimulus for this work, which spans a period of 35 years, was the disastrous fire which occurred in 1956 at the Bois du Cazier mine at Marcinelle in Belgium, resulting in 267 fatalities.

The general classifications of hydraulic fluids are given in ISO 6743/4 (Lubricants, Industrial Oils and Related Products - Class L - Classification, Part 4: Family H, Hydraulic Systems), guidelines for use have been developed in ISO 7745 (Hydraulic Fluid Power - Fire Resistant (FR) Fluid - Guidlines for Use), but no formal standards are available to interrelate fluid classification with the relative fire risk. Two fundamental parameters are considered when selecting tests for standardisation: **1. spray ignition tests and 2. flame propagation or wick tests.** This paper discusses the use of testing methods to characterize the performance of conventional fire resistant hydraulic fluids.

---

[1] Dipl.-Ing., Research and Testing Division
Deutsche Montan Technologie (DMT), D-45305 Essen, Germany

INTRODUCTION

Fire resistant fluids were first developed in the U.S.A. during World War II, primerally for aircraft and naval use. Industrial application followed. Two types of fluids were used initially: water-glycol hydraulic fluids (UCON® Hydrolubes by Union Carbide Corporation and phosphate esters by Monsanto Corporation).

Further development of fire-resistant fluids in Europe was prompted by a disastrous mine fire where 267 miners lost their lives in the Bois du Cazier mine, of Marcinelle, Belgium, in 1956. The disasterous accident occurred when a pipeline containing readily inflammable, pressurized mineral oil was ruptured resulting in a mineral oil spray which was ignited by an electrical ignition. At the request of the Council of Ministers and the High Authority of the European Coal and Steel Community (ECSC), the recommendation No. 36-M was subsequently made stating:

> "Research should be continued with the object of developing incombustible fluids to be used in place of inflammable oils for mechanical purposes e.g. in hydraulic equipment, couplings, balances, props, etc."

Requirements and tests applicable to fire-resistant hydraulic fluids used for power transmission and control (hydrostatic and hydrokinetic) have been published under the aegis of the Safety and Health Commission for the Mining and other Extractive Industries. The first of these "Luxembourg Reports" was approved on December, 1960. As part of an ongoing process of improving safety and health demands, the specifications and testing conditions for fire-resistant hydraulic fluids were repeatedly adapted to changing regulations and technical conditions and to other requirements over the 35 years to follow.

Of particular importance during the last 10 years was the fact, that fire resistant fluids containing components not readily biodegradble became considered as detrimental to the environment. For a number of years, the manufacturers of hydraulic fluids, working together with research and testing establishments, machinery manufacturers and users and by maintaining contact with the national authorities in the European Commission, have made continuous efforts to develop non-mineral oil based, readily biodegradable and hence environmentally-friendly "substitute fluids", which have much better fire resistance than mineral oil.

However, it proved difficult to assess the the fire resistant properties of these fluids using the "Community of six" spray test [1]. Health and Safety Executive (HSE) in Buxton, England, together with the Thermodynamics and Fluid Division at Manchester University (GB), have now developed a spray ignition test based on heat release from a stabilized flame (Buxton II test) [2]. Three new test units were installed, each in England, France and Germany.

The methods for assessing health hazards have been up-dated [3]. Further considerations to provide improved environmental protection were made. Testing procedures have been supplemented and updated in the view of the current ISO (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION) and CETOP (COMITÉ EUROPEAN DES TRANSMISSIONS OLEOHYDRAULIQUES ET PNEUMATIQUES) documents in order to to increase the in-service reliability of hydraulic machinery.

The **seventh edition of the Luxembourg Report** [4] harmonized by the experts from the EUROPEAN UNION (EU) Member States was approved by the Safety and Health Commission, Luxembourg, on March 3rd, 1994, for publication. The next step is for the European Commission to instruct the European Committee for Standardization CEN (Comité Européen de Normalisation) to incorporate the specifications and testing conditions on fire-resistant fluids in the European Standards (EN).

The Luxembourg Reports have enjoyed considerable standing and have been used in many parts of the world, not only by manufacturers but also by the users of hydraulic fluids and the independent testing laboratories. Besides the mining industry, other sectors are also interested such as the tunneling industry, the iron and steel industry, motor vehicle manufacturing, merchant and naval shipping, aerospace industry and others.

This paper will discuss the standardization of testing methods used to characterize the fire -resistance properties hydraulic fluids in Europe.

DISCUSSION

1. Fire-Resistant Hydraulic Fluids

According to ISO 6743/4, fire-resistant hydraulic fluids are subdivided in aqueous and water-free fluids as shown in Figure 1. Fire-resistance of water-free fluids is achieved by their chemical structure. The fire-resistance of aqueous fluids depends on the water content. The only "nonflammable" fluids are hydraulic fluids of class HFA containing at least 95 % of water.

Two notorious accidents; Seveso, Italy, in 1976 and Binghamton (N.Y.), USA, in 1981, which, however, although having nothing to do with hydraulic equipment, showed that the toxicity of possible pyrolysis products from halogenated hydrocarbons may have severe effects on humans and the environment. HFDS and HFDT hydraulic fluids contain hydrocarbons with low chlorine content. Although the EU guidelines on the restriction of the distribution and use of polychlorinated biphenyls (PCB) for hydraulic systems in underground mining equipment still contained some exceptions [5], these PCBs and PCTs fluids have been probibted since 1994 [6]. The same is true for the polychlorinated diphenyl-methane derivates (PCDM) and dibromobenzyl-toluene (DBBT) which have been used as PCB substitutes.

Table 1: Hydraulic Fluids for Coal Mining Applications

Category	Composition Typical Properties	Water Endanger. Category	Applications Operating Temperature	Flammability Rating (Method AMS-3150C)
Water Based Fluids				
HFAE	Oil-in-water emulsions Mineral oil/synthetic ester Concentration by Vol. <20%	3-1	Power Transmissions Powered Roof Support High Working Pressure	1
HFAS	Mineral Oil Free Aqueous Synthetic Solution Concentration by Vol. <20%	0	Hydrostatic Drives Low Working Pressure 5 to <55°C	1
HFB	Water-in-Oil emulsions Mineral Oil Portion <60%	3	Not approved in German mining	3
HFC	Aqueous Polymer Solutions Water Content >35%	0	Hydrostatic Drives -20 to <60°C	1
Non-Aqueous Synthetic Fluids				
AFDR	Phosphate Esters Water Insoluble	1	Not approved for German mining	3
HFDS	Chlorinated Hydrocarbons	3	Hydrodynamic Couplings <150°C up to 1984 PCB (Elaol Vi)	1
HFDT	Blends of Chlorinated Hydrocarbons and Phosphate Esters	3	Hydrostatic Drives 10 to <70°C Up to 1990 PCDM (Ugilec)	2
HFDU	Other Anhydrous Fluids	0-1	Hydrostatic Drives -35 tp <90°C	?
Non-Aqueous Environmentally Acceptable Fluids (Substitute for Mineral Oil)				
HEPG	Polyalkylene Glycol - Water Soluble	0	Hydrostatic Drives -30 to <90°C 1989 tied operation on ISO Cor E 40, Ukadol Nbr.	46
HETG	Vegatable Oil - Triglycerides (Water insoluble)	0	Hydrostatic Drives -20 to <80°C Not approved in German mining (Rape Seed Oil)	3
HEES	Synthetic Esters (Polyol Ester) Water Insoluble	0-1	Hydrostatic Drives -35 to <90°C	3

Thermally stable halogenated hydrocarbons must no longer be used as fire-resistant hydraulic fluids in any industrial hydraulic plant because of their potential biological and toxicological hazards. A systematic study on organic substances carried out in Germany [7] showed that among the water-free fire-resistant hydraulic fluids, only phosphate esters (HFDR) will be considered for future use in mining applications.

Synthetic esters (fatty acid esters or polyol esters) and polyalkylene glycol thickened - water/glycols (water/glycols) are not significantly hazardous to water. However, the water/glycols exhibit excellent fire-resistance properties in many applications, thus reducing the cost of otherwise required fire fighting equipment in industrial hydraulic installations.

Some assessment of the fire-resistance of hydraulic fluids, according to ISO 6743/4, is actually possible with aqueous fluids without testing. If fluids contain more than 80 % of water, they are considered nonflammable fluids. Water/glycol hydraulic fluids (HFC) containing more than 35 % water are practically unignitable in spray ignition tests. The fire-resistance of water free fluids is dependent on chemical structure. In this case, the phosphate esters (HFDR) are considered self-extinguishing fluids. They are also classified under category TCD of ISO 6743-5. The proper assessment of water-free synthetic fluids of other compositions than this (HFDU) is significant because hydrostatic drives in equipment with high thermal load cannot be operated on aqueous fluids due to the high vapor pressure of water.

The suitability of any test method to determine the fire resistance of water-free fluids (HFDU) ultimately depends on the ability to differentiate fire risk potential and this data must be reproducible. Pass/fail assessments are no longer sufficient.

2. Standardization of Test Methods for Fire-Resistant Fluids in Europe

2.1 Scope

The use of hydraulic fluids based on petroleum oils are not recommended if they are used in fire- and explosion-prone areas. High pressure in hydraulic systems may, whenever connection fittings or hoses leak, give rise to sprays of atomized fluid or to fluids containing larger oil droplets. Even if the fluid is less flammable, large amounts of petroleum in the form of fine sprays through pinhole leaks, may ignite and produce huge flames as shown in Figure 2. Ignition-proneness is influenced by many factors, such as droplet size distribution, spontaneous ignition temperature or by the heat of combustion.

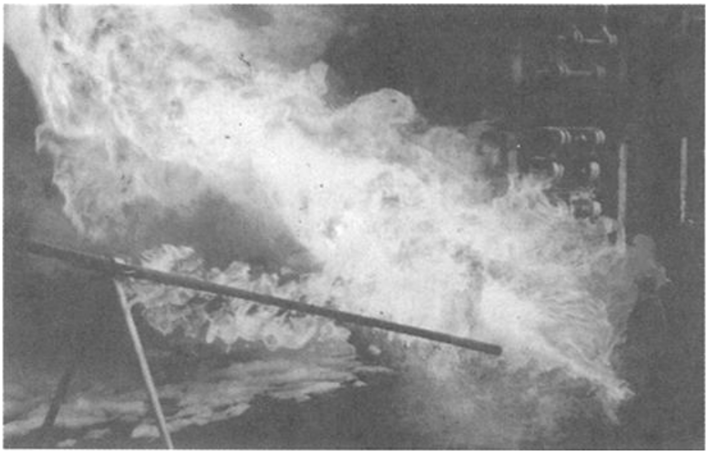


Figure 2 Spray Ignition of Mineral Oil HM 68

The droplet size may be influenced by the addition of high molecular weight polymers. These polymers reduce the tendency for formation of oil mist although they are highly sensitive to shear degradation due to the high shear fields present in hydraulic pumps and valves. The use of fire-resistant fluids of sufficient viscosity instrad of petroleum oil effectively reduce fire risk. Standardization of test methods is performed by several national and international agencies.

2.2 International Standardization Work by the ISO/TC 28 on "Petroleum Products and Lubricants Technical Committee

Standards on the technical requirements for fire-resistant hydraulic fluids are developed by ISO/TC28/SC4/WG3. The following listing summarizes current standardization activities:

2.2.1 International Standard ISO 6743/4-1982 (E)

Lubricants, industrial oils and related products (class L) - Part 4: Family H (Hydraulic systems) - Classification

2.2.2 International Standard Draft No. 4 CD 12922-1994

Lubricants, industrial oils and related products - Fire resistant hydraulic fluids for hydraulic systems - Specification

2.2.3 International Standard ISO 7745-1989 (E)

Hydraulic fluid power - Fire-resistant (FR) fluids - Guidelines for use

2.3 International standardization work by CETOP

The European Committee of Hydraulics and Pneumatics - CETOP - elaborated documents based on the Luxembourg Reports. These CETOP - Recommendations are established in cooperation by the manufacturers both of fluids and of hydraulic equipment in Europe. In CETOP, national standards of memberstates are used to develop international ISO and CEN standards.

CETOP Recommendation RP 55 H contains the primary test methods recommended to assess the fire-resistance of hydraulic fluids used by industry and in mining. These methods are identified and summarized in Figure 3. There is no longer any distinction between compulsory and additional test methods as in the past because of the specifics required individualized application. The order of different test methods does not represent any evaluation of their degree of stringency. Such an evaluation would be impossible since varying test criteria are applied e.g.: ignition of a spray by a flame, behaviour of fluids after impingement on hot or molten metal surfaces, or the ignition properties of fluid impregnated materials. More recent test methods on fire resistance tried to introduce some differentiation or classification of fire resistance. However, all of these methods only allow an evaluation by specific test criteria and have to be adapted to the individual hazard sources encountered during application in the different industrial branches.

2.4 Specifications According to the 7th Luxembourg Report

Besides fire resistance test methods, procedures to assess health hazards and environmental acceptability are contained in the 7th Luxembourg Report as shown in Table 3. Hydraulic fluids used in mining and other extractive industries within the European Union must successfully meet the requirements of one out of two spray ignition tests and one out of two tests for the determination of flame propagation. Compliance is necessary to obtain a certificate based on European Standards defined by European agencies, e.g. prEN 1710 for machinery in underground mining. This test protocol assures that for any fluid used in hydraulic systems, a fluid spray projected at some pressure, and in the presence of a flame, exhibits good fire-resistant properties and that any flame produced would not persist due to the hydraulic fluid.

Table 2 **Fire Resistance Tests from CETOP Recommendation RP55H**

Test Procedure	Test Criteria
Determination of spontaneous ignition temperature DIN 51, 794; ISO/DIS 3988	Spontaneous Ignition Point
Spray ignition test with screen (pressure = 70 bar) 7th Luxembourg Report, Part 3.1.1	Ignitability Spreading of Flames Rating is (1) or (2)
Spray ignition test, hollow cone spray (70 bar) 7th Luxembourg Report, Part 3.1.2	Subsequent Burning Time (<30 seconds)
Persistance of a flame on a wick (wick test) CETOP RP 66H 7th Luxembourg Report, Part 3.2.1	Time of exposure to flames, subsequent burning time
Inflammability on hot molten metal (aluminum, 800°C) proposed RWTÜV, Essen, Germany	Time from contact of hot metal to ignition
Effect of evaporation on non-flammability CETOP RP 64H	Non-flammabililty after heat impingement (evaporation of fluid fractions)
Stabilized flame heat release, spray test (In development, 7th Luxembourg Report, Part 3.1.3)	Non-flammability index, RI-index, length of flame, smoke development

Table 3 **Testing Conditions for Fire-Resistant Hydraulic Fluids Recommended in the 7th Luxembourg Report.** (Fire Resistant Fluids for use in power transmission systems are normally required to be tested by two of the tests shown below.)

1. Spray Ignition Tests
   - 1.1 Spray Ignition Test with Screen ("Community of Six" Spray Test).
   - 1.2 Spray Ignition Test With Hollow Cone Spray (The United Kingdom Spray Test).

1.3 Spray Ignition Test (In Development) - Stabilized Flame Heat Release Spray Test".

2. Flame Propagation Tests

2.1 Persistance of Flame on a Wick (Wick Test)

2.2 Flame Propagation in a Fluid-Coal Dust Mixture

2.5 European Committee for Standardization - CEN

The European Committee for Standardization CEN, namely CEN/TC 196, deals with standards for mining equipment. The standard draft prEN 1710 on "Machines for Underground Mines - Requirements for Applications in Areas of Mines with Firedamp Hazards-" requires the use of fire-resistant fluids. All European Standards for fire-resistant hydraulic fluids will include the test methods and specifications contained in the 7th Luxembourg Report.

Standardization of fire-resistance tests on fire-resistant hydraulic fluids is dealt with by the Technical Committee CEN/TC19 on "Petroleum Products, Lubricants and Related Products". Work will begin by standardizing two test methods already contained in the 7th Luxemburg Report and in CETOP RP 55 H. These spray ignition and flame propagation tests have been well established for many years.

The Technical Committee ISO/TC28 is also very interested in standardization of these methods to establish specifications for fire-resistant hydraulic fluids and fire-resistant turbine fluids.

CONCLUSIONS

For fire prevention, the use of fire-resistant fluids is frequently required in fire- and explosion-prone areas. Fire resistance of fluids can be assessed only by specific test criteria. Since it is impossible to determine uniform tests for any and all applications and industrial branches. In practice fire hazard has to be valuated depending on the type of ignition source. Working conditions and environmental influences have to be well considered.

The stringency of test methods for determining the fire-resistance of hydraulic fluids is of paramount importance if it comes to the classification of synthetic water-free fluids. The results must always be seen in comparison to petroleum-based products. Figure 2 represents the test results according to the new method, entitled "HEAT RELEASE OF A

STABILIZED FLAME" for different fluids, pursuant to ISO 6743/4. The tests were carried out in France with the test agency of HBL, Laboratoire Lubrifiants, in MARIENAU, F-57600 FORBACH. By this method it will become obvious that any differentiation of water-free fluids is quite difficult and that the only clear distinction is possible between phosphate ester HFDR 46 and mineral oil HM 46.

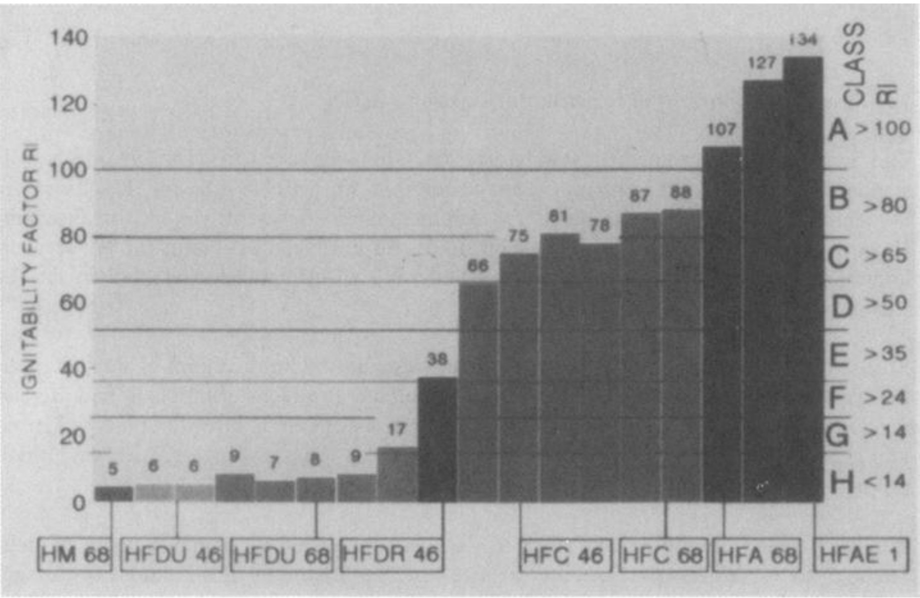


Figure 5 **Stabilised Flame Heat Release**

Essential for practicable application are specific criteria, e.g. spray ignition, smoke development, behaviour of the fluid after impingement on hot or molten metal surfaces, flame propagation of spilled fluids or of fluid-impregnated material. The CETOP suggestion RP 55H contains a list of the current test methods under due consideration of the influences from various industrial branches.

REFERENCES

1. "REQUIREMENTS AND TESTS APPLICABLE TO FIRE RESISTANT HYDRAULIC FLUIDS USED FOR POWER TRANSMISSION AND CONTROL (HYDROSTATIC AND HYDROKINETIC) Seventh Edition, 3rd March 1994, Doc. No. 4746/10/91 EN", 7th Luxembourg Report, Part III, Section 3.1.1, "The Community of Six Spray Test".

2. "REQUIREMENTS AND TESTS APPLICABLE TO FIRE RESISTANT HYDRAULIC FLUIDS USED FOR POWER TRANSMISSION AND CONTROL (HYDROSTATIC AND HYDROKINETIC) Seventh Edition, 3rd March 1994 Doc. No. 4746/10/91 EN", 7th Luxembourg Report, Part III, Section 3.1.3, "Determination of Flame Persistance or Propagation".

3. "REQUIREMENTS AND TESTS APPLICABLE TO FIRE RESISTANT HYDRAULIC FLUIDS USED FOR POWER TRANSMISSION AND CONTROL (HYDROSTATIC AND HYDROKINETIC) Seventh edition, 3rd March 1994, Doc. No. 4746/10/91 EN", 7th Luxembourg Report, Part III, Part IV, "Methods of Assessing Heath Hazards".

4. 7th Luxembourg Report, 3rd March 1994 , Doc. N° 4746/10/91, SPECIFICATION AND TESTING CONDITIONS RELATING FIRE -RESISTANT HYDRAULIC FLUIDS USED FOR POWER TRANSMISSION (HYDROSTATIC AND HYDROKINETIC). Publisher: Safety and Health Commission for the Mining and other extractive Industries. L-2920 Luxembourg, Commission of the European Communities DG V/E/4.

5. PCB-Prohibition (Council Directive 91/3309/EEC of June 1991 amending for the eleventh time Directive 76/769, OJ No. L 186, 12.7.1991, P. 64 (legislation in the European Union).

6. 91/339/EEC Council Directive of 18 June 1991 amending for the 11th time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations.

7. Engel, W. und H. Kihl: Schwerentflammbare und gesundheitsunschädliche Hydraulikflüssigkeiten der Gruppe HFD für den Bergbau. Glückauf 123 (1987) Nr.22 S.1423/1426.

7th Luxembourg Report is avaliable from:

Commission of the European Communities DG V
Jean Monnet Building C4,57
L-2920 Luxembourg

Carl E. Snyder, Jr.[1] and Lois J. Gschwender[1]

FIRE RESISTANT HYDRAULIC FLUIDS AND FIRE RESISTANCE TEST METHODS USED BY THE AIR FORCE

REFERENCE: Snyder, C. E., Jr. and Gschwender, L. J., **"Fire Resistant Hydraulic Fluids and Fire Resistance Test Methods Used by the Air Force,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: The concern about the fire resistance of hydraulic fluids by the Air Force and the rest of the Department of Defense (DoD) dates back to the introduction of the mineral oil based hydraulic fluid, MIL-H-5606 [1], into aircraft hydraulic systems. This concern has led to the development of two fire resistant hydraulic fluids that can be directly substituted into aircraft hydraulic systems that were designed to use MIL-H-5606, i.e., MIL-H-83282 [2] and MIL-H-87257 [3], and a nonflammable hydraulic fluid, MIL-H-53119 [4], that can be used only in hydraulic systems that were designed for that fluid or in subsystems originally designed for MIL-H-5606, MIL-H-83282 or MIL-H-87257, for which re-design of the components and retrofit of the system with compatible seals, if required, would be cost effective. Another fire resistant hydraulic fluid was developed for use in commercial aircraft hydraulic systems, a phosphate ester based hydraulic fluid described by Society of Automotive Engineers document AS1241, Fire Resistant Phosphate Ester Hydraulic Fluid for Aircraft The fire resistant properties of these fire resistant and nonflammable hydraulic fluids are discussed and the flammability test methods are presented.

KEYWORDS: flammability, fire resistant hydraulic fluids, Department of Defense

BACKGROUND

The flammability characteristics of aircraft hydraulic fluids have been of great concern for both military and commercial aircraft since the introduction of hydraulic systems to aircraft and flammable hydraulic fluids for their operation. In addition to the fire hazards associated with all hydraulic systems, i.e., high pressure lines in the vicinity of a variety of ignition sources, the DoD aircraft also must be concerned about survivability of aircraft to enemy gunfire. The selection of organic liquids rather than

---

[1] Research Materials Engineer, Air Force Wright Laboratory, Materials Directorate, WL/MLBT, 2941 P Street, Suite 1, Wright-Patterson Air Force Base, OH 45433-7750

water based fluids as hydraulic fluids for these systems was guided by their wide temperature range of operation, especially the requirement for good flow characteristics at temperatures as low as -54° C. At one time, the most widely used hydraulic fluid in both military and commercial aircraft was MIL-H-5606, a mineral oil based hydraulic fluid. In the 1950's, with the advent of jet aircraft, the commercial aircraft began to use a phosphate ester based hydraulic fluid, currently described in Society of Automotive Engineers document AS1241. The adoption of this fluid required the development of new, compatible materials since this fluid was not compatible with MIL-H-5606 or hydraulic systems designed to use MIL-H-5606. Compatible materials were developed for use with phosphate esters exclusively, but lacked compatibility with MIL-H-5606 systems which prevented the military from adopting this fluid. Nearly 20 years later, after a significant number of programs by the Air Force and the Navy, a compatible, fire resistant fluid that could be directly substituted for MIL-H-5606 without any need for redesign or retrofit of systems or system materials was developed. That fluid, MIL-H-83282, is currently the most widely used hydraulic fluid in DoD aircraft. The need to carefully consider the properties of candidate replacement hydraulic fluids is well demonstrated by the program conducted by Conte, et al [5] to develop a fire resistant direct replacement for MIL-H-5606 based on a chlorophenylmethyl silicone fluid, Nadraul MS-6. This program was conducted in parallel with the Air Force's program based on polyalphaolefin chemistry which led to MIL-H-83282. Most of the fluid properties were acceptable and the fire resistance properties were very good. The Navy's program even overcame the traditional poor lubricity usually demonstrated by silicone based fluids by developing a formulation with an effective lubricity additive. It was not until it was tested in a mock-up F-4 aircraft that it was found to be unacceptable for implementation. The inferior bulk modulus properties of MS-6 compared to MIL-H-5606, the fluid for which the hydraulic system was designed, resulted in unacceptable flight control performance in the aircraft. While it could have been used in future aircraft hydraulic systems which could have been designed around the inferior bulk modulus, this was not done.

Still concerned about the hydraulic fluid fire hazard, the Air Force initiated a program to develop a nonflammable hydraulic fluid in the late 1970's. It was recognized that a nonflammable hydraulic fluid would have properties so different that systems would have to be designed to use this fluid and it would not be a drain and fill replacement for MIL-H-5606 or MIL-H-83282. The criteria that were developed by the Air Force which had to be met to consider the hydraulic fluid to be nonflammable were very stringent. The fluid which was developed, MIL-H-53119, along with compatible seals, was successfully demonstrated in both full system mock-ups as well as in hydraulic subsystems that were redesigned and retrofitted with compatible components and seal materials. This fluid was based on a chlorotrifluoroethylene oligomer. Currently, that fluid has not been incorporated into any aircraft due to logistic considerations and the risk associated with the introduction of a radically new hydraulic fluid into an aircraft, but it is under consideration for use in some ground applications by the Army.

The last hydraulic fluid to be discussed is MIL-H-87257. This is the most recent development in fire resistant hydraulic fluids. It was developed to replace MIL-H-5606 hydraulic fluid in systems that could not convert to MIL-H-83282 because of low temperature operational requirements. The low temperature viscosity characteristics of MIL-H-83282 are not as good as those of MIL-H-5606. The temperature at which the fluid reaches 2500 cSt, generally considered to be the maximum viscosity at which the fluid can be pumped through the long, small diameter hydraulic lines in aircraft hydraulic systems, is reached at -40° C by MIL-H-83282 compared to -54° C for MIL-H-5606. For most DoD aircraft, this did not cause a problem, because after a relatively short warm up time, by exercising the hydraulic controls, MIL-H-83282 would work well at temperatures as low as -54° C. However, that warm up time would compromise the ability for some aircraft to conduct their mission, so they were not converted to MIL-H-83282. At that time, a requirement was developed for a -54° C to 135° C direct replacement hydraulic fluid that would have fire resistance approaching that of MIL-H-83282. That fluid, MIL-H-87257, was developed and is currently undergoing flight tests.

FLUID PROPERTIES

The physical properties of MIL-H-5606, MIL-H-83282, MIL-H-87257, AS1241 and MIL-H-53119 are shown is Table 1 along with the test methods used for their determination.

Table 1. Selected Typical Physical Properties of Hydraulic Fluids

Property /Test Method	MIL-H-5606	MIL-H-83282	MIL-H-87257	AS1241	MIL-H-53119
Temperature Range, ° C	-54 to 135	-40 to 205	-54 to 175	-54 to 110	-54 to 175
Kinematic Viscosity, mm/sec ASTM D445					
at -54 ° C	2450	20,000	2,480	1700	766
-40 ° C	490	2,140	520	300	150
38 ° C	14.2	14.2	9.0	10.5	3.1
99 ° C	5.1	3.6	2.6	3.5	1.0
Pour Point, ° C ASTM D97	<-59	<-59	<-59	<-59	<-59
Elastomer Compatibility, Rubber Swell, % ASTM D4289	24 (NBR-L)	20 (NBR-L)	18 (NBR-L)	13 (EPR)	11(EPR)

Note: NBR-L is the designation for Buna N Rubber and EPR is the designation for Ethylene Propylene Rubber

A deficiency of the current AS1241, phosphate ester based hydraulic fluids, is their limited high temperature use capability of 110 °C compared to 175°C and higher for the other fire resistant hydraulic fluids. This was not a limitation in the past, but as more extensive use of hydraulic power is being designed into more modern aircraft, the operational temperature continues to advance and more thermally stable hydraulic fluids are required.

FLAMMABILITY PROPERTIES

Flammability characteristics of hydraulic fluids are usually determined at three different levels to assess the hazards for DoD systems. Most commonly used are the standard laboratory flammability test methods which can provide relative fire resistance ranking of hydraulic fluids. These tests include: flash point, fire point, autoignition temperature and flame propagation rate. These methods are valuable because they have been standardized and have the benefits of significant development and widespread acceptance. They also usually require relatively small amounts of sample and are relatively safe to run. These flammability test methods are typically used during new fluid development programs. These methods and the data for MIL-H-5606, MIL-H-83282, MIL-H-87257, AS1241 and MIL-H-53119 are shown in Table 2. The outstanding fire resistance of MIL-H-53119 is easily observed as it surpasses all of the other fluids in all of these tests. One must be very careful in trying to read too much into the data from these tests, however. For example, the flash and fire points of AS1241 are inferior to those of MIL-H-83282. However, in most other flammability tests, AS1241 demonstrated superior performance. In general, AS1241 is considerably more fire resistant than MIL-H-83282 and MIL-H-87257. These standard test methods are usually used during fluid development.

After a candidate fire resistant fluid has been selected and a more realistic assessment of its performance, when subjected to a closer simulation of the fire hazards actually anticipated in aircraft applications can be made, another level of flammability testing is conducted. These tests include: spray flammability tests, hot surface ignition tests, etc. These tests, described in [6], are much less standardized and are generally designed to more closely resemble the actual conditions anticipated. For example, the hot surface ignition tests are usually conducted at hot surface temperatures resembling engine manifolds, hot brakes, etc. Spray flammability testing resembles ruptured hydraulic lines in the high pressure hydraulic system. A spray flammability test can either resemble a hot surface induced ignition or a spark or flame induced ignition depending on how one attempts to ignite the spray. Spray flammability tests are generally designed to reflect a given level of fire safety. For example for the nonflammable hydraulic fluid development program, an orifice was selected for the nozzle to generate an extremely fine mist with maximum surface area per unit of fluid volume. All of the other fluids were extremely flammable using this spray nozzle. However, if a coarser spray is used for the test, differences in flammability characteristics between MIL-H-5606 and MIL-H-83282 can readily be seen. Using the Navy coarse spray flammability test [7], MIL-H-5606 readily ignites and continues to burn when the ignition source is removed from the spray, whereas MIL-H-83282 readily ignites but when the ignition source is removed, the fire self-extinguishes. The hot surface ignition test is often used to predict how a fluid will behave if it is dripped or sprayed on a hot surface. The results of this test kept the Air Force from implementing MIL-H-83282 hydraulic fluid for nearly ten years because it showed MIL-H-83282 igniting at a lower temperature than MIL-H-5606. In studying a variety of other hydrocarbon fluids, it was found that the minimum hot surface ignition temperature was inversely proportional to the volatility of the fluid. For example, JP-4 jet fuel had a higher minimum hot surface ignition temperature than MIL-H-5606, MIL-H-83282 or MIL-L7808 (an aircraft turbine lubricant). This ranking was in direct opposition to the other flammability tests. In spite of the lower hot surface ignition temperature, the implementation of MIL-H-83282 in DoD aircraft has significantly reduced hydraulic fluid fire damage.

Table 2. Selected Typical Flammability Properties of Hydraulic Fluids

Property	MIL-H-5606	MIL-H-83282	MIL-H-87257	AS1241	MIL-H-53119	Test Method
Flash Point, ° C	102	210	166	170	None	ASTM D92
Fire Point, ° C	110	235	191	188	None	ASTM D92
Autogenous Ignition Temperature, ° C	232	354	243	524	643	ASTM D2155
Flame Propagation Rate, cm/sec	0.73	0.21	0.30	0.00	0.00	ASTM D5306
Gunfire Ignition Test, Number of Fires in 5 Shots	5	1	1	0	0	Military Specification MIL-H-83282

Finally, when a hydraulic fluid has been selected for a weapon system and a full survivability study needs to be conducted on the weapon system, even more realistic flammability tests are conducted. The survivability being determined is against hostile gunfire. These generally involve mock-up hydraulic systems utilizing the weapon system's actual operating pressure (up to 5000 psi) and simulated hydraulic fluid flow rates. In many cases, anticipated air flow rates for the weapon system are simulated and ammunition characteristic of the threat to which the weapon system will be subjected is used in the gunfire testing. A series of replicate tests are conducted and a survivability assessment is made. The fire resistance of the hydraulic fluid is usually a very big factor in the survivability assessment of weapon systems. These tests are considerably more expensive to conduct than either of the other two levels of flammability tests.

DISCUSSION

Developing and/or selecting a fire resistant hydraulic fluid for an application can be a very complex activity. First and foremost, the fluid must be capable of performing as a hydraulic fluid in the system for which it is being considered. This means it must have the appropriate physical properties and materials compatibility characteristics for it to be used in a system. In some cases, it may be possible to design a hydraulic system around any unique properties the fluid with the requisite fire resistance properties possesses, or it may be possible to make modification to or to retrofit the hydraulic system to make it possible to use that specific hydraulic fluid, but this usually is not within the scope of system changes that can be made. In most cases, a fire resistant fluid is being sought for an existing hydraulic system which is currently using a hydraulic fluid which is considered too flammable. In some cases, fire resistance requirements have been developed which are impossible to meet with fluids which could be substituted without retrofit into current systems. That was what DoD did for many years. DoD wanted a hydraulic fluid with the fire resistance properties of phosphate esters, but wanted to put in into MIL-H-5606 hydraulic systems without retrofit. While that was a noble goal, where DoD really made their mistake for many years was to eliminate any hydraulic fluids that could be substituted into MIL-H-5606 systems without retrofit that were significantly more fire resistant than MIL-H-5606, but slightly inferior to the phosphate esters. DoD just continued using MIL-H-5606 and living with the large fire damage losses that using that fluid caused. It was not until compatibility with MIL-H-5606 systems was made the number one requirement and the most fire resistant hydraulic fluid that met that requirement as the replacement was selected that it was possible to reduce hydraulic fluid fire losses. MIL-H-83282, the fluid that was developed and selected, has reduced hydraulic fluid fire losses by over 90% since it was introduced. Although MIL-H-83282 did not perform much better than MIL-H-5606 in the more severe flammability tests, the reduction in fire damage has been quite significant. In analyzing the hydraulic fluid fires experienced by the Air Force over the last 35 years, some very interesting data was found. First, the actual number of hydraulic fluid fires has not decreased as much as the reduced fire damage would predict. The major reason the fire damage has been so significantly reduced is that the extent of fire damage is so much less. This would indicate that the fire, although it did occur, was of much smaller magnitude than those experienced with MIL-H-5606. Another factor that was observed was that when entire aircraft were lost due to a hydraulic fluid fire, in most if not all cases, the loss of the airplane was the result of the hydraulic fluid fire propagating to the fuel system and the fuel fire actually consuming the aircraft. Therefore, the authors feel that the major flammability test that explains the observed improvement in hydraulic fluid fire losses is the flame propagation test. This test did not even exist during the MIL-H-83282 fluid development program.

SUMMARY AND CONCLUSIONS

The selection of fire resistant fluids for utilization in hydraulic systems can be a very challenging task. It is significantly more difficult to find a fire resistant fluid to use in an existing system which was originally designed to use a more flammable fluid. Since hydraulic systems are designed to most efficiently operate utilizing a fluid with specific properties, selecting a different operational fluid frequently results in unacceptable degradation in system performance. In addition to improved fire resistance, a replacement fluid must also have adequate properties and materials compatibility to enable equivalent or improved system performance. Frequently, that requires that a compromise be made in fire resistance properties.

It is very difficult to predict the extent of fire safety that will be achieved by substituting a more fire resistant hydraulic fluid in a specific system because it is very difficult to relate improvement in fire safety to flammability test results. An obvious exception to that is when a nonflammable hydraulic fluid can be used. In that case, total elimination of hydraulic fluid fires can be achieved. In the case of fire resistant fluids, the fire safety improvement achieved can frequently be best estimated by comparing flame propagation characteristics of the fire resistant candidate replacement with the original hydraulic fluid. In the case of DoD weapon systems, especially aircraft, the hydraulic fluid fire damage was reduced much more drastically than would have been predicted, based on the flammability tests on MIL-H-5606 and MIL-H-83282.

REFERENCES

1. Military Specification MIL-H-5606G, Hydraulic Fluid, Petroleum Base, Aircraft, Missile, and Ordnance, NATO Code H-515, 9 September 1994.
2. Military Specification MIL-H-83282C, Hydraulic Fluid, Fire Resistant, Synthetic Hydrocarbon Base, Aircraft, Metric, NATO Code Number H-537, 25 March 1986.
3. Military Specification MIL-H-87257, Hydraulic Fluid, Fire Resistant, Synthetic Hydrocarbon Base, Aircraft, Missile, and Ordnance, 2 March 1992.
4. Military Specification MIL-H-53119, Hydraulic Fluid, Nonflammable, Chlorotrifluoroethylene Base, 1 March 1991.
5. Conte, Jr., A. A., Hammond, J. L. and Stallings, L., "Status of Silicones as Fire Resistant Military Aircraft Hydraulic Fluids," *Lubr. Eng.*, **34**, pp. 486-494 (1978).
6. Parts, Leo, "Assessment of the Flammability of Aircraft Hydraulic Fluids," Air Force report AFAPL-TR-79-2055, July 1979.
7. High-Temperature - High Pressure Spray Ignition Test, Federal Test Method Standard 791, Method 6052.

W.D. Phillips[1]

FIRE RESISTANCE TESTS FOR FLUIDS AND LUBRICANTS - THEIR LIMITATIONS AND MISAPPLICATION

REFERENCE: Phillips, W. D., **"Fire Resistance Tests for Fluids and Lubricants—Their Limitations and Misapplication,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: A large number of tests are currently available for assessing the fire resistance of functional fluids and lubricants. Since it is extremely difficult to simulate fire conditions for fluids in laboratory tests, the main use for the different methods is a comparative assessment of the various fluids.

The fluids in commercial use, where fire resistance is a critical feature, can be divided into those which depend on water for their performance and non-aqueous fluids, where the fire resistance depends on the chemical composition. Ideally a fire resistance test should be capable of assessing the behaviour of all candidate fluids on an equal basis, but because the two groups of fluids behave in totally different ways comparison in most tests is not valid.

Although some tests suffer from indifferent precision or are unable to satisfactorily discriminate one type of fluid from another (within the same group), many rank the fluids in approximately the same order and therefore do not provide any additional information.

The introduction of two new spray ignition tests which enable all the different fluids to be compared under similar conditions is a major step forward. These tests, however, cannot simulate a condition where the water content of aqueous fluids can volatilise and leave behind a flammable residue. As a result, for the minimum assessment of the behaviour of both groups of fluid it is advisable to obtain both spray ignition test performance and performance in a 'hot surface' test.

KEYWORDS: Fire-resistant hydraulic fluids, fire resistance tests, spray ignition tests, hot surface tests, wick tests, cone calorimeter, flash/fire points,autoignition temperature, ignitability, propagating tendency, ignition delay, heat release.

INTRODUCTION

In 1966 at an ASTM Symposium on the fire resistance of hydraulic fluids, concern was expressed at the proliferation of tests claiming to measure the 'nebulous property' of the fire resistance of functional fluids [1]. It was further suggested that communication between testing groups was inadequate, resulting in a considerable

---

[1] FMC Corporation (UK) Limited

duplication of effort. Almost thirty years later the chairman of ASTM Committee N6 is quoted as saying "that a major problem confronting industry today is the lack of test standardisation and interpretation of test results to adequately measure the fire resistance of fluids"[2]. Certainly, while the development of tests has done much to improve safety in industry during a period when operating conditions have become increasingly severe, the downside has been the appearance of tests claiming particular relevance to every conceivable fire hazard.

A recent count revealed about 50 methods (excluding obvious variations or minor modifications of the same test) all claiming to measure various aspects of fluid fire-resistance. Test method development is still continuing with some recent techniques involving considerable sophistication. Perhaps this situation simply acknowledges that fire is an extremely complex phenomenon which is difficult, if not impossible, to reproduce in laboratory tests. It must be queried, however, whether it is necessary to have fifty tests to measure the fire resistance of perhaps 6-8 chemically different types of fluid. If not, how does the user select the relevant methods, and where possible correctly relate the fluid performance to the fire hazard.To do this, it is essential to have an understanding of what the test is trying to measure, and its limitations. The selection of the wrong test or the misinterpretation of the results could have alarming consequences for the user.

The object of this paper, therefore, is to examine the problems associated with the fire-resistance testing of fluids and lubricants with reference to the most commonly-used tests; to identify their limitations and how their results can be misinterpreted. A suggestion for the minimum tests required for a comparative assessment will be made.

TERMINOLOGY

A very basic requirement for any branch of science or technology is an agreed set of terms and definitions. A number of standards containing such definitions exist for the field of fire technology and fire-resistance testing. These include:

ISO/IEC Guide 52: Glossary of fire terms and definitions
ISO Standard 3261: Fire tests – vocabulary.
IEC Standard 695-4: Fire hazard testing – terminology concerning fire tests.
BS 6336: Development and presentation of fire tests and their use in hazard assessment.

BS 6336 also indicates terms which are not recommended, for example 'low inflammability' or 'not easily ignitable', on the grounds that they may give a misleading impression of performance or imply a judgement of performance in the unknown circumstances of a real fire situation. The use of the term 'less flammable' also requires an agreed reference point. For functional fluids this is normally mineral oil, and all other fluids across a wide spectrum of performance are loosely described in this way. The term 'fire resistance' is accepted because it is so well established that it 'would not be expedient to try to align its definition with that of other terms'[3]. Such a term would be unacceptable in France or Germany, where fire-resistant fluids are instead called ' les fluides de difficilement inflammables' or 'schwerentflammbare Flüssigkeiten' – fluids difficult to ignite! 'Fire resistance', however, is used to imply the general fire test behaviour of a material whereas ignitability is only one facet.

The term fire resistance will therefore be used in this text. Its use should not be equated with 'non-inflammability' since most organic materials will burn under the right conditions.

The ASTM definitions of fire terms can also be significantly different from those listed in the ISO and IEC Standards. A lack of common agreement on definitions will remain an obstacle to a greater understanding of fire resistance and its measurement.

THE MECHANISM OF FIRE

To understand what a test is measuring it is first necessary to understand a little of the nature of fire. The following information is a greatly simplified explanation of the major processes involved.

- Fire or combustion is an oxidation reaction. It normally consists of three stages: initiation, development and termination. There can be occasions, however, when no significant period of development occurs and the fire quickly terminates.

- Fire occurs in the vapour phase at the liquid surface and depends upon the availability of fuel, sufficient energy to volatilise the fuel, and oxygen. A reduction in, or the absence of, one of these components will result in the fire self-extinguishing.

- Fluid characteristics which determine its vapour pressure, that is viscosity and molecular weight, and reactivity with oxygen, specifically chemical structure and thermal stability, have a significant impact on the ease of ignition.

- As a result of the reaction between the 'fuel', vapour and oxygen, heat is released. This can be in the form of a cool flame (barely visible) with limited release of heat or a hot (visible) flame. Cool flames occur at lower temperatures, and in most tests are either unnoticed or unrecorded.

- Combustion of the fuel will continue after the initiation phase if the heat released by ignition provides sufficient energy to adjacent fluid (vapour) to ensure reactivity with oxygen. Heat release is therefore important in determining the growth of a fire. In fact, for continued combustion of a liquid the rate of heat loss due to convection and radiation through the air, and conduction through the liquid must be less than the sum of the rate of heat emitted by the ignition source and that available from the combustion process.

THE CLASSIFICATION AND SELECTION OF TEST METHODS

The tests available for assessing fire resistance can be categorised in different ways: by application (which would result in duplication) or by the fire resistance property they are attempting to measure such as:

- ease of ignition
- heat release or flame propagation
- smoke and/or products of combustion

As many tests claim to measure more than one parameter this classification is also unsatisfactory. A preferred scheme might be to categorise them according to the mode of ignition:

- bulk fluid ignition
- ignition when absorbed onto a substrate
- ignition of a spray or jet
- ignition by a hot surface

These methods can in turn be further subdivided into either:

- quality control methods (which may not relate to service performance)
- laboratory tests attempting to simulate a specific hazard or general fire behaviour
- full scale evaluations.

Tests can also be divided into those which simulate conditions where the fluid release initiates the fire – *the cause scenario* – (spray/hot surface ignition) and those involving bulk fluid ignition by a flame, which suggest that the fluid is involved in an external fire – *the victim scenario*. Obviously the former condition is much more important than where the fluid is a victim of a fire already in progress, but the latter can be of use in fire modelling.

One type of test which falls outside the above categories but is used for development and classificatory purposes is that which purports to measure an intrinsic property of the material; in this case, the heat of combustion or net calorific value of the fluid.

Table 1 identifies the most commonly-used procedures and classifies them according to the categories indicated above.

Such a classification is subjective and the boundary between some 'laboratory' procedures and full scale tests is not clearly defined. The spray ignition tests mentioned above, for example, would be beyond the ability of many laboratories to carry out.

As regards the selection of methods to simulate a particular fire hazard, the test conditions should simulate or reflect that hazard as closely as possible. 'If more than one hazard is present then different tests may be required for each hazard. In practice simplifications may be necessary to reduce the time and cost involved but the condition finally adopted should relate as nearly as possible to the actual environment in which the hazard is thought to arise. If a test is designed to assess different products for a specific use it is essential that the method be capable of being applied to all possible materials, and **on an equal basis**' [3].

It is also important that the method/equipment should be so designed that a feature of the equipment does not influence the results. Performance under one set of conditions should be minimised where possible since this may present a restricted view of the behaviour of the products. Tests should of course have good precision and preferably be simple and cheap to carry out. Lastly, the selection of methods which essentially measure the same parameter and which do not add to our knowledge of the behaviour of the product should be avoided.

The primary objective of a fire test is to be able to relate the performance of the product, i.e. ignitability or the tendency to propagate flame, to practice. Evaluation of products of combustion and smoke are a secondary consideration since they are dependant on the ignitability and propagating tendency of the material.

One assumption made in fire-resistance testing is that there is no change in performance in use. With fluids this is not necessarily the case. Changes to fire resistance can occur:

- in the case of the breakdown of emulsions resulting in the formation of a layer of free oil.
- if water is lost from water-containing products
- if polymeric materials shear down in use causing a reduction in viscosity
- if the material degrades thermally or oxidatively in use to form flammable degradation products.

TABLE 1 – The classification of fire test procedures for functional fluids

Test category	Mode of fluid ignition			
	Bulk fluid ignition	Absorbed on substrate	Spray ignition	Hot surface ignition
Quality control	flash/fire points oxygen index	wick tests	–	autoignition
Laboratory simulation of hazard or fire behaviour	cone calorimeter heat release tests	soaked cube test	Luxembourg Report and Factory Mutual tests	hot channel test hot manifold test molten metal ignition
Full scale tests	pool fire transformer fire	–	–	–

THE USE AND MISUSE OF SOME COMMON TEST METHODS

In this section the relevance of some widely used methods and their ability to satisfactorily discriminate between different fluid types is discussed.

Basic properties of combustion

An example of a test which is regarded as independent of the physical properties of the material, i.e. viscosity, volatility etc., is the heat of combustion (or net calorific value). Heat release is not an intrinsic property and is discussed later under an evaluation of the cone calorimeter and spray ignition techniques.

The heat of combustion, determined in a bomb calorimeter, is defined as the heat released by complete combustion of a unit mass of material, the water produced being the vapour state. The technique was developed for use with hydrocarbon fuels and in ASTM D240, for example, it specifically states that the fuel should contain only the elements carbon, hydrogen, oxygen, nitrogen and sulphur. It is assumed that the products of combustion are carbon dioxide, nitrogen, sulphur dioxide and water. As few fires take place in the presence of excess oxygen, it is an artificial condition unrelated to (most) practice.

On its own the data is also meaningless – there is no way of relating heat of combustion values to ignitability or the tendency of a fluid to propagate flame. For the data to be interpreted it is necessary to refer to fluid performance in tests which are often much less precise. Some heat of combustion data on different fluid types is given in Table 2. As can be seen the figures for the phosphate ester do not correlate well with results from other fire tests.

TABLE 2 – The relationship between heat of combustion data and other common fire tests

Fluid	Heat of combustion (ASTM D240) kJ/g	Open cup flash/fire points (ASTM D92) °C	Autoignition temperature (ASTM 2155) °C
ISO VG 10 mineral oil	46	166/180	320
ISO VG 46 triaryl phosphate	35	246/365	580
ISO VG 32 polyol ester	37	280/310	415
ISO VG 46 silicone fluid	32	300/340	470
ISO VG 7 Askarel (Polychlorinated Biphenyl)	13	190/none	>650

Despite the restrictions in the scope of bomb calorimetry methods mentioned above, these tests are also used for measuring the heats of combustion of non-hydrocarbon products,such as synthetic insulating liquids as specified in IEC 1100, *Classification of insulating liquids according to fire point and net calorific value.* Both silicone fluids and chlorinated hydrocarbons, for example, behave under such combustion conditions in a different way to hydrocarbons. When silicones combust completely, they produce particles of silica (sand) which absorb some of the heat released by the organic part of the molecule. The heat of combustion values for this material will therefore be understated. With chlorinated hydrocarbons a primary degradation product is hydrogen chloride. However, this undergoes a further reversible reaction [4].

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$$

Complete combustion of chlorinated materials does not therefore take place in a calorimeter. In a fire, the water and chlorine would be rapidly lost, driving the reaction to the right. Bomb calorimetry thus produces data on certain materials which does not relate to their behaviour in a fire and renders comparisons with other chemical types either invalid or, at best, only very approximate.

Test assessing bulk flammability behaviour

Flash and fire points – Both the open cup (ASTM D92) and the closed cup (ASTM D93) procedures have been widely used by industry for many years for quality control and standardisation/classification purposes. The technique involves heating a fixed volume of liquid from below at a standard rate and trying to ignite the vapour by means of a small pilot flame. The flash point is the lowest temperature at which the vapour ignites, while the fire point is the lowest temperature at which the vapours will sustain burning for a minimum of 5 seconds.

In the closed cup method it is only possible to measure flash point and the values are slightly lower than for the open cup test, probably because the loss of low boiling components is hindered in this procedure. Closed cup flash points are in fact thought to correlate with the lower limit of flammability [5].

Although these tests are simple and cheap to carry out they have been criticised for poor precision due to inadequacies in equipment design and its susceptibility to the external environment [5, 6]. Burgoyne [5] goes so far as to say the "flash point is an arbitrary quantity which does not relate to any known hazard". While it can be useful in detecting the presence of small amounts of volatiles, it does not necessarily relate to ignitability, as can be seen from the data on polychlorinated biphenyl in Table 1. Unfortunately, flash point is used in certain countries as the sole arbiter of fire resistance – a situation which is clearly untenable.

Fire point, however, is of value in predicting relative ignitability in the victim scenario. For the establishment of classification limits, reference to the hazard or operational conditions is necessary. An occasion when the fire point could have some relevance to a fire hazard would be when equipment or a fluid spill is involved in an external fire. As a result, both the US National Electrical Code and the IEC Standard 1100, *Classification of insulating liquids according to fire point and net calorific value* require a 300°C minimum value. Classification limits cannot be reliably established without reference to relevant applicational data.

In terms of the relationship between fire point and other fire-resistance tests, some data is given in Table 3. Fire point is seen to increase along with other test data but without an exact correlation. This will, in part, be due to the limited precision of the methods used but also to the fact that some fluids, for example silicones, degrade in a different way and produce data which is strictly non-comparable. This will be discussed later in more detail.

In common with most of the simple laboratory techniques it is not valid to evaluate or compare the fire test performance of water-based fluids under these conditions as the water volatilises, leaving a flammable organic residue. For the non-aqueous fluids a general trend in fire resistance emerges ranging from hydrocarbons, the most flammable, through carboxylate esters and phosphate esters to the chlorinated

TABLE 3 – A Comparison of the fire resistance behaviour of fluids in common laboratory tests

Fluid	Flash point	Fire point	Autoignition temperature	Wick test mean persistence of burning	Oxygen index	Hot manifold test
	(ASTM D 92)	(ASTM D 92)	(ASTM D 2155)	(CETOP RP 66H)	(IEC 1144)	(CETOP RP 65H)
	°C	°C	°C	seconds	%	
Carboxylate ester A (ISO VG 32)	245	295	400	continuous burn	–	fail
Carboxylate ester B (ISO VG 68)	266	313	415	continuous burn	17	fail
Silicone fluid (ISO VG 46)	300	350	430	7	23	–
Phosphate ester (ISO VG 46)	245	360	575	6	23	pass
Polychlorinated biphenyl (ISO VG 46)	190	>400*	650	no ignition	–	pass
Hydrocarbon Oil A (ISO VG 46)	145	150	–	continuous burn	17	fail
Hydrocarbon Oil B (ISO VG 150)	284	312	410	continuous burn	18	fail

* 400°C is the maximum fire point value that can be attained with the equipment

aromatic hydrocarbons. This ranking is also found in other tests as will be seen in subsequent sections.

Oxygen index test – Another potential quality control test is the measurement of oxygen index – otherwise the percentage volume of oxygen that will just support combustion of the fluid under specified conditions. The technique involves heating (and eventually igniting with a pilot flame) fluid held in an open glass dish. The oxygen content of a mixture with nitrogen flowing over the sample is then controlled until the minimum level that will support combustion for at least 60 seconds is found. The details are specified in IEC Standard 1144, *Test method for the determination of oxygen index of insulating liquids.*

This method enables the comparison of certain fluids under conditions which have been suggested as measuring 'ease of flame extinction' [7]. The method tells us nothing about the ignitability or propagating tendency of the fluid and lacks sensitivity. Oxygen content is, of course, impossible to control in a fire situation and oxygen index values greater than 21 are almost entirely artificial. They might (erroneously) suggest that products with these values would not burn! The IEC procedure is also not valid for fluids with viscosities greater than 50 cst at 40°C or for water-containing products.Although the precision of the IEC method has yet to be established, from the data available the method appears promising as a quality control procedure and is relatively cheap and simple to carry out. However, it is not apparent that it offers any significant advantage over fire point in this respect.

The cone calorimeter and similar heat release tests – In recent years much work has been carried out on investigating the heat released on combustion from solids such as building materials, plastics and fabrics. The technique most commonly used involves a cone calorimeter and variations thereof.

In this test a sample of specified dimensions is heated in a current of air from above by radiant elements with a heat flux of up to 100 kW/m^2 until ignition takes place by means of a spark or pilot flame. Measurements can be made under these specific conditions of the time to ignition, the heat released (from oxygen consumption or the temperature rise of the fluid gases), smoke density, the composition of the volatile degradation products, mass loss etc.

As a result of the development of standard procedures for solids, the utility of the equipment for assessing the fire resistance of liquids has subsequently been examined. In a slightly modified procedure a dish containing a known volume of liquid is heated under similar conditions.

The importance of heat release measurements in determining flame propagation tendency was indicated earlier and the method certainly enables a comparative assessment of the relative ignitability of non-aqueous fluids to be made. As with 'pool fire' tests this method is of little practical interest when considering the likelihood of an external source of ignition of 20-100 kW/m^2 in contact with a open container with a significant depth of liquid. Under these conditions a major conflagration is already in process and the ignition of the fluid becomes rather academic.

It is also of little or no relevance to measure smoke and combustion products if the fluid does not burn under practical conditions, or when the degradation products contribute little to the total fire effluent.

Unlike the heat release measurements of the spray ignition test (see below), the cone-calorimeter tests cannot be reliably used for assessing water-based products, as during the heating process, water is lost and heat release measurements are made on the fluid enriched in the organic component.

The method is mainly of use as a screening tool for non-aqueous fluids, but it does have the advantage of being a procedure capable of measuring most of the parameters involved in the combustion of liquids.

Pool fire tests – In fire scenarios involving electrical equipment such as transformers and cables, it has been assumed in the past that a significant hazard is a leak or spill of an ignitable fluid leading to a pool fire, and that a highly volatile and flammable cleaning fluid presents the same degree of hazard as a high fire point lubricating oil [8].

As a result, a method for determining the ignitability of a pool of liquid has been developed and used in the evaluation and comparison of less flammable (or high fire point) insulating liquids [9]. The procedure involves igniting 4 US gallons of heptane in an open circular trough which surrounds 40 US gallons of the fluid held in an inner, concentric, pan. The convective and radiative heat release rates of the fluid under 'steady state' burning conditions are measured.

A study of the 'Ignitability of high fire point liquid spills' was subsequently reported by Modak [8]. Factors investigated included the thermal energy available from the ignition source, the depth of the pool, the fire point and thermal conductivity of the fluid and the conductivity of the container floor and walls. His investigations (under more severe conditions than these indicated above) suggested that 'high fire point lubricating oils and hydraulic fluids in thin layers would require sustained heat fluxes of the order of 20 kW/m^2 to cause the liquid surface to reach the fire point.' However, the need for such a high heat flux suggests the presence of a substantial fire independent of any ignition of the fluid and therefore the latter will probably be of secondary concern.

For deeper spills, the surface temperature rises faster due to the lower thermal conductivity and heat capacity of the fluids in comparison with those of the container. Even so a considerable heat flux is still required to ignite a high fire point liquid, a level of 10 kW/m^2 for more than 1000 seconds, which is necessary to ignite a phosphate ester. The author concludes that "volatile flammable material represents a more immediate fire threat since it only requires an ignition source to become a flaming fire. At the other end of the scale, high fire-point, fire-resistant fluids such as phosphate esters represent little risk as they require both a heat source to raise the surface temperature and an ignition source".

In common with other bulk ignition tests the pool fire technique should not be used to compare non-aqueous fluids with water-containing products even though the latter could eventually ignite under these conditions.

Transformer fire tests – A transformer can initiate a fire as a result of internal arcing followed by an explosion and expulsion of the contents, or the insulating fluid can leak out and be ignited. It may also be involved in an external fire, when it is expected to retain its integrity for a minimum period of time while fire-fighting is undertaken. Information on the behaviour of the equipment in a fire is important in deciding the installation requirements for the transformer.

To date, the only way of simulating the effects of a major breakdown of insulation has been to deliberately contrive the effect in a transformer and to monitor the behaviour of the insulating liquids on expulsion. With most fluids a fireball is rapidly formed but in the case of less flammable (or high fire point) insulating liquids, the flame is rapidly self-extinguished.

Similarly there is no alternative way of checking the resistance of the transformer and its insulant to an external fire than to test the unit in an external heat flux, either in the form of burning wooden cradles or large radiant panels mounted around the unit. Thermocouples inside the transformer monitor the change in temperature of the fluid in the windings and any tendency of the fluid to escape and ignite is noted. At the end of the test the transformer is checked to see if it is still capable of operation.

Such full scale tests are expensive to carry out but should not require repeating unless there were major changes in the design or a different insulating liquid was used.

Ignition of fluid absorbed on to a substrate

The absorption of fluid onto a substrate, such as pipe lagging, cotton waste or paper and board, as a result of leaks etc. frequently exposes a thin layer of fluid to oxygen, which aids combustion. (A 'wick' can easily turn a non-ignitable liquid at room temperature into one which is readily combustible.) If the fluid is absorbed into a medium that is itself highly flammable, for example paper, the fluid may reduce the ease of ignition of the paper (particularly high fire point fluids), but ignition of the paper may provide sufficient heat for the fluid itself to combust – perhaps after driving-off any aqueous component.

If, however, fluid is absorbed into a medium which is non-flammable, such as pipe-lagging, then the fire hazard will depend on the density of the medium (and hence oxygen availability), its temperature and heat transfer characteristics, fluid viscosity and type. The absorption properties of the medium are also important, as will be shown later.

In order to assess the hazards arising from different fluids in this situation a variety of tests have been developed. These include:

CETOP RP 66H (*Wick test*)
7th Luxembourg Report, Section 3.2.1 (*Determination of the persistence of flame on a wick*)
7th Luxembourg Report, Section 3.2.2 (*Determination of flame propagation in a fluid/coal dust mixture*)
ASTM D5306 (*Linear flame propagation rate of lubricating oils and hydraulic fluids*)
US Bureau of Mines Schedule 30,Part 35 (*Test to determine effect of evaporation on flammability*)
IEC 1197 (*Method for the linear flame propagation of insulating liquids using a fibre glass tape*)
EPRI Report NP-1447 (*Soaked cube fire test*)

The methods fall basically into three types:

1 The ignition of a pre-soaked wick with varying applications of an igniter flame. Measurements are made of the time for self-extinguishment of the flame and, in certain circumstances, the rate of flame propagation along the 'wick'. The wick is commonly an aluminosilicate or glass fibre tape or board but can also be formed from coal dust.

2 An evaluation of the effects of evaporation on fire resistance by cycling a fluid-soaked wick through an ignition source until the fluid ignites

3 The measurement of exothermic reactions taking place inside a sample of insulating material containing a known amount of fluid as the temperature is increased.

Wick tests in the first group are a mixture of pass/fail types and those which attempt to discriminate between different fluid types. The degree of discrimination, however, is generally not very good as indicated in Table 4 with reference to the most commonly used methods. Water-based fluids do not ignite under these conditions and the methods are therefore limited in use to certain non-aqueous fluids.

The other test in the same category involves ignition of a paste of fluid and coal dust formed into a thin rectangular layer of known thickness. An igniter flame is applied at one end and measurement made of the flame propagation and the time to extinction. The 'wick' in this case is combustible and heat is released from combustion of both the coal and the fluid. Of obvious relevance to the mining industry, the test can be used to assess the propagating tendency of different fluids. In reality there are

TABLE 4 – The ability of different wick tests to discriminate between fluid types

Method	Fluid type	Mineral oil	Synthetic hydrocarbons	Carboxylate esters	Silicone fluids	Phosphate esters	Water-glycol fluids
CETOP RP 66H	poor discrimination-most fluids burn continuously				flame quickly self-extinguished - no propagation		no ignition
ASTM D 5306	good discrimination in flame propagation rate				no data	no ignition	no ignition
IEC 1197	moderate - good discrimination in flame propagation rate					no ignition	no ignition

circumstances underground when an aqueous fluid on soaking into coal dust could lose its water content owing to localised elevated temperatures and/or forced evaporation, and the test would then be more appropriate to fluid with a low (or no) water content.

The coal used in this test is ground to a specific particle size range and has a known calorific value. If these parameters change so too will the test results, though the same ranking will probably remain. At present the future of the test is uncertain owing to the impending closure of the pit which was previously the source of the coal dust.

In the US Bureau of Mines test an 'ordinary' pipe cleaner is soaked in both aged (2-4 hours at 150°F) and unaged test fluid. After draining excess fluid, the cleaner is cycled in a horizontal plane through a Bunsen burner flame at 25 ± 2 cycles/minute. The number of cycles required to obtain a self-sustaining flame is noted. The rationale for the use of this test is difficult to understand as it does not relate to any obvious hazard, and the test conditions favour the non-aqueous fluids.The viscosity dependence of this test is such that an ISO VG 100 mineral oil can meet the test limits! This test therefore seems to discriminate in favour of fluids which under other conditions would be regarded as quite flammable.

In view of the limited comparability information offered by these tests their value in practical terms is also restricted. Clearly, propagation rates can be of value in fire-modelling techniques but the main value of this type of test must be for quality control – particularly as the tests are simple and cheap.

Fires attributed to spontaneous ignition can occur when combustible fluids leak into pipe lagging and other insulation covering hot surfaces. They can occur even if the lagging material is at temperatures well below published autoignition temperature values – but not necessarily below the minimum autoignition temperature.

The relative ignitability of fluids soaked into insulation can be assessed by comparing the temperatures at which the initial exotherm takes place as a sample of insulating material of specified dimensions, and containing a fixed volume of fluid is heated. The temperature rise due to the exotherm will depend both on the extent of oxidation and the rate at which energy is lost to the atmosphere and adjacent insulation where the fluid is not combusting.

Data published by EPRI [10] comparing a range of non-aqueous fluids in a 'soaked cube test' using calcium silicate insulation are given below in Table 5 and compared with their autoignition temperature.

TABLE 5 – A comparison of initial exotherm temperatures in insulation with autoignition temperatures

Fluid	Initial exotherm temperature °C	Autoignition temperature D 2155 °C
Mineral oil (ISO VG 46)	190	350
Silicone fluid (ISO VG 46)	204	430
Diester (ISO VG 32)	218	405
Phosphate ester 1 (ISO VG 32)	232	500
Phosphate ester 2 (ISO VG 32)	329	570

The fact that an exotherm occurs does not necessarily mean that the fluid will ignite. That will depend on the amount of heat generated by the exotherm, oxygen availability etc. With mineral oil, for example, although an initial exotherm was found at 190°C, ignition did not occur until between 218-250°C while neither of the phosphates tested ignited up to oven temperatures of 450°C.

Evaluation of different types of lagging reveals a decrease in the spontaneous ignition temperature in the order:

glass fibre > calcium silicate > absestos

suggesting that the controlling factors are material density and oxygen availability.

The ASTM has previously examined the possibility of developing a lagging test procedure but this foundered, it is thought, on the difficulty of specifying a suitable lagging material and also on test precision. This was unfortunate as the method has obvious application and does emphasise the inadequacies of the existing autoignition test procedures. The hazard this test simulates is applicable to water-based products, most of which would be expected to ignite under these conditions after first losing the aqueous content.

Spray ignition tests

The possibility of fluid escaping under pressure from a hydraulic system and being ignited by a flame or spark has been recognised as a major fire hazard for many years. Currently the following standard procedures are used for assessing this aspect of fire resistance:

7th Luxembourg Report, Section 3.1 (3 tests)
Factory Mutual Standard 6930
US Bureau of Mines Schedule 30, part 35
Nordtest 031 Fire Test
AMS 3150 C

Most of the above procedures involve high pressures (up to 70 bar) but none operate at the very highest pressures found in industrial hydraulics (~350 bar).

Traditionally spray ignition tests have attempted to measure ignitability and flame propagating tendency of fluids under specified conditions of pressure, fluid temperature, nozzle dimensions and ignition energy. Unfortunately there has been no general agreement as to what these conditions should be reflecting, perhaps, the different requirements of different applications. Until recently the tests have also been of the pass/fail type and therefore have not permitted a ranking of different fluids. They also did not have good precision primarily due to the difficulties of obtaining a repeatable spray pattern and droplet size.

The apparent duplication of methods in the Luxembourg Report arises for the following reason. In Europe two spray ignition tests of differing conditions and severity were used for many years by the UK and Continental Europe. The continental test was originally written around the performance of polychlorinated biphenyls. The UK test, however, was less severe and permitted the use of other water-free products. In an attempt to harmonise European requirements both spray tests were incorporated into the 6th Luxembourg Report and the competent authority was allowed to select a procedure appropriate to its needs. This situation was a temporary expedient while a new test designed to rank all the current types of fire-resistant fluids was developed [11]. This latest test is essentially an 'ease of flame stabilisation method' which uses the heat released from burning fluids to classify their performance in terms of an 'Ignitability Factor' – although the fluid is pre-ignited. The test is also included in the latest (7th) edition of the Luxembourg Report, and it is the intention for this test to replace the earlier methods when sufficient experience with its use has been obtained.

Results of the new spray test on fluids of various types are indicated in Figure 1.

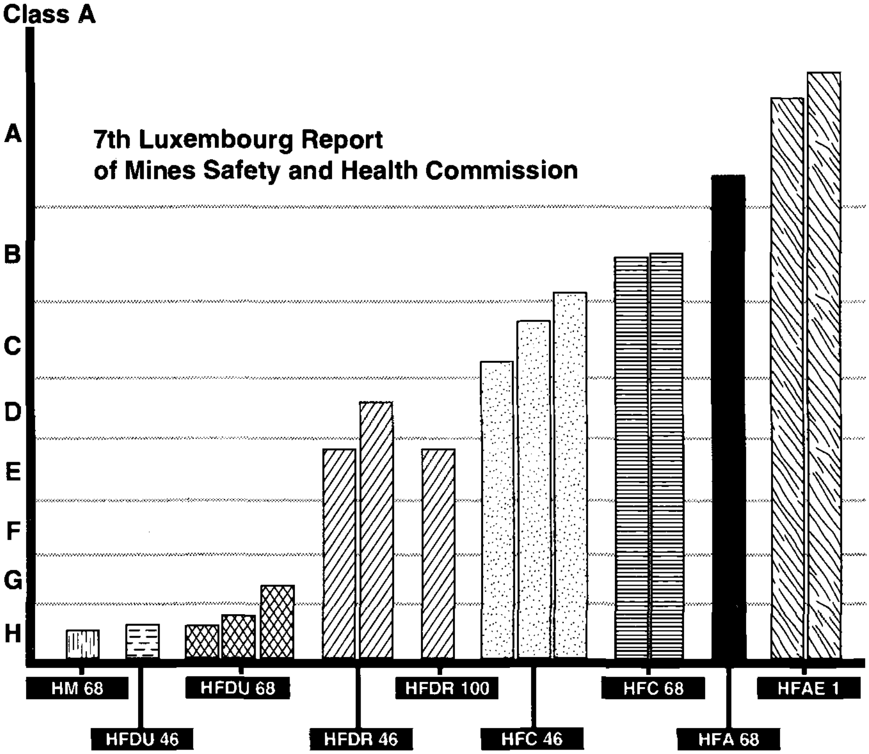


FIGURE 1 – Stabilised flame heat release test

As can be seen the performance varies considerably, with the water-based fluids excelling. The ability to assess all fluids on an equal basis is an important advantage of the new test.

Another new spray ignition method [12] has been developed by the Factory Mutual Research Organisation and features in the latest version of Factory Mutual Standard 6930 draft, *Specification Test Standard for Flammability of Hydraulic Fluids*. The grounds for developing this method were also to replace an earlier, less discriminating procedure. Although both of the new methods have similarities, for example they measure heat release from a stabilised flame at low fluid pressure, the treatment of data is somewhat different. In the Factory Mutual procedure a non-dimensional spray flammability parameter is derived from the chemical heat release rate and the critical heat flux for ignition.

The chemical heat release rate is calculated from the generation rates of carbon monoxide and carbon dioxide. It presupposes that in flaming combustion, heat is released with the production of these gases. As was indicated earlier, however, this is not necessarily valid for compounds which contain elements other than C, H and O.

The critical heat flux for ignition is defined is the heat flux below which (piloted) ignition is not possible. This parameter is measured separately in a test similar to a flash/fire point determination but where the heat source is above rather than below the sample. The rationale for including this parameter is because ‘spray fires of highly volatile liquids, e.g. methanol, ethanol and heptane, would otherwise be classified as relatively low heat release rate fires’[12] (another instance of a single characteristic that when used independently could produce misleading information). As a result it was felt necessary to take volatility into account.

The results of the determination of the spray flammability parameter for various classes of fire-resistant fluid by the new method are indicated in Figure 2 [13] and related to their performance in the previous Factory Mutual approval test procedures.

At high fluid exit velocities the performance of the different fluids are ranked approximately in the same order as found in the European test above.

A further advantage of both the above methods is that by measuring the heat release of combusted fluid, the effect of additives which increase the droplet size in a spray (reducing the surface area exposed to oxygen) and make the fluid more difficult to ignite, are largely negated. This is a wholly artificial means of increasing fire resistance which suffers from the following disadvantages.

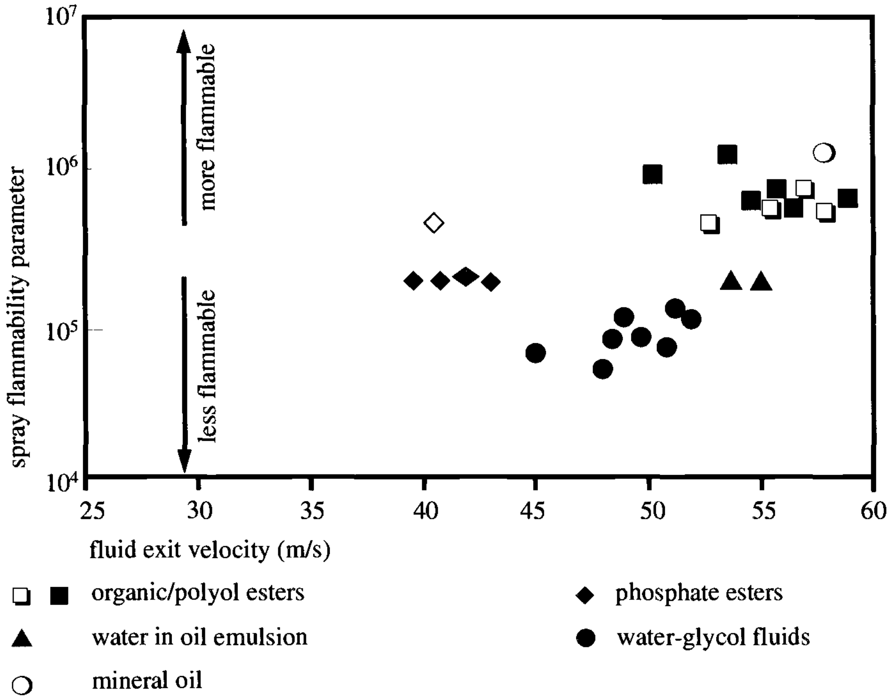
- the polymeric materials used for viscosity modification can result in the use of higher viscosity products than would be ideal for the application.

- the polymers tend to shear-down in use with a consequent reduction in spray ignition performance.

- the incorporation of a polymer offers no significant beneficial effect when the fire resistance is evaluated under other conditions, for example hot surface ignition.

- the fire-resistance of a spray depends on droplet size and hence bulk fluid temperature. The higher the temperature the lower the viscosity and drop size and also the spray ignition performance. Table 6 shows the effect on fluid burn times of raising the bulk fluid temperature of a polymer-thickened ester in comparison with a triaryl phosphate. Depending on the fluid temperature the ester performance varies from no ignition to continuous burning.

Although suffering from similar limitations as other tests in not fully reproducing the exact behaviour in a fire because of the limited selection of test conditions, spray tests are probably closer to reality than most. These methods are also advantageous in that they enable the whole spectrum of fire-resistant fluids to be compared and ‘the



open symbols indicate that fluids failed in previous Factory Mutual approval tests
closed symbols indicate that fluids passed in previous Factory Mutual approval tests

FIGURE 2 – Spray flammability parameter as a function of fluid exit pressure at 6.9 MPa nozzle pressure

TABLE 6 – Effect of fluid temperature on spray ignition test performance

Polyol ester (ISO VG68)		Phosphate ester (ISO VG46)	
Temperature (°C)	Burn time (seconds)	Temperature (°C)	Burn time (seconds)
19	0	21	3
25	0	34	3
50	6	49	4
60	continuous	60	4
77	continuous	77	4
...	...	90	3
...	...	100	5
...	...	120	4

effect of drop size on combustion behaviour can be eliminated and fluids classified on the basis of their fire resistance only' [12].

Hot surface ignition

According to Early and Hatton [1], the ASTM in 1939 collected and analysed data on fires involving hydraulic fluids in aviation, mining and general industry. In 46% of all fires studied the source of ignition was found to be a hot surface – by far the most common cause. Molten metal ignition was found to be of particular importance in industrial applications while spark ignition was the dominant feature in mining fires. Open flame and frictional ignition sources were regarded as of minor importance.Today, hot surface and open flame ignition whether of a spray or jet of liquid, remain the most important hazards. Spark ignition, by contrast rarely appear to be a concern and there are now no standard procedures for evaluating this aspect of fluid behaviour.

Test falling into the 'hot surface' category include both hot surface and molten metal procedures. The most well known tests of this type are:

Autoignition temperature (ASTM: D286, D2155 and E659)
Hot manifold test (VV-L-791b Method 6053 and CETOP RP 65H)
Hot channel test (Factory Mutual Standard 6930)
Molten metal ignition (Rheinisch Westfälischer Technischer Überwachungsverein [TÜV])

Autoignition temperature – The measurement of autoignition or spontaneous ignition temperature is another procedure that is widely misunderstood and misquoted. The fact that over the years there have been three different ASTM methods (D286, D2155 and E659), each requiring different equipment and involving increasing sophistication, has not helped.

Each method involves injecting a small quantity of liquid into a test vessel of prescribed size under specific conditions. Depending on the test procedure, the hot flame (visible) ignition is measured and also, in recent variants, the presence of cool flames and the ignition delay time. This last parameter is the time required after injection for the sample to volatilise and combust with the production of a visible flame.

Autoignition temperature is very much dependent on a number of variables including:

- sample mass
- vapour pressure of sample
- system pressure
- shape and vessel size (hence fuel/air ratio)
- vessel material

As a result, several papers have been published highlighting the variation in results that can be obtained, (e.g. references 14-15). Of these variables, perhaps the most significant is the vessel size. Changing from a 125cc flask (as specified in the D286 method) to a 500cc vessel as specified in the most recent test (E659) can result in reductions in autoignition temperature of 30-60°C. Ignition in even larger vessels may result in further reductions. There is in fact a direct relationship between autoignition temperature and ignition delay time; the higher the former the shorter the delay time [15]. Cool flames appear to behave in a similar way, but, of course at lower temperatures.

In reporting autoignition test data and particularly when comparing results on different fluids it is essential to know which test condition was used and preferably the ignition delay time as well. Although in theory the D286 and D2155 methods are extinct, results of these tests are still widely quoted. This is probably because the original test data that was published on many fluids was generated by these methods. In the event of lower results being reported for the E659 method on the same product, some customer confusion would inevitably occur and such a move would necessitate accompanying user awareness. Specification requirements are also slow to adapt to method changes.

A further limitation of the autoignition method is that the results should not be regarded in isolation. In Table 7, for example, hot flame data on some common fluids and highly flammable solvents is listed. Little difference is seen and the solvents would be classified as fire-resistant on the basis of this data. Autoignition information in isolation therefore does not necessarily enable a predication of fire resistance behaviour and comparative testing should preferably be undertaken in association with other forms of assessment.

TABLE 7 – A comparison of autoignition temperatures of some common solvents and hydraulic fluids with flash and fire point data

Fluid/solvent	Autoignition temperature ASTM D2155 (°C)	Flash and fire point (open cup) ASTM D92 (°C)
Mineral oil (ISO VG 46)	350	200/225
Carboxylate ester (ISO VG 68)	415	266/313
Phosphate ester (ISO VG 46)	575	245/360
Toluene	536	4/see note
Ethanol	402	12/ see note
Acetone	519	–19/see note
Pentane	313	–40/see note
Heptane	223	–8/see note

Note – Fire point data for solvents is seldom quoted but values are usually very close to the flash point. The latter is determined for solvents by the closed cup procedure.

The high autoignition values of some volatile solvents can be partly attributed to their high thermal stability which determines their reactivity with oxygen but the main reason is probably due to their very high volatility. This results in loss of vapour from the test vessel and/or the rapid production of a vapour/air mixture which exceeds the upper flammability limit. In contrast, higher molecular weight products would be expected to volatilise more slowly and to remain within the limits of flammability long enough for ignition to take place. The difference between autoignition temperature (and other hot surface tests) and fire point illustrates the ability of a small but hot pilot flame to promote ignition compared with a surface at a somewhat lower temperature. The extent to which this difference is due to the catalytic effect of the free radical content of the flame is unknown but could be significant.

Autoignition temperatures of water-based hydraulic fluids are not normally quoted. Available data given in Figure 3 [16] in fact suggests that the water content of water-in-oil emulsions and water-glycol fluids has little effect on autoignition and that

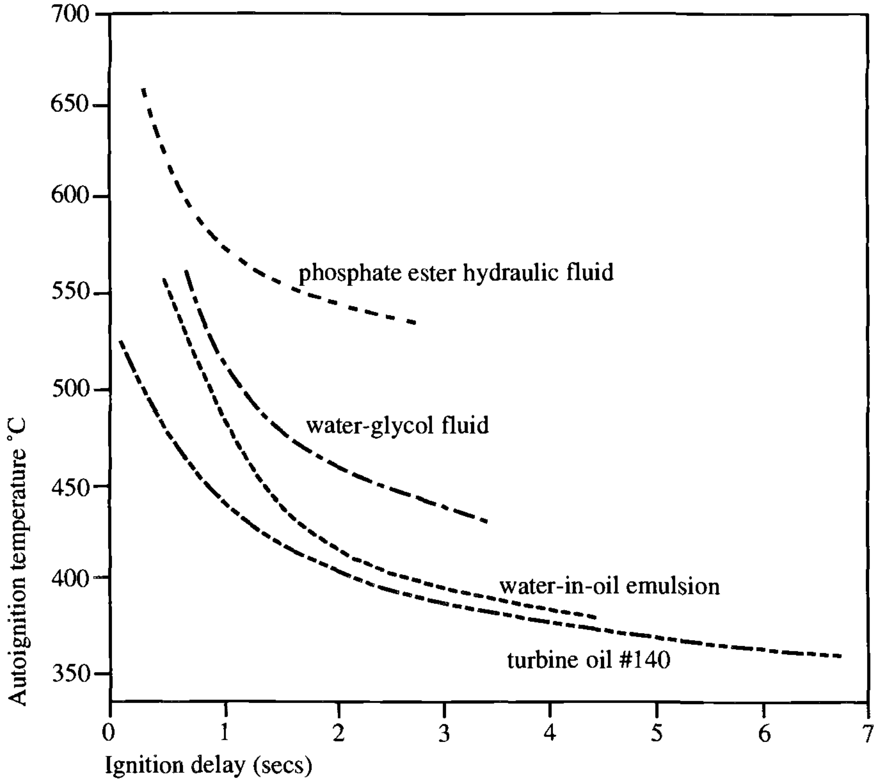


FIGURE 3 – Relationship between autoignition temperature and ignition delay

the minimum values correspond closely to those of the organic components of the fluids. Unsurprisingly, therefore, under these conditions, phosphate esters are seen to be less flammable than water-based fluids.

Hot Manifold and Hot Channel tests

The other most widely used 'hot surface' tests which are regarded as being performance-related are the so-called Hot Manifold test and the Factory Mutual Hot Channel test. In the former case, fluid at ambient temperature is dropped at a prescribed rate on to the surface of a tube heated from within to 704°C (1300°F) and maintained at an angle of ~5° to the horizontal. The fluid is observed for ignition on the tube and, if this occurs, whether the fluid continues to burn when it is collected in a catchment tray below the tube. In the Hot Channel test, fluid is sprayed at 1000 psi and 60°C on to a steel channel inclined at 30° to the horizontal and heated initially to 704°C. The flammability of the fluid is noted. In the latter test, however, the heaters are turned off prior to the spraying of the liquid and there is subsequently no control over the surface temperature. This reduces more rapidly in the case of water-based fluids as a result of their better cooling behaviour.

Both these are normally used as pass/fail tests at a fixed temperature. The use of an arbitrary limit, however, can result in a failure to discriminate between different fluids (Table 3), and although comparison may be possible by varying the tube or channel temperature (Table 7), precise control in the latter case is difficult.

TABLE 7 – Hot Manifold ignition temperatures on different fluids

Fluid	Ignition temperature (°C) (CETOP RP 65H)
Mineral oil (ISO VG 46)	350
Carboxylate ester (ISO VG 46)	400
Phosphate ester (ISO VG 46)	800
Water-glycol fluid (ISO VG 46)	>800

We should also not necessarily expect the two tests to give identical results on the same fluid because of the different modes of application, i.e. drops or a stream as opposed to a spray, and particularly as a result of differences in residence time on the metal surface. In the Hot Manifold test water-based fluids perform well owing to the rapid formation of steam around the drop as it hits the surface. This encourages the drops to 'bounce off' rather than to maintain contact. A further potential disadvantage of this procedure is the lack of control in the rate of application of the fluid.

With the Hot Channel test, the situation is more complicated. Some of the fluid (including non-aquous media) will bounce-off the channel as a result of the speed and angle at which it hits the surface. Other fluid will hit the surface and ignite providing a flame and a further heat source for the ignition of fluid sprayed onto the surface.

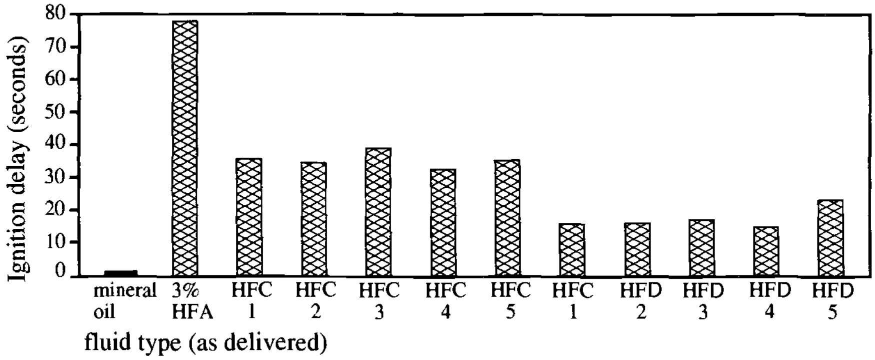
Water-based fluids will not normally ignite under these conditions because limited residence time on the surface is encouraged by the equipment design and, in the hot channel test, by the use of a spray which encourages volatilisation of the fluid. The dropping of fluid or even a low pressure spray on to a flat surface maintained at a lower temperature could produce totally different data.

It has been proposed that hot surface ignition is autoignition taking place in a container of infinite volume. Monwa and Honma [16] in fact suggest that an empirical relationship exists between the two parameters expressed as follows:

Hot Manifold ignition temperature = 2 x minimum autoignition temperature – 280°C

On the limited data available this may have some validity, for non-aqueous fluids.

Ignition delay time, which is a feature of both autoignition and other hot surface tests is the criterion evaluated by the TÜV molten metal test [17]. In this method a known volume of fluid is poured on to the surface of molten aluminium at 800°C (1472°F) and the ignition delay time measured. Typical results for fire-resistant fluids (see Figure 4) show delays of 30-40 seconds for water-glycol fluids and 15-22 seconds



for phosphate ester fluids respectively.

FIGURE 4 – Ignition delay times for different fluid types at 800°C on molten aluminium

The concept of ignition delay as 'escape time' in fact goes back many years and results reported earlier [18] indicated that phosphate esters exhibited no ignition up to 1400°F (745°C) whereas the water-glycol fluid ignited at all temperatures from 800°F (427°C) upwards (Table 9). This is perhaps another example of the misleading picture obtained by using a single temperature for comparison. Below 1400°F it could be argued that phosphates are the safer fluid but this position is reversed at higher temperatures.

TABLE 9 – Ignition delay times at different temperatures for water-glycol and phosphate ester fluids on molten aluminium

Fluid type	Ignition delay time (seconds)											
	Test temperature (°C)											
	800°F	900°F	1000°F	1100°F	1200°F	1300°F	1400°F	1500°F	1600°F	1700°F	1800°F	1900°F
Water-glycol fluid (ISO VG 46)	305	165	128	75	78	55	45	38	38	38	32	26
Phosphate ester (ISO VG 46)	← no ignition →							4				

THE PRINCIPLE OF COMPARABILITY

It was indicated earlier that valid comparisons of the behaviour of different materials in fire tests could only be made if the products behave in the test in a similar fashion. It will also have become apparent that the performance of fire-resistant hydraulic fluids varies with their chemical composition and physical form. There are, in fact, three major areas in which the fluids differ from each other:

- homogeneity – contrast single phase products like the esters with emulsions
- volatility – both relatively low volatility non-aqueous fluids and volatile water-based materials are used
- composition of gaseous degradation products – some fluids degrade to form only oxides of carbon while others also form oxides of nitrogen, phosphorus etc.

Each of these characteristics impacts on fluid behaviour in a fire and as a result comparisons between fluids with different characteristics are, strictly speaking, invalid.

These differences are very obvious. Less obvious is the typical behaviour of silicone fluids in fire tests. The production of silica (or silicon dioxide) is readily observable and this has a significant effect on mass loss as well as on the actual measurement of heat released, particularly in heat release tests like the cone calorimeter, where the solid deposit can function both as a wick and as a heat shield from the ignition source radiating down on the surface. What is less obvious is the fact that silicones are reported to undergo two other irreversible reactions as a result of being subjected to thermal and oxidative stress [4]. Unlike many other organic molecules, which change their physical state from liquid to gas without undergoing any other transformation, the silicone fluid molecule is unable to vaporise without first being converted into low boiling cyclic materials – mainly tetramers and pentamers (with flash points of 60°C and 82°C respectively). The presence of these molecules can be expected to influence the flammability of the liquid to an extent varying with their content.

As a result of the disproportionation reaction silicones also cross-link or gel. Bastian [19], in fact suggests that owing to the repetitive flame impingement on the fluid surface in the Cleveland open cup method, gel formation occurs, which eventually hinders volatilisation and makes the determination of the true flash and fire points impossible.

It is obvious that such behaviour makes a valid comparison between silicones and other fluids in laboratory tests untenable, and for this reason it is important that these fluids are assessed under full scale conditions.

CONCLUSIONS

The simulation of the behaviour of an oil or hydraulic fluid in a full scale fire by a laboratory test is a difficult and often impossible task. No simple method can satisfactorily reproduce all the variables that are involved. As a result test methods have grown both in numbers and complexity as researchers try to duplicate more closely the conditions found in different fire hazards. Unfortunately, the results of new tests often tell us no more than could be intelligently extracted from existing procedures – particularly as those tests capable of discrimination rank the different fluid types in approximately the same order.

At best, therefore, laboratory fire resistance tests can compare different fluids in terms of their relative ignitability or tendency to propagate flame, but cannot guarantee the performance of a fluid in an actual fire.

Comparisons are also frequently made of fluids under strictly non-comparable conditions, for example in the heat of combustion test. Non-aqueous and water-containing fluids also behave in different ways owing to their different physical and chemical nature and cannot readily be compared on an equal basis. While new spray tests are useful in this respect the ranking of fluids in this test clearly does not apply to the situation where water evaporates from a fluid leaving behind a flammable residue. Under these conditions some products normally regarded as highly fire resistant can ignite at only moderate temperatures.

The selection of methods for identifying the fire resistance of fluids depends initially on whether they are aqueous or non-aqueous and also on whether an inter-group comparison is required. In both cases a spray test and a hot surface test would ideally be required (see Table 10). For comparisons of aqueous fluids the use of a spray test measuring heat release is necessary, but for non-aqueous fluids an alternative combination of a hot surface test and a fire point, cone calorimeter or wick test should be considered.

TABLE 10 – Recommended procedures for specific fire test parameters

Property	Test procedure
Ignitability	Hot surface*
Self-propagation	Wick, hot surface*
Ignition delay	Hot surface, cone calorimeter
Heat release	Cone calorimeter, spray**
Smoke	Cone calorimeter, spray**
Thermal degradation products	Cone calorimeter
Relevance to major fire hazards	Spray**, hot surface*, wick
Ability to evaluate all fluid types on equal basis	Spray**, hot surface* – selected tests

Notes

*Hot surface in this context means hot manifold or hot channel tests

**Applies to new Factory Mutual test and section 3.1.3 of the 7th Luxembourg Report

REFERENCES

1 Early, C.L. and Hatton, R.E., 'Industrial and ASTM fluid fire test programs', *Fire resistance of hydraulic fluids*, ASTM STP 406, pp105-132

2 Totten, G.E. and Webster, G.M., 'Review of testing methods for hydraulic fluid flammability', *SAE paper 932436.*

3 British Standard 6336, 'Development and presentation of fire tests and their use in hazard assessment'. British Standards Institute, 1982

4 Bastian, J., 'The comparability of 'silicones', with particular reference to current standardisation efforts and transformer norms', unpublished paper.

5 Burgoyne, J.H. *et al*, 'The significance of open flash points', *J.Inst. Pet.*, vol 53, 526, pp 338-341 (1967).

6 Sundquist, K, 'Flash point – unreliable method', *Nynas Naphthenics*, No. 2, pp 10-11 (1991).

7 Weil, E.D. *et al*, 'Oxygen index: Correlations to other fire tests', *Fire and Materials*, vol 16, pp 159-167 (1992).

8 Modak, A.K., 'Ignitability of high fire point liquid spills', *EPRI Report NP 1731* (1981).

9 Factory Mutual Standard, 'Less flammable transformer fluids – Class 6933"

10 'Evaluation and test of improved fire-resistant fluid lubricants for water reactor coolant pump motors', *EPRI Report NP 1447*, vol. 1, section 10 (1980).

11 Yule, A.J. and Moodie, K., 'A method for testing the flammability of sprays of hydraulic fluid', *Fire Safety Journal*, vol 18, pp 273-302 (1992).

12 Khan, M. and Brandao, A.V., 'Method of testing the spray flammability of hydraulic fluids', *SAE Paper 921737.*

13 Factory Mutual Specification Test Standard for flammability of hydraulic fluids – Class number 6930

14 Kuchta, J.M., and Cato, R.J., 'Ignition and flammability properties of lubricants', *SAE Paper 680323.*

15 Hilaldo, C.J. and Clark, S.W., 'Discrepancies and correlations of reported autoignition temperatures', *Fire Technology*, vol 8, 3, pp 218-227 (1972).

16 Monwa, Y., and Honma, Y., 'Fire resistance of lubricating oils', *Junkatsu*, vol 16, 5, pp 364-369 (1971).

17 Beyer, R. and Bauer, K., 'Schwerentflammbarkeit von Drückflüssigkeiten beim Kontakt mit Metallschmelzen', *Ölhydraulik und Pneumatik Sonderdruck* No.6, 1988.

18 McDonald, W.F., 'Escape time – an important new concept in fire resistance', *The Houghton Line*, vol 34, 4, pp 1-12, 41-43 (1970).

19 Bastian, J., private communication, 1 March1995

Ted A. Marolewski[1] and Edward D. Weil[2]

A REVIEW OF PHOSPHATE ESTER FIRE RESISTANCE MECHANISMS AND THEIR RELEVANCE TO FLUID TESTING

REFERENCE: Marolweski, T. A. and Weil, E. D., **"A Review of Phosphate Ester Fire Resistance Mechanisms and Their Relevance to Fluid Testing,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: The fire resistance of phosphate esters is primarily a result of properties imparted by the phosphate nucleus. These properties make triaryl phosphate esters difficult to ignite and cause them to self-extinguish. Fluid fire resistance is a function of different chemical and/or physical characteristics depending on fire test configuration. Studies performed on phosphate esters for flame retardant and fire extinguishing applications provide useful analogies to fluid fire resistance. The soaked cube fire test predicts the oxidation exotherm temperature of a fluid on steam pipe lagging. The impact of fluid properties on the decomposition and ignition temperature is discussed. A simple extension of the fire point test was used to illustrate the fire resistance of various phosphate ester/polyol ester mixtures. The transition to a self-extinguishing mixture occurs over a narrow phosphate ester concentration range.

KEYWORDS: triaryl phosphate esters, fire resistant fluids, flame retardant mechanisms, lagging fires, self-extinguishing fluids

---

[1] Research Manager, Akzo Nobel Chemicals Inc., 1 Livingstone Avenue, Dobbs Ferry, NY 10522.
[2] Professor, Polymer Research Institute, Polytechnic University, Brooklyn, NY

Phosphate esters have been used in a variety of industrial applications for many years due to their excellent fire resistance. Phosphate ester fire resistance encompasses two critical features:

1. Phosphate esters are difficult to ignite
2. If ignited, phosphate esters will self-extinguish

The performance of phosphate esters in these two areas can be illustrated with a variety of standard tests. These tests are designed to provide information on the relative performance of hydraulic fluids and lubricants. Since fluid applications vary significantly, fire tests cover a broad spectrum of configurations. Some tests, like the autoignition temperature (AIT), provide information applicable to many uses. Other tests, like the compression ignition test, are more focused on a specific critical application [1]. The physical state of the fluid varies significantly in different fire tests. For example, the fire point test uses a small pool of fluid, whereas the fluid is present as a film on a glass surface in the AIT, or as small droplets in spray tests. The relative contributions that various fluid chemical and physical properties make in a given test will be highly dependent on test configuration and fluid state.

Certain chemical and physical properties of phosphate esters can be related to fire resistance in a relatively direct manner for a given test. High thermal and oxidation stability are controlling factors in the autoignition test [2]. Low volatility is important in the fire point and spray flammability tests [3]. Low heat of combustion is a significant factor in the new Factory Mutual spray flammability test method [3]. All of these factors contribute to the frequently cited inherent self-extinguishing properties of phosphate esters [4,5]. But these physical and chemical properties may not be sufficient to explain the fire resistance of phosphate ester fluids. Chemical flame retardant activity should also be considered when describing potential modes of action for phosphate ester fire resistance.

The literature on phosphate esters as flame retardants for plastics distinguishes between condensed phase and vapor phase mechanisms [6]. The proposed vapor phase mechanisms are most pertinent to our discussion. These can be broken down into chemical and physical modes of action. From a chemical perspective, phosphorus compounds have been shown to strongly inhibit flame reactions. Phosphate esters break down in a flame to form fragments which could scavenge hydrogen atoms and induce hydrogen atoms to recombine. This would inhibit the following rate-controlling, branching step in flame chemistry:

$$H\bullet + O_2 \rightarrow HO\bullet + O$$

Oxidation of phosphate esters generates finely divided particles of polyphosphoric acid and phosphorus oxides which also contribute to radical quenching reactions by providing sites for radical recombination.

The physical mode of action appears to be operative in recent studies on phosphorus flame retardants in polystyrene[7]. A comparison of triphenyl phosphate and triphenylphosphine oxide, which have very different chemistries but very similar flame retardant action in polystyrenes, suggests that the action may be more physical (heat capacity, low fuel value, volatility at preignition temperatures) than chemical. A critical Damkoehler Number must be reached for ignition[8,9]. The Damkoehler Number is defined as the ratio of the fuel's time in the combustion zone divided by the time required for combustion. The volatile slow-burning phosphorus compounds sweep the fuel out of the combustion zone (reducing the numerator of the Damkoehler Number) at the same time they retard the combustion by dilution, cooling and possibly chemical inhibition (increasing the denominator of the Damkoehler Number). Phosphate esters can cool the flame by endothermic vaporization and potentially by endothermic dissociation reactions [6]. To assess the relative contribution of chemical and physical flame retardant mechanisms requires careful study.

In addition to the extensive literature on the use of phosphate esters as flame retardants for plastics, a recent patent teaches that organophosphorus compounds significantly enhance the fire extinguishing properties of halon compositions [10]. Specifically, it was shown that the addition of 30% of a triaryl phosphate to a halon mixture will extinguish an oil fire 40% faster and with 60% less extinguisher composition than the halon mixture alone. Halon extinguishing compositions are regarded as chemical action agents because they decompose in the flame forming fragments which terminate combustion reactions. The synergy with triaryl phosphates suggests a similar radical quenching mechanism for the phosphate ester in the flame. However, the chemical action theory for halon compositions has been challenged on the grounds that physical effects are sufficient to explain the flame suppression [11,12,13]. This illustrates the difficulty of postulating mechanisms in this complex area.

DISCUSSION

Data from two fire tests will be reviewed in the context of fluid physical and chemical characteristics which may be important parameters in each case. The potential role of the flame retardant chemical mode of action will be discussed.

Soaked Cube Fire Test

Phosphate ester fluids are used extensively in the electro hydraulic control systems of thermal and nuclear powered steam turbine generators. Phosphate esters obviate one of the primary hazards in a power station, fire resulting from mineral oil hydraulic fluid soaking into steam pipe insulation or lagging and spontaneously igniting [14]. Similar hazards from steam turbine oils still exist. This problem is being addressed in Russia where phosphate esters have been successfully used to lubricate large steam turbines for over ten years [15].

Lagging fires will occur with mineral oil even though the lagging is below the AIT of the oil. The porous lagging provides a high surface area for oxidation to occur. The oxidation decomposes the oil generating volatile, combustible products. Oxidation also creates a localized hot zone exceeding the AIT of the oil. Spontaneous ignition and a fire is the eventual result of the oil spill.

Westinghouse developed the soaked cube fire test to simulate this phenomenon and rank fluids for fire resistance [14]. The soaked cube fire test is performed using cubic specimens, 2.54 cm (1.0 inch) on a side, of calcium silicate pipe insulation. A flat-bottom, fluid well is drilled in the top of the cube and a hole is drilled at the center line in the side for a thermocouple. The cube is heated at 538°C for 72 hours to burn off the insulation binder. The cube is now ready for fluid testing. The cube is placed in a furnace and allowed to stabilize at the oven temperature. One mL of fluid is injected into the well in the cube via a hole in the top of the oven. The soaked cube exotherm point is defined as the highest temperature to which the cube can be heated without the exothermic temperature rise of the cube exceeding 28°C (50°F) after fluid injection. The exotherm points of several triaryl phosphate esters were higher than the typical in-service lagging temperature of 288°C (Table 1). Other fluids, such as carboxylate esters, petroleum oil lubricants, and silicone oils, all exhibited exotherm points significantly below 288°C even though their AIT's were all higher.

Differences were also observed among the triaryl phosphate esters. The soaked cube fire test exotherm point increased going from methyl to tertiary-butyl substituents on triaryl phosphate esters. This is consistent with data showing that t-butylphenyl diphenyl phosphate esters are very stable to oxidation [16]. This is attributed to the absence of benzylic hydrogens which are sites for oxidation.

Another significant observation from this work was that none of the phosphate esters produced flames, while all of the other fluids flamed at exposure temperatures lower than the phosphate ester test conditions. This fire resistance was observed in spite of the fact that the internal temperature of the lagging reached or exceeded the AIT of the phosphate esters, and the fluid test well in the lagging cube glowed red hot at an oven temperature of 427°C. Phosphate ester fire resistance with lagging was confirmed by Westinghouse in larger scale simulations and has also been observed in power stations.

TABLE 1--Soaked cube fire test results

Fluid	Initial Exotherm, °C	Max. Oven Temp., °C	Observation at Max. Temp.
t-butylphenyl diphenyl phosphate	329	427	no flame
trixylyl phosphate	302	427	no flame
tricresyl phosphate	232	427	no flame
ditridecyl adipate diester lubricant	218	385	flame
dimethyl silicone	204	371	flame
petroleum oil turbine lubricant	191	260	flame

The absence of flames under conditions which will fragment the phosphate ester to volatile, combustible products suggests that organophosphorus fragments are suppressing flaming reactions of combustible vapors emitted from the cube. This would be somewhat analogous to one proposed flame retardant mechanism of triaryl phosphate esters in blends of polyphenylene oxide and high impact polystyrene [6]. In this material, the polyphenylene oxide provides char while the phosphate ester provides the flame inhibition needed to suppress the combustion of hydrocarbon pyrolysates. Alternate explanations for the absence of flame are lower heat of combustion and/or lower volatility; however, the alkylated silicone fluid has a lower heat of combustion than the triaryl phosphate ester (6.4 vs. 7.7 kcal/g) [17], but flames were observed with this fluid at an exposure temperature of 371°C.

Fire Point Test

The fluid fire point conducted in accordance with ASTM Flash and Fire Points by Cleveland Open Cup (D92) defines the temperature at which burning of the fluid can be sustained for at least 5 seconds following ignition with the test flame. For the fluid to continue burning, the vapor-air mixture must be rich enough in combustible content and at a high enough temperature to be over the lean limit of flammability [3]. Generally, more volatile fluids with higher vapor pressure ignite at lower temperatures.

The relevance of fire point as a measure of fluid fire resistance has been questioned [2]. In fact, the fire point method itself incorporates a disclaimer concerning the use of fire point data for this purpose. However, fire point is an important factor in the new Factory Mutual Spray Flammability Parameter [3]. Fire point also was found to correlate with the time to ignition of a fluid spill [18]. This study was conducted by Factory Mutual under EPRI sponsorship. They found that a phosphate ester hydraulic fluid takes twice as long to ignite as a mineral oil turbine lubricant when exposed to a heat flux simulating a fire adjacent to the fluid spill.

As mentioned earlier, the fire point is defined as the temperature where there is sustained (>5 seconds) burning of the fluid. It was observed that a phosphate ester flame at the fire point is not as steady as polyol ester, mineral oil, or silicone oil flames. Based on this observation, several fluids were ranked by time of sustained combustion which is defined as the time it takes for the fluid to stop burning with no ignition source after the fire point heater is turned off. Table 2 lists the fire points, time of sustained combustion, and heats of combustion for a triaryl phosphate ester, a polyol ester, a mineral oil, and a silicone oil under these conditions. The phosphate esters self-extinguished shortly after the heat source was turned off. The mineral oil lubricant, the polyol ester, and the silicone oil continued to burn for two minutes. They were extinguished at this point.

A series of polyol ester / triaryl phosphate ester mixtures were examined to probe the relationship of fire point and propensity of the fluid vapor to sustain a flame. A commercial polyol ester gas turbine lubricant was selected for the study because it had a fire point of 296°C which was significantly lower that the 360°C fire point of a commercial triaryl phosphate ester gas turbine lubricant. The fact that the two lubricants formed homogeneous mixtures in all proportions was also a criteria for selecting this polyol ester lubricant. Figure 1 shows the fire point as a function of increasing amounts of phosphate ester. There was a rapid increase in fire point with the addition of 20% phosphate ester. The increase in fire point was more regular with further additions of phosphate ester. In contrast to the steady increase in fire point, the series of mixtures showed a distinct discontinuity in sustained combustion. The polyol ester mixtures burned for two minutes up to a level of 30% phosphate ester. The mixture containing 40% phosphate ester self-extinguished in <30 seconds. The mixtures with higher levels of phosphate ester self-extinguished in the same manner.

TABLE 2--Fire point and combustion data

Fluid	Fire Point, °C	Sustained Combustion, s	Heat of Combustion, kcal/g
phosphate ester turbine lubricant	360	15	7.7 [3]
trimethylol propane trioleate lubricant	326	>120	8.6 [3]
dimethyl silicone	393	>120	6.4 [17]
petroleum oil turbine lubricant	296	>120	11.0 [3]

The triaryl phosphate ester and several phosphate ester/polyol ester mixtures only sustain combustion for a short time without an external heat source. This implies that the radiation from the flame is not sufficient to maintain the surface of the fluid at its fire point. The fuel value of the vapor will vary according to the heat of combustion and volatility of the mixture components. The rather abrupt change in sustained combustion at 30-40% phosphate ester may be related to the lower heat of combustion of the mixture or the chemical effect of organophosphorus fragments in the vapor. Additional studies would be required to establish how the phosphate ester controls the sustained combustion of these mixtures. However, the work cited earlier on flame retarded plastics and halon extinguishing agents suggests that this would be a complex problem.

CONCLUSION

The inherent fire resistant characteristics of triaryl phosphate ester fluids can be attributed to either physical effects or to chemical effects imparted by the phosphate nucleus. While the fire resistance of phosphate esters is apparent in a variety of fire tests, identifying a given mode of action in a test is a complex problem.

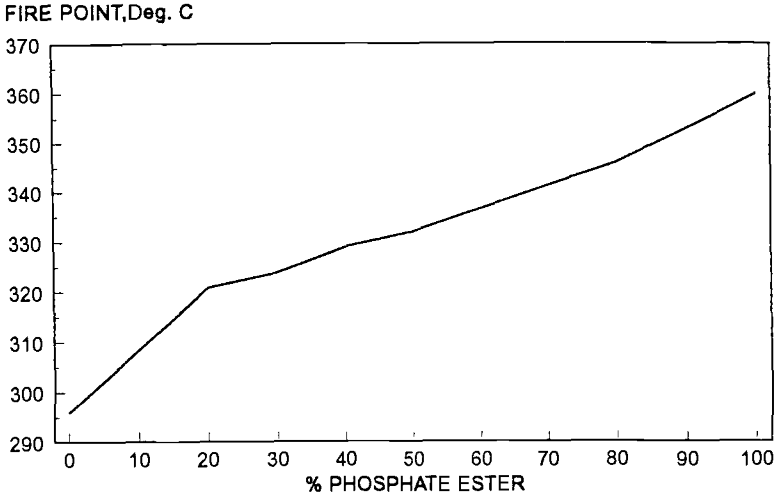


FIG. 1--Fire point of polyol ester/phosphate ester mixtures.

REFERENCES

[1] United States Military Specification MIL-H-194570(SH) for Fire Resistant Hydraulic Fluid, 1989.

[2] Gunderson, R.C. and Hart, A.W., Synthetic Lubricants, Reinhold Publishing Corp., New York, 1962.

[3] Khan, M.M., "Spray Flammability of Hydraulic Fluids and Development of a Test Method," Report FMRC J.I. OTOW3. RC, Factory Mutual Research Corporation, Norwood, MA, 1991.

[4] "Turbine Lubricants - for Steam, Gas, Wind and Water Turbines," Industrial Lubrication and Tribology, September/October, 1994, pp 8-17.

[5] Placek, D.G. and Shankwalkar, S.G., "Flammability Limits of Synthetic Lubricant Basestocks as Measured by a Modified Oxygen Index," Lubrication Engineering, May 1993, pp 415-7.

[6] Weil, E.D., "Flame Retardants Based on Phosphorus," Handbook of Organophosphorus Chemistry, R. Engel, Editor, Marcel Dekker, Inc., New York, Chapter 14, pp 683-739, 1992.

[7] Weil, E.D., "Meeting FR Goals Using Polymer Additive Systems," Proceedings of the International Conference on Fire and Smoke Resistant Materials, National Research Council, Washington DC, 1994 (to be published).

[8] Williams, F., "A Unified View of Fire Suppression," Journal of Fire and Flammability, Vol. 5, 1974, pp 54-63.

[9] Sohrab, S.H. and Williams, F., "Extinction of Diffusion Flames Adjacent to Flat Surfaces," Journal of Polymer Science, Polymer Chemical Education, Vol. 19, 1981, pp 2955-2976.

[10] Song, C.E., et al., "Liquid Fire Extinguishing Composition," U.S. Patent 5,219,4747, 1993.

[11] Sheinson, R.S., Penner-Hahn, J.E. and Indritz, D., "The Physical and Chemical Action of Fire Suppressants," Fire Safety Journal, Vol. 15, 1989, pp 437-450.

[12] Larsen, E., "Mechanism of Flame Inhibition II: A New Principle of Flame Suppression," Journal of Fire and Flammability/Fire Retardant Chemistry, Vol. 2, 1975, pp 5-19.

[13] Freemantle, M., "Search for Halon Replacements Stymied by Complexities of Fires," Chemical & Engineering News, January 30, 1995, pp 25-29.

[14] Pietsch, H., "Evaluation and Test of Improved Fire-Resistant Fluid Lubricants for Water Reactor Coolant Pump Motors," EPRI Research Project 893-1, NP-1447, Vol. 1, Westinghouse Electric Corporation, East Pittsburgh, PA, 1980.

[15] Lysko, V.V., "Experience in Russian Turbines with Phosphate Ester, Fire Resistant Lubricants," Abstracts of the 49th STLE Annual Meeting, STLE, Park Ridge, IL, 1994.

[16] Cho, L. and Klaus, E.E., "Oxidative Degradation of Phosphate Esters," ASLE Transactions, Vol. 24, 1980, pp119-124.

[17] Lipowitz, J., "Flammability of Poly (dimethylsiloxanes). I. A Model for Combustion," Journal of Fire and Flammability, Vol. 7, 1976, pp 482-503.

[18] Modak, A.T., "Ignitability of High-Fire-Point Liquid Spills," EPRI Research Project 1165-1, NP-1731, Factory Mutual Research Corporation, Norwood, MA, 1981.

W. HEYN[1]

GENERAL VIEW AND CRITICAL CONSIDERATIONS OF SPRAY IGNITION TESTS IN FIRE-RESISTANCE EVALUATION OF HYDRAULIC FLUIDS

REFERENCE: Heyn, W., **"General View and Critical Considerations of Spray Ignition Tests in the Fire-Resistance Evaluation of Hydraulic Fluids,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: The need for a spray-ignition test method for hydraulic fluids to be used in underground mining is described. The current spray-ignition testing method as recommended by the European Commission and a proposed "heat release of a stabilised flame"testing method are discussed. The limitations of laboratory spray ignition fire-resistance testing methods, especially for non-aqueous fluids is considered. Additional measures for minimising the fire hazards in the workplace and the potential use of jet spray ignition testing for hydraulic fluids used in non-mining applications are also included in this discussion.

KEYWORDS: oil, hydraulic fluids, spray-ignition, fire-resistance.

---

[1] Retired From: Deutsche Montan Technologie
Tremonia Experimental Mine
Dortmund, Germany

INTRODUCTION

In 1956, 267 miners were killed in a coal mine fire in Marcinelle, Belgium. The fire was caused by damage to a main hydraulic line containing mineral oil in the mine shaft. The mineral oil spray contacted a nearby electrical cable producing an electric arc which ignited the mineral oil.

In view of this disasterous fire, the mining countries of the European Community for Steel and Coal (ECSC) refrained from using mineral oil hydraulic fluids for hydrostatic and hydrokinetic power transmissions. (The six member countries of ECSC are: Belgium, Germany, France, Italy, Luxembourg, Netherlands.) In the early 1960's, a testing method was developed to experimentally demonstrate the fire-resistance properties of various hydraulic fluid compositions relative to mineral oil. This method was integrated into the 7th issue of the Luxemburg Report [1] as the spray ignition test method of the "Community of Six". The development and testing results of this testing methodology will be described here.

DISCUSSION

1. Spray Ignition Test Method of the Community of Six

In this spray ignition test, a standard oxy-acetylene flame which simulates an electric arc as ignition source is manually moved along the axis of a fluid jet under pressure. Observations are made whether the jet is ignited and whether the flames from the spray-jet reach a steel-sheet-baffle at a distance of 1.75 m from the nozzle. The test configuration is illustrated in Figure 1. In this test, "Mark 1" indicates that the spray is not ignited. "Mark 2" indicates that the spray jet is ignited but the flames do not reach, or do not continuously reach, the baffle. "Mark 3" indicates that the spray is ignited and the flame reaches the baffle.

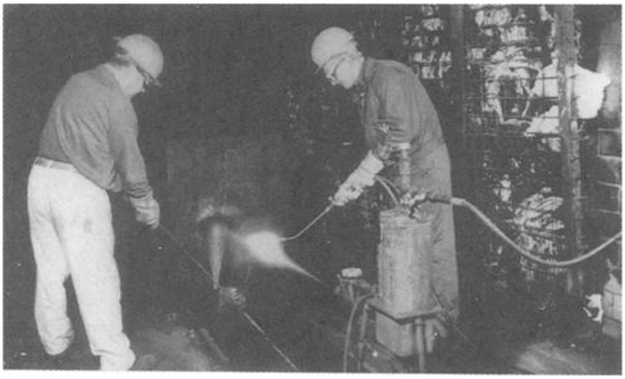


Figure 1 Spray Ignition Test Method of the Community of Six
Rating: Mark 1, Spray is not ignited, Hydraulic Fluid HFDT 46

2. Spray Ignition Test Method of the United Kingdom

Since the United Kingdom's entry into the European Community, an alternative testing method has been used since 1980. This spray ignition testing procedure is described in the 7th issue of the Luxembourg Report [1].

With this method, the fluid under test is sprayed under pressure in the form of a fine droplet mist as shown in Figure 2. A defined oxy-acetylene flame is introduced at various positions within the mist. After the mist is ignited, the flame is removed. In contrast to the above method, the ignition criteria of the spray jet and the flame length is related only to the post-combustion time of the spray after removal of flame. This time is not to exceed a relatively long period of 30 seconds. Representative fluids and results comparing the "Community of Six" and the "United Kingdom" test methods is provided in Table 1.

Table 1 **Hydrauic Fluids and Comparative Test Results For Two Spray Ignition Test Methods.**

			Method of "Community of Six"		Method of United Kingdom	
VG-No.	Category ISO-VG-46	Fluid Composition	Rating	Judgement	Subsequent Burning Time(s)	Judgement
14/173	HM	Mineral Oil	3	-	730	-
14/174	HEES	Synthetic Ester	3	-	730	-
14/163	HEPG	Polyalkylene glycol	3	-	730	-
14/165	HFDU	Polyalkylene glycol	3	-	11	+
14/171	HEPG	Polyalkylene glycol	3	-	>30	-
14/160	HFDR	Phosphate Ester	3	-	3	+
14/161	HFDR	Phosphate Ester	3	-	4	+
14/165	HFDR	Phosphate Ester	3	-	3	+
14/169	HFDR	Phosphate Ester	3	-	3	+
14/176	HFDT	PCDM	2	+	2	+
14/177	HFC	Water/glycol	1	+	0.5	+
14/178	HFC	Water/glycol	1	+	0.5	+
14/172	HFB	Water/oil/emulsion	3	-	2	+

Figure 2 Spray Ignition Test Method of the United Kingdom
Subsequent Burning Time 4 Seconds - Hydraulic Fluid HFDR 46

3. Spray Ignition Test Method "Heat Release of a Stabilised Flame"

Concurrent with the German endeavours in the mid 1980's to replace chlorinated biphenyl fluids with more biologically degradable fire-resistant fluids, the Health and Safety Executive (HSE) in Buxton, United Kingdom developed a novel spray ignition testing method to quantify the relative fire-resistance of hydraulic fluids. Scientific support was provided by the University of Manchester [2]. This method will be presented in detail in a subsequent paper.

4. Hydraulic Fluid Summary

In the countries of present-day European Union, hydraulic fluids for use in underground mining must not only meet safety-related criteria, but also hygienic and technological specifications. In many applications, good thermal properties such as operating temperatures from -20°C to 150°C are also required. These fluids include synthetic, anhydrous fluids of the "HFD" category. Up to approximately 4 years ago these included fluids such as PCDM (polychlorinated diphenyl methane derivative) basis named Tetrachlorobenzyltoluene was used under the trade name Ugilec 141.

As with the chlorinated biphenyls (PCB's), environmental compatibility , which includes both biological degradability and environmental toxicity, became critically important criteria for all hydraulic fluids. Potential alternative candidates included HFD fluids, such as phosphate esters (HFDR) and polyalkylene glycols (HEPG). A hydraulic fluid classification table is provided in Table 2. In addition to biological degradability, low toxicity is also important, especially in underground use.

Manufacturers claims for the fire-resistance of these fluids suggested that both HFDR and HEPG (or HFDU) hydraulic fluids are better than mineral oils but they are not as fire-resistant as PCB- or PCM-containing fluids. However, these claims had to be independently validated.

5. Comparative Fire-Resistance Testing Results

To experimentally determine the relative fire-resistance of typical classes of hydraulic fluids, 14 different fluids were tested by the two older spray ignition tests; the "Community of Six" and the United Kingdom tests described above [3]. To better differentiate the fire-resistance results, mineral oil was not included in that study. However, since there was a need for non-aqueous hydraulic fluids, HFD hydraulic fluids were included in this study. The objective of this work was to learn whether these older methods also permitted an adequate assessment of the fire-resistance properties of hydraulic fluids, especially for underground mining applications.

5.1 Spray Ignition Test Method of the "Community of Six"

On the basis of this work, the spray ignition test method of the "Community of Six" does not allow for differentiation of the fire-resistance properties of the different hydraulic fluid classes. The problem seems to be due to the "pass/fail" rating of the fluids. The assessment "Mark 2" given to one fluid only implies that some of the flame tips reach the baffle. However, this is not an objective test. The relative rankings are subjectively determined by the experimentalist. Therefore, these results of this study should be viewed with caution. Table 1 provides a tabulation of the results obtained with various hydraulic fluids.

Table 2: Hydraulic Fluids for Coal Mining Applications

Category	Composition Typical Properties	Water Endanger. Category	Applications Operating Temperature	Flammability Rating (Method AMS-3150C)
Water Based Fluids				
HFAE	Oil-in-water emulsions Mineral oil/synthetic ester Concentration by Vol. <20%	3-1	Power Transmissions Powered Roof Support High Working Pressure	1
HFAS	Mineral Oil Free Aqueous Synthetic Solution Concentration by Vol. <20%	0	Hydrostatic Drives Low Working Pressure 5 to <55°C	1
HFB	Water-in-Oil emulsions Mineral Oil Portion <60%	3	Not approved in German mining	3
HFC	Aqueous Polymer Solutions Water Content >35%	0	Hydrostatic Drives -20 to <60°C	1
Non-Aqueous Synthetic Fluids				
AFDR	Phosphate Esters Water Insoluble	1	Not approved for German mining	3
HFDS	Chlorinated Hydrocarbons	3	Hydrodynamic Couplings <150°C up to 1984 PCB (Elaol Vi)	1
HFDT	Blends of Chlorinated Hydrocarbons and Phosphate Esters	3	Hydrostatic Drives 10 to <70°C Up to 1990 PCDM (Ugilec)	2
HFDU	Other Anhydrous Fluids	0-1	Hydrostatic Drives -35 tp <90°C	?
Non-Aqueous Environmentally Acceptable Fluids (Substitute for Mineral Oil)				
HEPG	Polyalkylene Glycol - Water Soluble	0	Hydrostatic Drives -30 to <90°C 1989 tied operation on ISO Cor E 40, Ukadol Nbr.	46
HETG	Vegatable Oil - Triglycerides (Water insoluble)	0	Hydrostatic Drives -20 to <80°C Not approved in German mining (Rape Seed Oil)	3
HEES	Synthetic Esters (Polyol Ester) Water Insoluble	0-1	Hydrostatic Drives -35 to <90°C	3

5.2 Spray Ignition Test Method of the United Kingdom

Generally, the UK spray ignition testing method permits differentiation between phosphate ester hydraulic fluids (HFDR) and water-glycol hydraulic fluids (HFC). The HFDR and HFDT fluids exhibit substantially shorter "after-burn" times by this test. Mineral oil and anhydrous polyalkylene glycol (HEPG) fluids exhibit similarly unfavorable fire-resistance properties by this test.

As with the "Community of Six" spray ignition method, the measurement technology and process pattern of the United Kingdom method should be updated to incorporate current technology.to obtain objectively measured results. The results tabulated in Table 1 show that the fire-resistance of the United Kingdom method are not as stringent as those of the "Community of Six" test method.

5.3 Spray Ignition Test Method - "Heat Release of a Stabilised Flame"

Initial trials with the spray jet heat release method were run in the late 1980's. It was found that this method could comply with the measurment and handling-related requirements discussed in Section 5.1 above to provide reproducible results. Furthermore, this method is expected to allow differentiated assessment of the fire-resistance of non-aqueous fluids. This method could be introduced into the mining countries of the European Union to replace the previously described spray ignition tests. Details of these test results will be provided in a subsequent paper to be presented by K. Holke [4].

6. General Comments on the Spray Ignition Test Methods

Spray jet testing of hydraulic fluids must be continued in the mining countries of the European Union. This is a practical method but it must be updated to incorporate current technology. The method should permit the differentiation of the fire-resistance of fluids ranging from water to mineral oil. The test results should be reproducible while incorporating cost effective equipment modifications. Neither laboratory methods, e.g. flash point, fire point or wick test, nor semi-industrial scale methods, e.g. fighting and extinguishing pool fires, perfectly model fires as they occur in industrial applications. However, relative comparisons of the potential fire risk of the use of hydraulic fluids in industrial environments can be made [5].

Special, more application-related, full-scale tests such as hydraulic point welding robotics equipment used in automobile production are more conclusive than the laboratory tests discussed above. However, such testing is no longer feasible in Europe because of environmental protection regulations. For example, in Germany open air fluid fire fighting excercises are no longer allowed.

7. Fire Hazard Minimization

The three prerequisites for a fire are: inflammable materials, an ignition source, and the presence of oxygen. If only one of these factors is lacking, a fire is excluded. To optimize fire protection, complete analysis of the factory or mine to be protected with respect to these prerequisites is necessary. As hydraulic systems are exposed to fire hazards, their solid as well as liquid synthetic components should exhibit good fire-resistance properties. For example, it may be necessary to use "fire-resistant" mining quality [6] hydraulic hoses, where the presence of an ignition source can not be excluded. Consideration should also be given to the installation of powder, nitrogen, or waterspray mist fire extinguishing systems to provide an inert operating environment if oxygen exclusion is necessary.

Limited access industrial environments such as those present in underground mining have been, and continue to be, subjected to increasingly stringent high fire safety standards to save human lives. Even in applications where the possibilities of escape are substantially better, certain safety regulations should be adapted from those practiced by industry, especially if high-value property is to be protected.

CONCLUSIONS

For all hydraulic fluid applications the technological and safety-related aspects need always to be given priority, and the fire-technological properties need to be proven by spray ignition tests. In many applications however, toxicological, cleanliness, and environmental compatibility must be considered. Economic aspects are also a decisive factor in the selection of hydraulic equipment and system design.

REFERENCES

1. Europäische Kommission: Anforderungen und Prüfungen schwerentflammbarer Hydraulikflüssigkeiten zur hydrostatischen und hydrokinetischen Kraftübertragung und Steuerung, Siebente Ausgabe, Dok. Nr. 4746/10/91 DE, April 1994 (Doc No. 4746/10/91 DE, April 1994 Requirements and testing of fire-resistant hydraulic fluids for hydrostatic and hydrokinetic power transmission and control, 7th issue)

2. S.F. Jagger, Health and Safety Laboratory, Buxton, Derbyshire, U.K.; A. Yule, Institute of Science and Technology, Manchester, U,K.; and K. Moody, Health and Safety Laboratory, Buxton, Derbyshire, U.K.; "The Development of a New Test for the Assessment of the Flammability of Sprays of Hydraulic Fluids".

3. Heyn, W.: Entwicklung eines harmonisierten Sprühstrahlverfahrens zur brandtechnischen Differenzierung von Hydraulikflüssigkeiten. Glückauf-Forschungshefte 51 (1990), Heft 2, S. 66-71 (Development of a harmonized spray ignition test method for differentiated fire-technological assessment of hydraulic fluids)

4. K. Holke, "Testing and Evaluation of Fire-Resistant Hydraulic Fluids Using the Stabilized Heat Release Spray Test" in Fire Resistance of Industrial Fluids ASTM STP 1284, George E. Totten, Jurgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1995.

5. J. Reichel, "Standardization Activities for Testing Fire-Resistant Fluids in Europe" in Fire Resistance of Industrial Fluids ASTM STP 1284, George E. Totten, Jurgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1995..

6. Landesoberbergamt NRW: Prüfbestimmungen für Betriebsmittel aus Kunststoffen in Bergwerken unter Tage, Ausgabe März 1993, Verlag Glückauf GmbH, Essen, Verlagsnummer 530 (Testing regulations issued by the Central Inspectorate of the state of Northrhine Westphalia for plastic material for use in underground mines)

Karl Holke[1]

TESTING AND EVALUATION OF FIRE-RESISTANT HYDRAULIC FLUIDS USING THE STABILIZED HEAT RELEASE SPRAY TEST

REFERENCE: Holke, K., **"Testing and Evaluation of Fire-Resistant Hydraulic Fluids Using the Stabilized Heat Release Spray Test,"** Fire Resistance of Industrial Fluids ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: Hydraulic fluids for use in coal mining applications must be fire-resistant. Fire-resistance is defined by the particular standardized testing methods being used. In Europe, the required fire-resistance testing procedures are specified in 7th Edition of The Luxembourg Report [1]. In this report, there are three acceptable spray testing procedures; 1.) the Community of Six spray test, 2.) the United Kingdom spray test and 3.) the "stabilized heat release spray test" (Buxton Test). Of these three tests, the Buxton Test offers the greatest and most reliable quantitative characterization of the fire-resistance properties of a hydraulic fluid. The results of investigations conducted to evaluate the experimental reproducibility of the Buxton Test are discussed in this report.

KEYWORDS: fire-resistance, hydraulic fluids, Buxton Test, spray flammability

---

[1]. DMT-Gesellschaft für Forschung und Prüfung mbH, Institut für Brand - und Explosionsschutz - Versuchsgrube Tremonia, Dortmund, Germany

INTRODUCTION

Hydraulic fluids for use in hard coal mining, must be fire-resistant. The term "fire-resistant" is defined with reference to a fire-testing method. In Europe, the required fire-resistance testing methods are given in the 7th Edition of The Luxembourg Report [1]. According to this report, the fire-restistance properties of hydraulic fluids used in hard coal mining must be determined by one of the three permitted spray ignition test procedures:

1. spray test of the Community of Six,
2. spray test of the United Kingdom (UK),
3. stabilized heat release test (Buxton Test).

The Community of the Six and the United Kingdom spray ignition tests are well established procedures and are relatively easy to conduct. These test methods are discussed in Reference [2]. Typically, the fire-resistance properties of a hydraulic fluid are classified as either "flammable" and "non-flammable". The terms flammability and non-flammability refer generally to the ability of a fluid to ignite when in contact with a flame (or heat) source, the amount or size of the resulting flame, the amount of heat evolved from the combustion process and the ability of the flame to propagate back to the heat source. However, the specific definitions and fluid classifications may vary and depend on the particular test procedure being used. Therefore, these classifications offer poor quantification of the relative fire-resistance provided by a hydraulic fluid. With the Buxton Test, a more precise differentiation of the fire-resistance properties of a hyraulic fluid is possible [3]. However, the experimental apparatus used for the Buxton Test is substantially more complex and the experimental results obtained by different laboratories with different test apparatus, although the same design, have not been reproducible, even if the experimental conditions are carefully controlled.

The goal of the European Union is to "harmonize" all spray ignition test methods. To successfully complete this task, reproducible test results are necessary. In this paper, the results of investigations conducted to determine the conditions of experimental into the reproducibility of the Buxton Test are discussed.

DISCUSSION

Spray Ignition Test Procedures from the Luxembourg Report

The Community of Six Spray Ignition Test -- In this test method, a spray is generated using a pressure vessel and a nozzle [2]. An oxyacetylene flame is brought near to the hydraulic fluid spray. Spray ignition properties and the ability of the flame to reach a tin screen 1.75 m away from the spray nozzle is determined.

Spray Ignition Test of the United Kingdom (UK) -- This test is similar to the Community of Six Spay Ignition Test since a spray mist is also generated using pressure vessel and a nozzel [2]. An oxyacetylene flame is then introduced into the spray mist. The "after" ignition time of the spray mist is measured after the burner flame is removed. The limiting value of the afterignition time is 30 seconds.

Heat Release of a Stabilized Flame (Buxton Test) -- The Buxton Test is conducted by generating a spray and igniting it with a propane flame. Although the Buxton Test is formally known as the "heat release of a stabilized flame" throughout Europe, the heat released from the burning spray is not actually measured. Instead, the increase in the exhaust temperature of the stream from the burning spray, which is proportional to the heat released is measured as shown in Figure 1. From the measured temperature, the so-called Relative Ignitability Index (RI-Index) is derived. The RI-Index is a dimensionless characteristic number which reflects the fire-resistance of a hydraulic fluid.

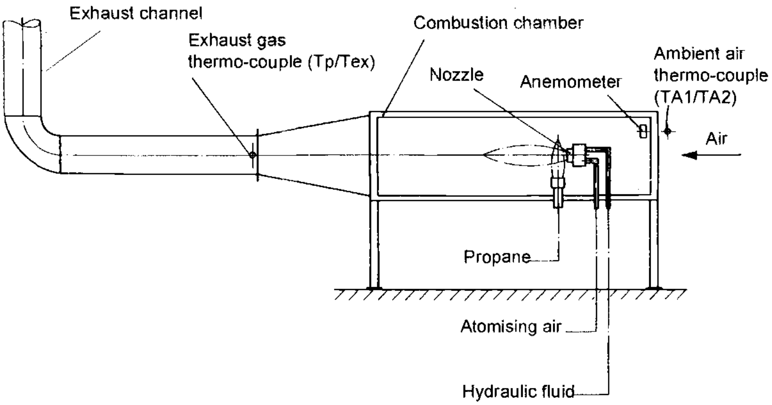


Figure 1: Schematic representation of the test chamber used for the Buxton Test.

There are two variants of the Buxton Test which are dependent on the RI-Index.

1. Hydraulic fluids with an RI-Index < 50 (Low Propane Region Fluids) are tested with a burner flame having a propane flow rate of 0.13 Nm^3/h. The RI-Index is calculated by:

$$RI = \frac{500\ (T_P - T_{A1})}{7\ (T_{EX-} - T_{A2})} \qquad (1)$$

where:

T_p is the exhaust temperature (°C) of the propane burner operated without spray,
T_{A1} is the air temperature (°C) at the combustion chamber entry without spray,
T_{EX} is the exhaust temperature (°C) with spray,
$T_{A2}$is the air temperature (°C) at the combustion chamber entry with spray.

2. Hydraulic fluids with an RI-Index $\geq$ 50 (High Propane Region Fluids) are tested with a burner flame having a propane flow rate of 0.4 Nm^3/h. In this case the RI-Index is calcutated by :

$$RI = \frac{100\ (T_P - T_{A1})}{T_{EX} - T_{A2}} + 30 \qquad (2)$$

The test method for High Propane Region Fluids will not be discussed further here since this procedure has been discussed in detail previously by S.F. Jaegger, et al. [5].

Interlaboratory Reproducability of The Buxton Test

The reproducibility of the Buxton Test was established by comparing fire-resistance properties of a series of hydraulic fluids obtained with the original apparatus at Health and Safety Executive (HSE) in Buxton, UK with results obtained with a different test apparatus of the same design constructed at HSE (see Figure 2) and delivered to DMT-Tremonia Experimental Mine in Germany.

Comparative fire-resistance tests were carried out with 10 different hydraulic fluids. Two of these fluids were obtained by mixing the original fluid with 25% and 50% water. The original fluid was an anhydrous polyglycol, VG-No. [14/190]. The VG-No is a DMT-Tremonia Experimental Mine registration code of the fluid.

The experimental results obtained by HSE and DMT were not reproducible as shown in Figure 3. However, although the RI-Index values were not reproducible they do correlate well as shown in Figure 4. Further analysis of this data showed that the RI-Index values were dependent on:

- temperature measurement in the exhaust channel (T_{Ex} and T_p),
- the exact adjustment of the fluid throughput,
- uniformity of the propane burners.

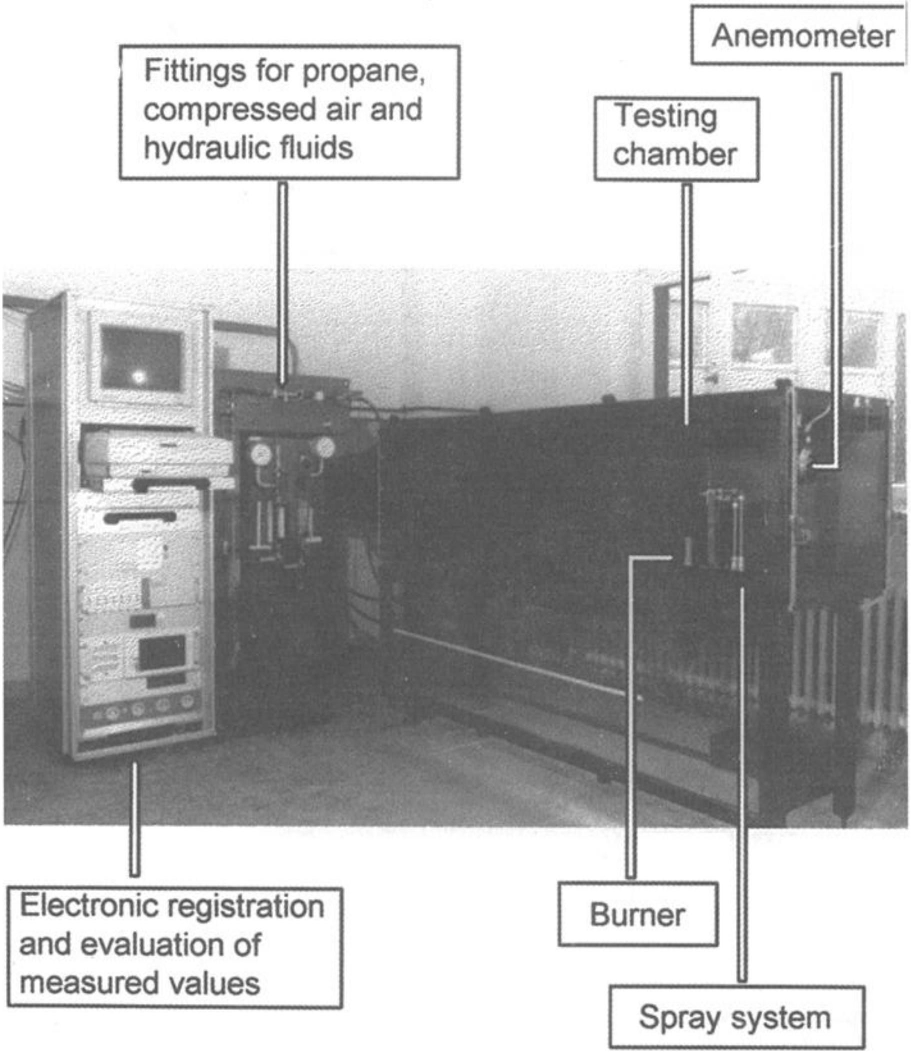


Figure 2: DMT-Trenia Experimental Mine Buxton Test Apparatus

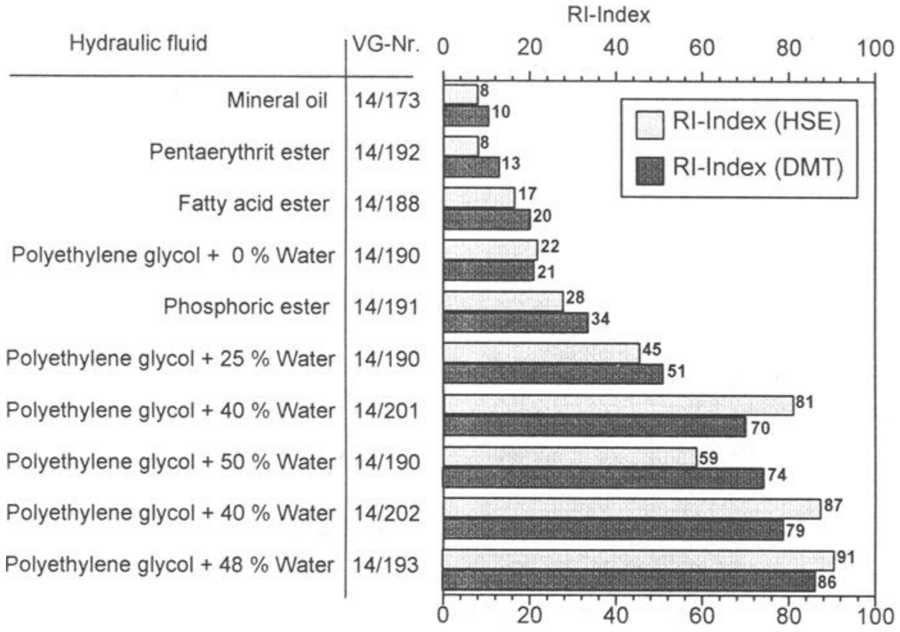
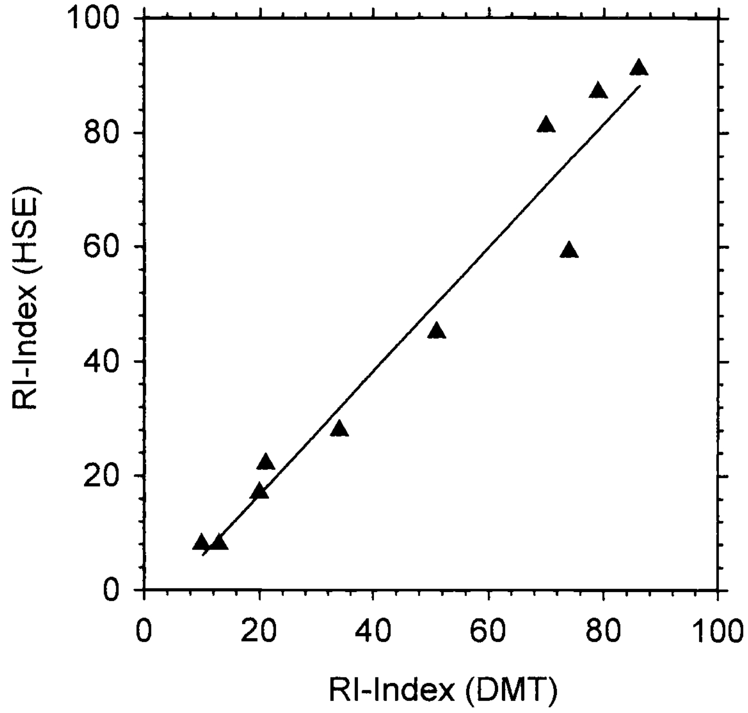


Figure 3: Comparison of RI-Indices of Different Hydraulic Fluids Obtained by DMT and HSE.

Because the temperature in the exhaust channel is not evenly distributed over the channel cross-section, the temperature measurement depends on the position of the thermocouple in the cross-sectional area. This means that slight variatons in the position can influence the RI-Index.

The temperature in the exhaust channel also depends on the heat release of the burning spray. This heat quantity is a ratio of the fluid quantity necessary for the generation of a spray. Therefore the fluid throughput has to be measured exactly and adjusted.

Because the exhaust temperature of single burner operation enters into the calculation of the RI-Index according the equations (1) and (2), the burners of each apparatus must burn with an identical flame. The burner flames are characterized and compared by the axial and radial temperature profiles.



Polynom - Regression: (N = 10)

$y = a + bx$

$a = -4.894782125$

$b = 1.080672099$

Correlation coefficient = 0.97496

Figure 4: Comparative test results obtained by DMT and HSE (HSE results as a function of DMT results).

In 1994 another testing apparatus has been commissioned in France. From the technical-scientific point of view it would be necessary to carry out comparative tests with hydraulic fluids with all three testing apparatus.

Test Apparatus Calibration

Comparative Tests With Ethylene Glycol-Water Mixtures -- Further comparative tests with calibration fluids were carried out at HSE and DMT in a further attempt to obtain reproducible interlaboratory results. The results obtained at HSE were published as "standard values" in the 7th Luxembourg Report. The values obtained at DMT (and other potential testing laboratories) will be converted to these standard values by correlation. (Any changes in the test apparatus, such as thermocouple replacement, requires the recalibration.)

Ethylene glycol ($\geq$ 98 % pure) was selected as the calibration fluid because:

- it is commercially available at this level of purity to all member states of the European Union,
- it can be mixed with water in any proportion,
- defined ethylene glycol-water mixtures can be readily prepared as calibration fluids,
- by varying water content ethylene glycol water mixtures from easily-ignited to fire-resistant may be prepared,
- These calibration mixtures are analagous to poly(alkylene glycol), with and without the addition of water, which may be used for hydraulic fluids formulation.

The following round-robin test procedure was used:

- 10 different ethylene glycol-water mixtures with exactly defined water content were tested,
- With each fluid mixture, 10 measurements were conducted to determine the mean value,
- The RI-Indexes, obtained with the HSE test apparatus were used in the 7th Luxembourg Report,
- By statistical evaluation of the RI-Indexes of HSE and DMT the equations for the correlation curves were determined,
- With these correlation equations, the DMT RI-Index values were converted to the standard values.

Figure 5 shows that the individual results are scattered and overlapping. The mean values, however, increase as the water content of the fluids increase. This indicates that it is necessary to state the RI-Index as mean value of a larger number of single measurements.

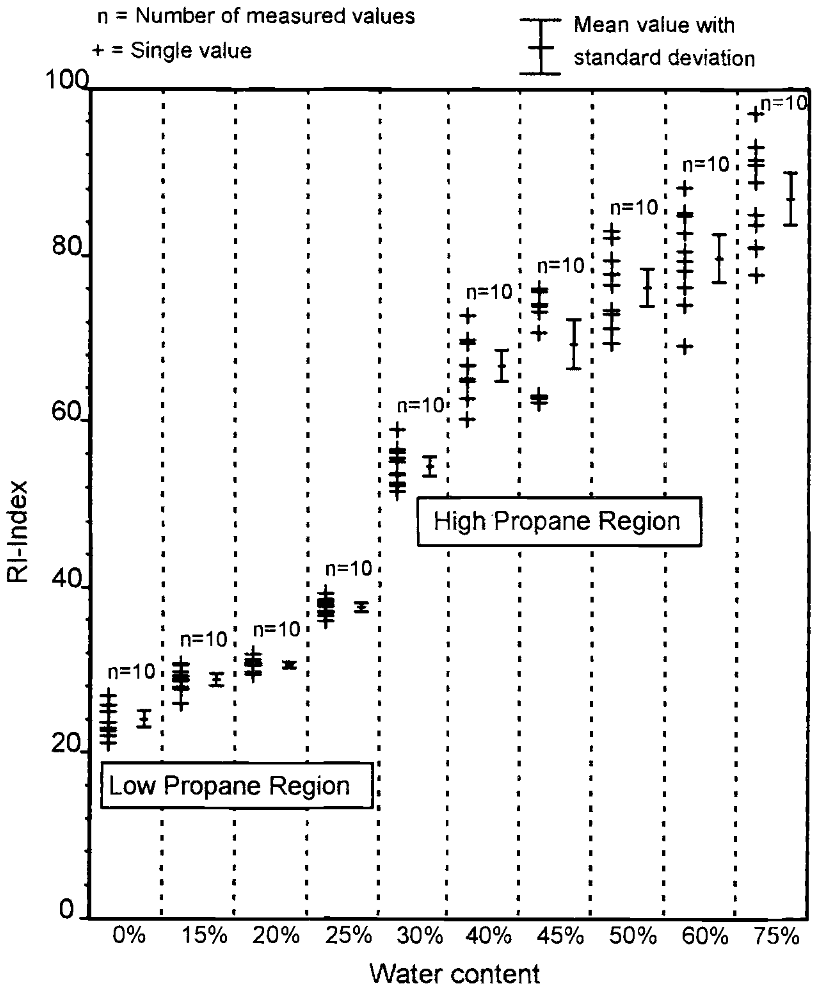


Figure 5: Calibration test results obtained with ethylene glycol/water mixtures at DMT - distribution of single and mean values as a function of water content.

In Figure 6, it is shown that the mean values of the RI-Indexes increase with increasing water content for both DMT and HSE although both laboratories obtained different absolute values.

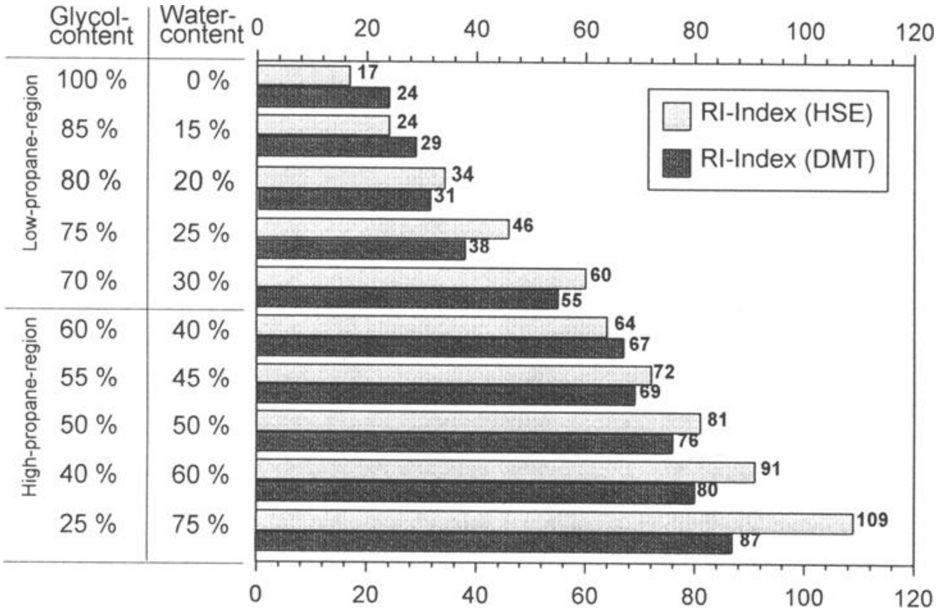


Figure 6: Comparison of DMT and HSE RI-Indices of different water/glycol mixtures used for calibration.

Test Result Correlation -- Preliminary analysis and evaluation of the results was done by Dr. Yule at the University of Manchester (UK), who had contributed considerably to the development of the Buxton Test [4]. It was found that the regression curves were non-linear and are generally described by equations (3) and (4):

For the Low-Propane Region:

$$Y = ax + bx^2 \tag{3}$$

or the High-Propane Region:

$$Y = a + bx + cx^2 \tag{4}$$

The coefficients a, b and c had been calculated at DMT with an appropriate PC-software according to the method of the smallest deviance. The equations for the conversion of DMT-RI-Indexes to the standard RI-Indexes are:

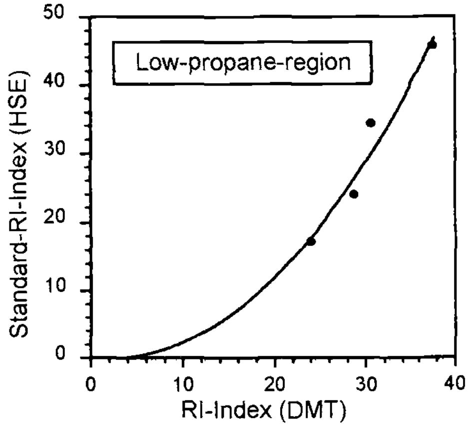
For the Low-Propane Region:

$$RI(stand.) = 0.13358 * RI(DMT) + 0.03647 * RI(DMT)^2 \tag{5}$$

For the High-Propane-Region:

$$RI(stand.) = 201.56419 - 5.21299 * RI(DMT) + 0.04777 * RI(DMT)^2 \tag{6}$$

These results are illustrated by the two regression curves shown in Figure 7 which appear to be in good agreement with the experimental values.



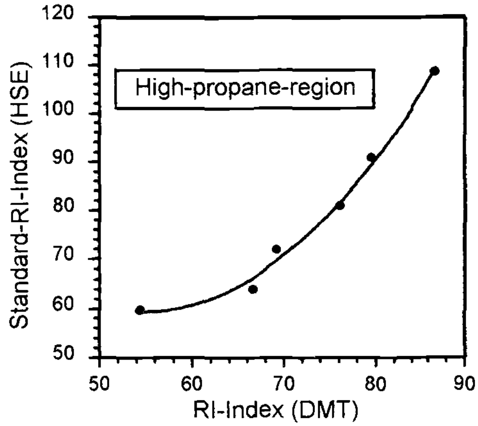
Non-linear regression: (N = 4)

$y = ax + bx^2$

a = -0.13358

b = 0.03647

Correlation coefficient = 0.96645



Non-lineare regression: (N = 6)

$y = a + bx + cx^2$

a = 201.56419

b = -5.21299

c = 0.04777

Correlation coefficient = 0.99623

Figure 7: Calibration tests results obtained with ethylene glycol/water mixtures at DMT -Correlation of RI-Indices of DMT and HSE.

Hydraulic Fluid Characterization

In the 7th Luxembourg Report the hydraulic fluids are classified by RI-Index obtained by the Buxton Test into 8 classes, from A to H as follows:

Class	A	B	C	D	E	F	G	H
RI-Index	> 100	100-80	79-65	64-50	49-36	35-25	24-14	< 14

Hydraulic fluid fire resistance increases with increasing RI-Index. According to these classifications, fire resistance decreases from class A to class H.

Requirements for hydraulic fluids for use in underground hard coal mining.have not yet been defined. These requirements will established at the conclusion of a two year testing phase when sufficient experience and results with the Buxton Test are obtained. It is estimated that this will be in 1997. During this interim period, the Community of Six or of the United Kingdom spray ignition tests will continue to be used in addition to the Buxton Test [1].

Ideally,it is desirable to conduct additional comparative tests with different hydraulic fluids. Future work should be conducted to demonstrate that the results obtained with the calibration tests are not limited to ethylene glycol-water mixtures but are generally valid for all fire-resistant hydraulic fluids.

Some of this work may be performed now that a French laboratory, the central testing laboratory of Marienau-Ferbach of the Lothringian coal mining region, has just completed the construction of a Buxton Testing apparatus.

SUMMARY

Up until now, the evaluation of the fire-resistance of hydraulic fluids using currently available and approved testing procedures by the member states of the European Community have been insuffucient, because they only require the classification "flammable" or "not flammable". These classifications do not adequately differentiate the fire-resistance between fluids.

Therefore, a new testing method has been developed at HSE in Buxton, which now internationally is known as Buxton Test. The basic principle of this testing methhod is to evaluate the heat release of a stabilized flame of a hydraulic fluid spray. Currently, there are two apparatus to conduct the Buxton Test. One is located at the HSE laboratory in the UK in Buxton and the other is located at the DMT-Tremonia Experimental Mine in Dortmund, Germany. Although both test apparatus have been construced in England, they are not identical, therefore, different results are obtained with the same hydraulic fluids. This problem was resolved with the using comparative tests conducted with calibration fluids. Apparatus-dependent factors were determined which permit the conversion of the experimentally derived data to standardized non-apparatus dependent results. In this way, hydraulic fluids the fire-resistance properties of different hydraulic fluids can be comparitively evaluated by different laboratories.

Currently, Buxton Test the Buxton Test is being introduced as the preferred fire-resistance testing method for hydraulic fluids by the member states of the European Union which is part of an overall effort to harmonize all test methods within the EU.

REFERENCES

1. Luxembourger Bericht über Anforderungen und Prüfungen schwerentflammbarer Hydraulikflüssigkeiten zur hydostatischen und hydrokinetischen Kraftübertragung und Steuerung, vom 3.3.1994, Dok.Nr. 4746/10/91 DE

2. The spray ignition test method of the "Community of Six" and the Spray Ignition Test Method of the United Kingdom are described in "General View and Critical Considerations of Spray Ignition Tests in Fire-Resistance Evaluation of Hydraulic Fluids", Fire Resistance of Industrial Fluids ASTM STP 1284, George E. Totten, Jurgen Reichel, Eds., American Society for Testing and Materials, Phiiladelphia, 1995.

3. DMT-Gesellschaft für Forschung und Prüfung mbH Versuchsgrube Tremonia (Heyn, W.); Versuchsstand „Harmonisierte Entflammbarkeitsprüfung für Flüssigkeiten zur hydraulischen Kraftübertragung“, KEG-Forschungsvereinbarung Nr. 7258-02/01/141, Dortmund (1992)

4. A.J. Yule and K. Moodie, Fire Safety Journal, 18, 273, (1992).

Mohammed M. Khan[1]

SPRAY FLAMMABILITY OF HYDRAULIC FLUIDS

REFERENCE: Khan, M. M., **"Spray Flammability of Hydraulic Fluids,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: The spray flammability characteristics of several hydraulic fluids, and mineral oil, methanol, ethanol, and n-heptane, sprayed vertically upward in the open through a pressure-jet hollow cone nozzle and stabilized by a propane-air ring burner, have been evaluated using the Factory Mutual Research Corporation (FMRC) Fire Products Collector. A spray flammability parameter (SFP) has been defined, which combines the combustion intensity of spray fires in terms of chemical heat release rate with the fluid volatility described by the critical heat flux for ignition. An SFP value has been identified at or below which a range of hydraulic fluids cannot be stabilized as spray flames using a standard flame stabilization test. Mineral oil, some hydraulic fluids, and highly volatile fluids such as n-heptane, methanol and ethanol, have high SFP values and are easy to stabilize as spray flames. SFP appears to be useful in discriminating between flammable and less flammable fluids.

Experimentally, it was found that the burning of multi-component fluids, such as water-in-oil emulsion and polyglycol-in-water on a wick (porous ceramic disc), does not simulate burning of such fluids in an atomized spray. Thus, a spray fire test appears to be a much better method for characterizing the flammability of all types of hydraulic fluids.

KEYWORDS: hydraulic fluids, spray flammability, spray flames, flammability of fluids on a wick.

---

[1] Senior Research Scientist, Factory Mutual Research Corporation, Norwood, MA 02062

INTRODUCTION

The typical fire hazard scenario involving hydraulic fluids is the release of fluid as an atomized spray near a source of ignition, following rupture of a pipe or hose at high pressure. A torch-like long flame with high heat release results. Another scenario involves the spillage (or slow leakage) of hydraulic fluid, forming a pool on the floor and then igniting. Generally, fluids may not be as flammable in bulk as they are when finely divided, such as in an atomized spray. The surface-to-volume ratio of a droplet in a spray is larger than that of a large drop or pool of liquid. This larger ratio enhances the transfer of heat to the liquid droplets, thereby promoting evaporation, ignition and efficiency of combustion. Thus, hydraulic fluid spray fires have a greater potential for hazards than pool fires in terms of fire protection.

The burning of a mixed fluid (multi-component fluid) soaked on a wick is expected to be similar to a mixed fluid in an atomized spray. Whatever the difference in fire points (or boiling points) of the components of the fluid, the components will vaporize (or undergo combustion) in proportion to their concentration, similar to the combustion in an atomized spray. On the other hand, in the combustion of a mixed fluid in a pool or a large drop without a wick, the more volatile component would dominate the gas phase and result in an increasing concentration of less volatile residual components.

At Factory Mutual Research Corporation (FMRC), a study [1] was undertaken to develop quantitative test methods to help identify less flammable hydraulic fluids. The objectives of the study were: a) to develop a technique for quantifying the flammability of fluids on a wick, simulating spray flammability; and b) to develop a quantitative method for characterizing spray flammability.

EXPERIMENTS

Commercially available hydraulic fluids (organic and phosphate esters, water-in-oil emulsion, and polyglycol-in-water), which differ from one another in terms of water content, additives, fire retardant and chemical structures, etc., were examined in this study. In addition, pharmaceutical-grade mineral oil and some well characterized fluids such as ethanol, methanol and n-heptane were used. The following experiments were conducted:

Fire Point

Fire point was determined using the ASTM Standard Test Method for Flash and Fire Points (D92) by Cleveland Open Cup (COC). In the standard test procedure, fluid was heated in an open container at a controlled rate, and a small pilot flame was passed over the surface periodically. Fire point is determined as the temperature at which burning can be sustained for at least 5 s.

Ignition

Ignition experiments were performed in the FMRC Small-Scale (50 kW-Scale) Flammability Apparatus shown in Figure 1. Descriptions of the Apparatus are given in Reference 1. An aluminum dish, 10 cm in diameter (2.54 cm lip height), containing 100 mℓ of fluid, was placed on a platform and surrounded by four pre-calibrated radiant heaters in order to expose the fluid surface to a heat flux. A premixed ethylene-air horizontal pilot flame about 0.01 m in length, located about 0.01 m above the fluid surface, was used to ignite the combustible vapor-air mixture produced due to the exposure to the heat flux. The experiments were performed under natural ventilation (without a quartz tube around the aluminum dish). Fluids were exposed to several values of radiant heat flux (up to 60 kW/m^2), and time to sustain ignition was measured.

Net Heat of Complete Combustion

The net heat of complete combustion, ΔH_T, of each fluid was measured in the oxygen bomb calorimeter. ΔH_T refers specifically to the condition where water as a product is in the vapor state. ΔH_T is less than the gross heat of complete combustion (which specifies that the reactants and products are in their standard states) by an amount equal to the latent heat of vaporization (2.26 kJ/g of water).

Flammability of Fluids on Flat Porous Diffuser Wick

Experiments were performed in the FMRC Small-Scale (50 kW-Scale) Flammability Apparatus, shown in Figure 1. Round discs of porous ceramic paper, 0.098 m in diameter and 3 mm in thickness, saturated with fluid, were placed horizontally inside a 10 cm (4 in.) diameter aluminum dish (2.54 cm lip height), surrounded by a quartz tube. Experiments were performed with an oxygen concentration of 40% in the environment, flowing at a rate of 0.0033 m^3/s to simulate large-scale pool fire radiation conditions [2]. The fluid was ignited by touching the fluid surface with the pilot flame. External radiant heat was not used in these experiments. Measurements were made for the chemical heat release rate, calculated from the generation rates of carbon monoxide (CO) and carbon dioxide (CO_2) [3]. The mass loss rate (or mass flow rate) was measured using a load cell, under the platform where the sample dish was placed.

Spray Flammability Experiment

The experiments were performed in the FMRC Fire Products Collector [4] shown in Figure 2. In order to emphasize details of the spray setup, the figure is not drawn to scale.

The fluids were sprayed vertically upward in the open from an 80° hollow-cone nozzle with an exit diameter of 0.38 mm (5.68 liters/hour @ 0.69 MPa). The nozzle was located 1.5 m from the floor, in the center of a 15 kW, 0.14 m diameter propane-air ring burner with a flame height of about 0.20 m. The tip of the nozzle was in the same plane as the ring burner head. The nozzle was connected to a fluid container through a 3 m long stainless steel flexible tube (0.0064 m I.D.) lined with Teflon. The fluids in the

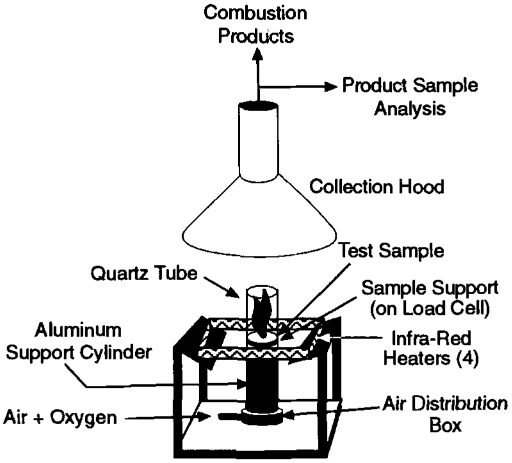


Figure 1. Factory Mutual Research Corporation Small-Scale (50-kW) Flammability Apparatus (not drawn to scale).

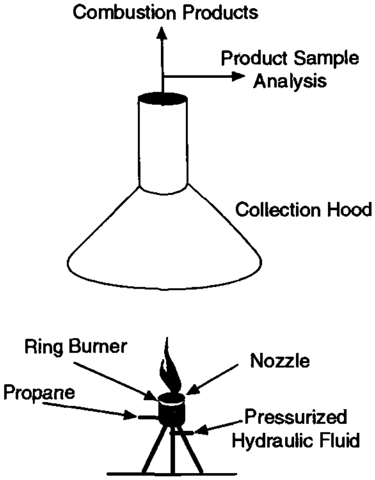


Figure 2. Factory Mutual Research Corporation Fire Products Collector and Fluid Spray Setup (not drawn to scale).

container were heated to 60°C, except for methanol, ethanol and n-heptane, and pressurized with nitrogen. Experiments were conducted at 6.9, 5.2, 3.5, and 1.7 MPa pressures.

All the combustion products along with the ambient air were drawn into the sampling duct of the apparatus, where measurements were made for the volumetric flow rate of the mixture of fire products and entrained air, gas temperature, generation rates of CO, CO_2, and consumption rate of oxygen (O_2). The chemical heat release rate [3] was calculated from the generation rates of CO and CO_2, and also from the consumption rate of O_2. The average steady state values of chemical heat release rates are reported in this paper. Other details have been described in References 1 and 5.

The average chemical heat of combustion was calculated by time integrating the chemical heat release rate to obtain the total energy released and dividing by the total mass of fluid injected into the spray.

After the fluid was heated and pressurized, the propane ring burner was turned on and the background data were recorded for one minute, at which time the nozzle valve was opened. The fluid was released as a spray and was ignited immediately. The propane burner remained on throughout the experiments to ensure a stable spray flame. Steady state conditions were achieved quickly (in about 20 s); the flames were well defined.

The fluid flow rate through the nozzle was determined from the initial and final weights of the fluid in the container and the time duration.

Flame Stabilization Test

This is a standard Approval test [6] which uses the same 80° hollow-cone nozzle (exit diameter of 0.38 mm). The atomized spray at 6.9 MPa pressure is directed horizontally into the open and a propane-air torch flame (about 100 mm in length) is introduced into the spray envelope at locations 152 mm and 457 mm downstream from the nozzle. If a spray flame is stabilized for more than 6 s after removal of the pilot flame for any one of the ten tests at each location, the fluid is considered to have failed the test.

DATA ANALYSIS

Physical properties of the fluid (such as volatility), degree of atomization (the size and size distribution of drops in spray) are expected to influence flame propagation [7]. It is known that flame propagation can influence minimum energy for ignition requirements (a measure of fluid volatility) and flame stabilization [8]. It has also been shown [7] that fluids with higher volatility have higher flame propagation rates (flame speeds) than fluids with lower volatility. In the following section, an attempt has been made to establish semi-empirical relationships based on measurable data to define a parameter which is expected to be a measure of flame propagation:

A spray flame is established when fluid is sprayed in the open at a constant nozzle pressure and is stabilized by an ignition source at the spray origin. It is assumed that combustion in a spray flame is primarily governed by the amount of heat transfer from the flame zone to the incoming spray droplets (near the nozzle exit) and the heat required to vaporize the droplets to produce a flammable mixture with air [9,10].

It is further assumed [3,11] that the amount of heat transfer to the droplets is proportional to the heat generation by combustion, i.e., chemical heat release rate, $\dot{Q}_{ch}$ (kW):

$$\dot{Q}_{ch} = \chi_{ch}\ \Delta H_T\ \dot{m}_f \qquad (1)$$

where $\dot{m}_f$ is the fluid mass flow rate (g/s) through the nozzle; χ_{ch} is the global efficiency of combustion,

$$\chi_{ch} = \Delta H_{ch}/\Delta H_T \qquad (2)$$

where ΔH_{ch} is the average chemical heat of combustion (kJ/g); and ΔH_T is the net heat of complete combustion (kJ/g). Note that ΔH_{ch} differs from ΔH_T by χ_{ch}. ΔH_{ch} is the amount of energy associated with the chemical reactions that generate CO_2 and consume O_2.

The efficiency of combustion, χ_{ch}, is expected to depend on the chemical and the physical nature of the fluids, degree of atomization, droplet size and spatial distribution, rate of vaporization of fluid, and amount of air available for combustion [5].

In order to create a flammable mixture, the droplets must be exposed to at least the critical heat flux $\dot{q}''_{cr}$ (kW/m^2) required for ignition (i.e., minimum ignition energy), which can be estimated from the fire point (assuming $\dot{q}''_{cr}$ is equal to the amount of radiation emitted from the fluid surface at the fire point temperature) as follows:

$$\dot{q}''_{cr} = \alpha\sigma T_f^4 \tag{3}$$

where α is the fluid surface absorptivity, assumed to be unity; σ is the Stefan-Boltzmann constant (5.67 x 10^{-11} kW/m^{2}k^4); and T_f is the fire point temperature (K) at ignition, a measure of volatility of the fluid. $\dot{q}''_{cr}$ represents the minimum heat flux required to raise the temperature to the fire point, at or above which the vapor pressure of a fluid is high enough to allow formation of a combustible vapor-air mixture.

Eq. (1) can be rewritten by defining $\dot{m}_f$, using an equivalent nozzle diameter, d_s(m),

$$\dot{Q}_{ch} = \chi_{ch}\,\Delta H_T\left(\frac{\pi}{4}\,d_s^2\,\rho_a u_o\right) \tag{4}$$

Note that $\dot{m}_f = \frac{\pi}{4}\,d_o^2\,\rho_f u_o = \frac{\pi}{4}\,d_s^2\,\rho_a u_o$, if $d_s = d_o\,(\rho_f/\rho_a)^{1/2}$; where d_o is the nozzle exit diameter (m), ρ_f and ρ_a are the fluid and ambient air densities (g/m^3), respectively, and u_o is the fluid exit velocity (m/s),

$$u_o = C_d\,(2\Delta P/\rho_f)^{1/2} \tag{5}$$

where C_d is the discharge coefficient of the nozzle; and ΔP is the pressure differential.

From the ratios of Eqs. (4) to (3) and normalizing with $\frac{\pi}{4}\,d_s^2$, a nondimensional spray flammability parameter (SFP) can be defined as follows:

$$\text{SFP} = 4\,\dot{Q}_{ch}/\pi d_s^2\,\dot{q}''_{cr} = \chi_{ch}\,\Delta H_T \rho_a u_o/\alpha\sigma T_f^4 \tag{6}$$

The droplet heating to ignition is expected to depend on the magnitude of $\dot{Q}_{ch}$ and on volatility (in terms of $\dot{q}''_{cr}$ or T_f), initial temperature of the fluid, degree of atomization and temperature of air entrained into the jet. SFP combines the chemical heat release rate from the spray fire with the fluid volatility as described by the critical heat flux for ignition. The value of SFP is expected to be a predictor of burning rate (or flame propagation rate). The fluids with higher SFP values are associated with a higher burning rate, and are expected to be easier to stabilize as spray flames than the fluids with lower SFP values.

RESULTS AND DISCUSSION

Experimental data are presented in Table 1.

TABLE 1--Experimental Data for Spray Flammability of Fluids [1,11]

Fluids	Nozzle Pressure (MPa)	ρ_f^a (kg/m^3)	$\dot{m}_f$ (g/s)	u_o (m/s)	$\dot{Q}_{ch}$ (kW)	ΔH_T (kJ/g)	ΔH_{ch} (kJ/g)	χ_{ch}	T_f (K)	$\dot{q}''_{cr}$ (kW/m^2)	SFP (10^4)
Organic/Polyol Esters:											
#1	6.9	924	5.85	55.5	220	36.6	35.8	0.98	553	5	49.86
	5.2		5.05	47.9	188		35.4	0.97			42.60
	3.5		4.07	38.6	151		35.3	0.97			34.22
	1.7		2.70	25.6	90		29.5	0.81			20.40
#2	6.9	922	5.87	55.8	216	35.7	35.0	0.98	541	5	48.96
	5.2		4.97	47.3	183		35.1	0.98			41.47
	3.5		4.11	39.1	151		35.0	0.98			34.22
#3	6.9	911	5.84	56.2	232	40.3	37.8	0.94	569	6	44.69
	5.2		4.92	47.4	194		37.5	0.93			37.31
	3.5		4.15	40.0	158		36.3	0.90			30.37
	1.7		1.80	17.3	62		25.0	0.62			11.89
#4	6.9	924	6.11	58.0	228	37.0	35.5	0.96	566	6	43.06
	5.2		5.0	47.5	191		36.3	0.98			36.03
	3.5		4.26	40.4	158		35.3	0.96			29.81
	1.7		2.70	25.4	76		23.9	0.65			14.39
Phosphate Esters											
#5	6.9	1130	5.13	39.8	158	ND	29.3	ND	593	7	21.02
#6	6.9	1110	5.20	41.1	166	31.8	29.7	0.93	589	7	22.42
	5.2		4.54	35.9	129		29.2	0.92			17.40
	3.5		3.72	29.4	102		28.8	0.91			13.81
	1.7		2.72	21.5	70		22.3	0.70			9.46
#7	6.9	1110	4.86	38.4	157	32.0	30.3	0.95	586	7	21.22
	5.2		4.51	35.6	130		29.5	0.92			17.57
	3.5		3.80	30.0	108		29.0	0.91			14.60
	1.7		2.80	22.0	72		21.8	0.68			9.73

TABLE 1--Experimental Data for Spray Flammability of Fluids [1,6] (continued)

Fluids	Nozzle Pressure (MPa)	$\rho_f{}^a$ (kg/m^3)	$\dot{m}_f$ (g/s)	u_o (m/s)	$\dot{Q}_{ch}$ (kW)	ΔH_T (kJ/g)	ΔH_{ch} (kJ/g)	χ_{ch}	T_f (K)	$\dot{q}''_{cr}$ (kW/m^2)	SFP (10^4)
Water-in-Oil Emulsion:											
#8	6.9	920	5.60	53.4	164	27.6	27.1	0.98	CM	9	20.63
	3.5		4.58	43.7	115		23.9	0.87			14.50
	1.7		3.68	35.1	94		ND	ND			11.83
Polyglycol-in-Water:											
#9	6.9	1078	5.91	48.1	65	11.0	10.5	0.95	CM	6	10.58
	3.5		4.21	34.2	45		10.2	0.93			8.82
	1.7		3.21	26.1	26		7.7	0.70			4.24
#10	6.9	1078	5.34	43.4	63	11.9	11.2	0.94	CM	7	8.82
	3.5		4.10	33,4	47		11.0	0.92			6.57
	1.7		3.18	25.9	27		8.1	0.68			3.79
#11	6.9	1079	6.05	49.2	78	14.7	12.3	0.84	CM	7	10.87
	3.5		4.44	36.1	56		12.0	0.82			7.84
	1.7		3.23	26.3	32		9.4	0.64			4.51
#12	6.9	1073	6.14	50.2	70	12.1	10.9	0.90	CM	7	9.79
	3.5		4.67	38.2	50		10.2	0.84			6.95
Mineral Oil:	6.9	874	5.71	57.2	255	46.0	44.6	0.97	525	4	76.81
	5.2		5.18	52.0	230		44.3	0.96			69.0
	3.5		4.45	44.7	202		44.1	0.96			60.60
	1.7		3.0	30.1	131		41.4	0.90			39.61
Methanol:	6.9	791	4.0	44.4	81	20.0	19.6	0.98	290	0.40^b	271.0
	5.2		3.20	35.5	64		19.7	0.99			215.0
	3.5		2.60	28.8	52		19.4	0.97			173.0
	1.7		2.24	24.9	44		19.6	0.98			148.0

TABLE 1--Experimental Data for Spray Flammability of Fluids [1,11] (continued)

Fluids	Nozzle Pressure (MPa)	ρ_f[a] (kg/m^3)	$\dot{m}_f$ (g/s)	u_o (m/s)	$\dot{Q}_{ch}$ (kW)	ΔH_T (kJ/g)	ΔH_{ch} (kJ/g)	χ_{ch}	T_f (K)	$\dot{q}''_{cr}$ (kW/m^2)	SFP (10^4)
Ethanol:	6.9	789	3.70	41.0	100	26.8	26.4	0.99	295	0.43[b]	309.0
	5.2		3.20	35.6	86		26.2	0.98			265.0
	3.5		2.71	30.0	72		26.0	0.97			223.0
	1.7		2.20	24.5	58		26.3	0.98			179.0
Heptane:	6.9	684	3.52	45.1	151	44.6	40.2	0.90	275	0.32[b]	717.0
	5.2		3.10	39.8	136		41.0	0.92			644.0
	3.5		2.47	31.7	108		40.7	0.91			512.0
	1.7		1.90	24.4	79		39.2	0.88			376.0

---

[a]: At 20°C

ND: Not determined.

CM: Could not measure.

[b]: Estimated by using Eq. (3).

Effects of Fluid Exit Velocities on the Efficiency of Combustion in Spray Flames

Figure 3 shows the relationship between the fluid exit velocity, u_0 (at 1.7 - 6.9 MPa nozzle injection pressures) and the efficiency of combustion, χ_{ch}, for the various hydraulic fluids, including mineral oil, methanol, ethanol and n-heptane spray flames [1,11,12]. It should be noted that variations in u_0 among fluids at a specific nozzle pressure are probably due to the differences in density and viscosity.

Figure 3 indicates that for hydraulic fluids, χ_{ch} decreases with decrease in u_0 at about u_0 <30 m/s (i.e., when the nozzle is operated at low pressure, 1.7 MPa). At u_0 >30 m/s (i.e., nozzle pressure approximately equal to or greater than 3.5 MPa), χ_{ch} reaches its maximum value and remains independent of u_0 within the range of nozzle pressures (3.5 - 6.9 MPa) tested. With increasing fineness of atomization (due to the increased nozzle injection pressure, i.e., increasing u_0), droplet size is expected to decrease and the evaporation and burning rates of fuel are expected to be rapid, enhancing efficiency of combustion.

For highly volatile fluids, such as methanol, ethanol and n-heptane, the efficiency of combustion appears to be independent of u_0 (between 1.7 to 6.9 MPa nozzle pressures). Droplets of highly volatile fluids are expected to vaporize rapidly with high efficiency of combustion.

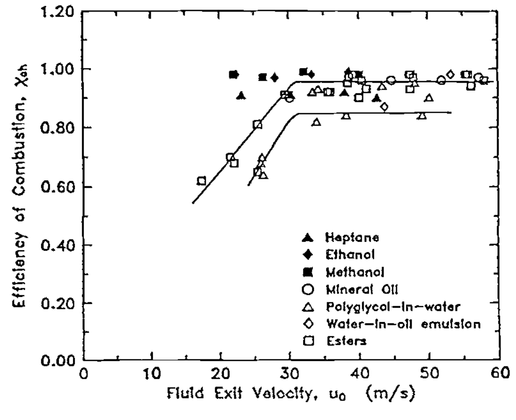


Figure 3. Efficiency of combustion as a Function of Fluid Exit Velocity.

Critical Heat Flux for Ignition

Critical heat flux for ignition, $\dot{q}''_{cr}$ (kW/m^2) can be determined from the fire point temperature, T_f of the fluid by using the relationship in Eq. (3). The value of $\dot{q}''_{cr}$ can also be estimated (especially for fluids whose fire point temperature cannot be measured, e.g., water-in-oil emulsion and polyglycol-in-water) from the ignition experiments.

Figures 4 and 5 present the reciprocal of time to piloted ignition as a function of external radiant heat flux per unit fluid surface area for mineral oil and water-in-oil emulsion, respectively.[1,11,12] Mineral oil, organic/polyol esters, and phosphate esters are single component fluids and exhibit a non-linear relationship, as indicated in Figure 4, where only mineral oil is shown for example. For the mixed fluids such as water-in-oil emulsion and polyglycol-in-water, the relationship is linear (in Figure 5, only water-in-oil emulsion is shown). However, $\dot{q}''_{cr}$ is estimated by extrapolating the curve (in Figs. 4 and 5) on the external heat flux axis. It should be noted in Figure 4, that $\dot{q}''_{cr}$ estimated by this extrapolation method and calculated by Eq. (3) shows excellent agreement.

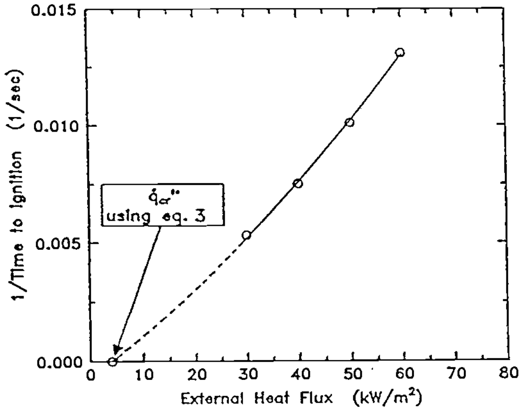


Figure 4. Relationship Between Time to Ignition and External Heat Flux for Mineral Oil.

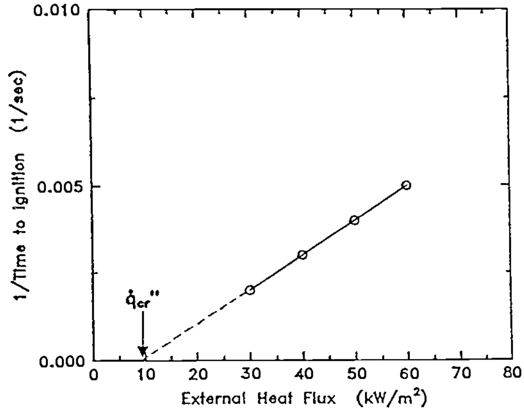


Figure 5. Relationship Between Time to Ignition and External Heat Flux for Water-In-Oil Emulsion.

Spray Flammability Parameter (SFP)

SFP values for all the fluids investigated in this study at various fluid exit velocities, u_o, are presented in Figure 6, where families of curves are shown for each group of fluid [6]. Figure 6 shows that SFP increases with the increase in u_o. Straight lines have been drawn for each group of hydraulic fluid at about $u_o > 30$ m/s, where χ_{ch} reaches the maximum and remains fairly constant (between 3.5 -6.9 MPa nozzle pressure, see Fig. 3). It should be noted that since χ_{ch} is constant, the increase in SFP with increasing nozzle pressure (or u_o) results from the increase of $\dot{Q}_{ch}$ because of increasing $\dot{m}_f$ (see Eqs. 1 and 4). At about $u_o < 30$ m/s (i.e., at 1.7 MPa pressure), the solid lines appear to deviate because of poor degree of fluid atomization, which probably produces larger droplets resulting in decrease in χ_{ch}.

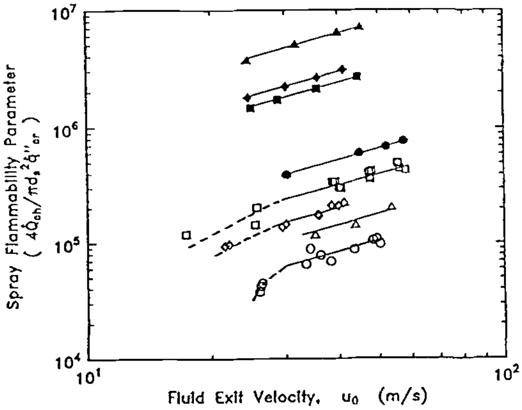


Figure 6. Spray Flammability Parameter as a Function of Fluid Exit Velocity:
□ organic/polyol esters; ◊ phosphate esters;
Δ water-in-oil emulsion; O polyglycol-in-water;
■ methanol; ◆ ethanol; ▲ heptane; ● mineral oil.

Data in Table 1 and in Figure 6 indicate that generally the higher the volatility of the fluids, the higher the SFP values. The fluids with higher SFP values are associated with a higher burning rate (or flame propagation rate), and are expected to be easier to stabilize as spray flames than the fluids with lower SFP values. As mentioned earlier, spray flame stabilization tests were conducted at a high fluid exit velocity (6.9 MPa nozzle pressure). At an SFP $\leq 25 \times 10^4$, a range of hydraulic fluids consistently could not be stabilized as spray flames. Mineral oil (which is considered to be more flammable than most hydraulic fluids), along with some hydraulic fluids, consistently stabilized as spray flames in the tests and has SFP values higher than 25 x 10^4. Although flame stabilization tests were not conducted for methanol, ethanol and n-heptane, they are expected to be easier to stabilize as spray flames because of higher SFP values. SFP (in the region where χ_{ch} reaches its maximum value and remains invariant with the increase in nozzle pressure or u_o) appears to be useful in discriminating between flammable and less flammable fluids in terms of ease of spray flame stabilization. It is, therefore, suggested to conduct the test for determining SFP value for hydraulic fluid at a high nozzle pressure (i.e., 6.9 MPa) to create a high degree of atomization so that the effect of drop size on combustion behavior can be eliminated and the fluids can be classified on the basis of their fire resistance only.

It should be pointed out that based on the hydraulic fluid samples investigated in this study, it appears (see Table 1) that if $\Delta H_T \leq 32$ kJ/g and $T_f \geq 590$ K, the fluid satisfies the condition: SFP $\leq 25 \times 10^4$.

Flammability of Fluid on Wick

Figure 7 shows the efficiency of combustion (from Eq. (1)), $\chi_{ch} = \dot{Q}_{ch}(t)/\Delta H_T \dot{m}_f(t)$, which is presented as a function of time for hydraulic fluids in small pool fires, using a round disc of porous ceramic paper soaked with fluid in an aluminum dish. 30% water-in-methanol has also been included in Figure 7. It can be noted in the figure that χ_{ch} remains approximately constant, and thus there is an insignificant separation of water from methanol during most of the combustion period. The ester, which is a single component fluid, burns as a single component fluid because its χ_{ch} remains approximately constant, as expected. The polyglycol-in-water solutions and water-in-oil emulsions, however, show that in the initial stages χ_{ch} keeps increasing, which suggests that water is the dominant component (preferential distillation), and in later stages the oil and the polyglycol are the only dominant components without water in the combustion.

Figure 8 presents the efficiency of combustion time-history for the same hydraulic fluids in spray fires (6.9 MPa nozzle pressure). The combustion efficiency remains fairly constant, indicating that the preferential combustion of the individual components in the water-in-oil emulsion and polyglycol-in-water fluids is negligible in the spray combustion experiments, as expected.

The experimental results indicate that burning of multi-component hydraulic fluids (such as water-in-oil emulsion and polyglycol-in-water) on a wick do not simulate burning of such fluids in an atomized spray. Results indicate that tests with a wick represent liquid pool or large drop combustion, but do not characterize realistic flammability behavior for multi-component hydraulic fluids. Thus, an atomized spray fire test which simulates the realistic mode of fire hazard appears to be a much better method for characterizing the potential flammability of all types of hydraulic fluids.

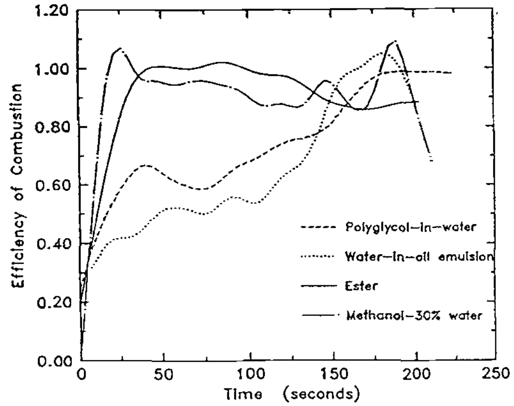


Figure 7. Efficiency of Combustion of Fluid on Wick as a Function of Time.

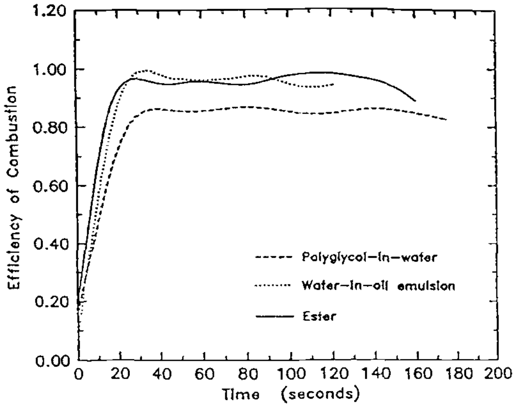


Figure 8. Efficiency of Combustion of Fluid in Spray as a Function of Time.

CONCLUSIONS

1. Hazards associated with hydraulic fluid spray fires were quantitatively characterized using a spray flammability parameter (SFP), which combines the chemical heat release rate from the spray fire with the volatility of fluids as described by the critical heat flux for ignition.

2. An SFP value of 25 x 10^4 was identified at or below which a range of hydraulic fluids cannot be stabilized as spray flames using a standard Approval flame stabilization test. SFP thus has been shown to be useful for identifying less flammable fluid in a spray.

3. Based on some experimental results, it is found that the burning of mixed hydraulic fluids, such was water-in-oil emulsion and polyglycol-in-water on a wick (porous ceramic paper disc) does not simulate burning of mixed fluids in an atomized spray.

4. Based on this study, a new test method for determining SFP for hydraulic fluids has been incorporated as part of a proposed FMRC Approval Standard.

REFERENCES

[1] Khan, M.M., "Spray Flammability of Hydraulic Fluids and Development of a Test Method," Technical Report, FMRC J.I. OTOW3.RC, Factory Mutual Research Corp., Norwood, MA., May 1991.

[2] Tewarson, A., Lee, J.L., and Pion, R.F., "The Influence of Oxygen Concentration on Fuel Parameters for Fire Modeling," Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, p. 563, 1981.

[3] Tewarson, A., "Generation of Heat and Chemical Compounds in Fires," Chapters 1-13, pp. 1-179 in the SFPE Handbook of Fire Protection Engineering, P.J. DiNenno (Editor). The National Fire Protection Association Press, Quincy, MA., 1988.

[4] Heskestad, G., "A Fire Products Collector for Calorimetry into the MW Range," Technical Report, J.1. OC2E1.RA, Factory Mutual Research Corporation, Norwood, MA., June 1981.

[5] Khan, M.M. and Tewarson, A., "Characterization of Hydraulic Fluid Spray Combustion," Fire Technology. November 1991.

[6] Approval Standard: Less Hazardous Hydraulic Fluids, Class Number 6930, Factory Mutual Research Corporation, Norwood, MA, 1975.

[7] Richards, G.A. and Lefebvre, A.H., "Turbulent Flame Speeds of Hydrocarbon Fuel Droplets in Air," Combustion and Flame, 78: 299-307 (1989).

[8] Lefebvre, A.H., Gas Turbine Combustion, Hemisphere, New York, 1983.

[9] Williams, A., "Fundamentals of Oil Combustion," Progress in Energy and Combustion Science, Vol. 2, pp. 167-179, 1976.

[10] Lin Cherng-Yuan, and Gollahalli, S.R., "Prediction of the Diluent Effects on the Structure of a Spray Flame," 1990 Fall Technical Meeting, the Eastern Section of the Combustion Institute, Dec. 3-5, Orlando, Fl.

[11] Khan, M.M., "Characterization of Liquid Fuel Spray Fires," HTD Vol. 223, Heat and Mass Transfer in Fire and Combustion Systems, ASME Winter Annual Meeting, 1992, pp. 37-44.

[12] Khan, M.M. and Brandao, A.V., "Method for Testing the Spray Flammability of Hydraulic Fluids," Society of Automotive Engineers (SAE) Technical Paper Series #921737; International Off-Highway & Powerplant Congress & Exposition, Milwaukee, Wisconsin, September 14-17, 1992 (SAE International, 400 Commonwealth Dr., Warrendale, PA 15096-0001, USA).

Armand V. Brandao[1]

IMPLEMENTATION OF REVISED EVALUATIONS OF LESS FLAMMABLE HYDRAULIC FLUIDS

REFERENCE: Brandao, A. V., "**Implementation of Revised Evaluations of Less Flammable Hydraulic Fluids,**" Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: Factory Mutual Research Corporation (FMRC) has evaluated and certified ("Approved") less flammable hydraulic fluids since the 1950s. This Approval is widely recognized among users, insurance interests, and regulators. However, the two traditionally used flammability tests (ignition of specifically defined sprays by open flame and a heated steel channel) have been shown to lack consistent repeatability. Consequently, the development of a new test methodology has been undertaken. The new protocol involves separate measurements of ease of ignition and heat release of the same spray discharge. These two measurements are then combined mathematically into a dimensionless "spray flammability parameter" (SFP), which becomes a unitary measure of the flammability hazard of the fluid. The revised methodology has been incorporated in the first significant revision to the Approval Standard for less flammable hydraulic fluids since the 1970s.

KEYWORDS: Certifications, combustion, fire resistance, flammability tests, hydraulic fluids, spray flammability.

---

[1] Senior Engineer & Fuels Approvals Manager, Factory Mutual Research Corporation, Norwood MA 02062

INTRODUCTION

The revised Approval Standard has progressed to the "outside review" stage, in which fluid producers, users, and other interested parties are invited to comment on the draft. Because of comments received, a variety of changes have been made. The most extensive of these has been the conversion of the standard from the traditional pass-fail evaluation to a “specification test” format. In this latter format, all fluids may be classified with regard to flammability and so listed.

If the new standard achieves adequate consensus, it will be adopted for future FMRC certifications of new fluids. It will also be used to reexamine all currently Approved fluids over a one-year grace period as a condition of their maintaining listing. To expedite this process, detailed test procedures will be developed to attempt to further improve consistency and repeatability of these evaluations by tightening controls on sample handling and measurements of test variables. Software will be written to allow automated completion of test records and calculation of SFP, as each test is completed, thereby reducing manual intervention and improving timeliness and accuracy.

A pre-screening algorithm has been written to allow producers to approximate the SFP of new fluids before committing to the expense of Approval evaluation. Making use of relatively easily measured properties such as fire point and net heat of combustion, some fluids can be shown to be "less flammable" without access to the large-scale apparatus used by FMRC. A second level of approximation can also be made by taking into account the typical combustion efficiency of similar fluids. Where the results of such pre-screening evaluations are unfavorable, a reduced scale spray flammability test may ultimately be developed to obviate the need for large scale testing.

BACKGROUND

Traditional flammability evaluations used in loss prevention engineering have incorporated scenario simulation testing. That is, attempts have been made to construct either full size or scaled down simulations of the process or machinery using the material and available ignition sources. Usually, these simulations incorporated some factor of safety by attempting to model realistic, but severe, incidents of deployment of the material and exposure to the ignition source.

Two problems have resulted from this approach. First, each industry has developed independent test protocols, the results of which are not easily correlated. Second, there is a great deal of art involved in designing such tests, even after the hazard to be modeled has been identified. Often, the most severe, reasonable scenario cannot be agreed upon. It is thus difficult to determine whether results incorporate a safety factor, and of what magnitude. Results can also vary after the protocol has been developed due to the necessity for observations of subjectively defined criteria, such as “full involvement in flame” or “complete charring”.

Conversely, more scientific laboratory tests of material flammability have suffered from an inability to correlate their results to material performance in the actual geometry of usage. Factors not easily scaled up include the effects of surface area to volume ratios, proportion of radiant energy supplied from the flame to preheat new material approaching the ignition source, and the effects of large scale heat-induced drafts. For example, some insulating materials with low flame propagation indexes, as determined by the industry-standard ASTM Test Method for Surface Burning Characteristics of Building Materials (E 84), have been shown to exhibit violent burning in FMRC’s 7.6 and 15.2 m (25 & 50 ft) high building corner tests [1].

However, in recent years pressure has been growing from all segments of industry to reduce the scale of testing in an attempt to reduce the attendant costs of introducing new materials. These costs include not only internal development costs, but also the costs of third-party certification testing where required by customer specifications or jurisdictional code authorities.

DEVELOPMENT OF THE SFP APPROACH

The current Approval Standard for less-flammable hydraulic fluids [2] incorporates two scenario simulation flammability tests. In each, an ignition source is introduced to a highly atomized spray of the fluid under test. One test uses an open flame for the ignition source, the other a heated steel surface. Multiple trials are attempted in each test. Success is based upon either non-ignition or self-extinguishment, when the ignition source is removed. These tests have not been significantly changed since the Approval standard was last revised in the 1970s. In the intervening years, there have been minor improvements in the apparatus in an attempt to improve fidelity to the stated test conditions and repeatability from trial to trial. By and large, these tests have been widely accepted across a broad spectrum of users, but not in some “severe application” industries, such as hot metal forming. These industries have continued to require additional testing to their own protocols.

In recent years, the offering of less flammable fluids using polyol ester chemistries has challenged the ability of these tests to discriminate clearly in marginal situations. Some of these fluids approached the limits of flammability to bring their other desirable performance characteristics to new applications. As a result, the traditional flammability tests began to be suspected of either inappropriately accepting or rejecting various fluids. In fact, some fluids were observed to apparently clearly “pass” one or the other of these tests on one occasion and to clearly “fail” on another. Further, an attempt in the 1980s to conduct round-robin verifications of the repeatabilities of these tests also yielded disappointing results.

For these reasons, the Research Division was enlisted to research existing methodologies for applicable flammability tests and to recommend improvements for the certification program. The results of that investigation are discussed in a Technical Report, Spray Flammability of Hydraulic Fluids and Development of a Test Method (FMRC JI 0T0W3.RC) [3]. This report concluded that no existing test methods assessed flammability of these fluids in a manner that would suggest that the results would be applicable in a wide range of deployment and ignition scenarios. It then proposed a new approach, which utilized established flammability research techniques to measure the fundamental characteristics of a fluid's ignitability and heat release rate. These two aspects of the flammability hazard were then mathematically combined into a single measure which was termed "Spray Flammability Parameter", or SFP. This parameter was established for a variety of commercially available hydraulic fluids and also some control substances, the characteristics of which are well known. These included mineral oil, methanol, ethanol, and normal heptane.

The proposed SFP can be considered a measured property of the fluid, much as is density or viscosity. As such, it is scenario independent and may be indicative of the fluid's flammability hazard in any application. Further, the research program indicated that this measurement is not significantly affected by viscosity. Therefore, the effects of deterioration of viscosity improvers in applications in which the fluid is subject to shearing should not affect its established flammability.

For these reasons, it was decided to adopt the new methodology in a revision of the Approval Standard, in an attempt to improve the accuracy of the certification process. Accordingly, a new draft has been written and circulated to interested parties for comment. These included representative users, producers, and technical experts (both within and outside FMRC).

As a result of that review and the comments received, the draft of the standard has been extensively revised. Rather than making a strict pass-fail distinction, the latest draft now proposes a classification system. Fluids will be classed as follows:

<u>Group 1</u>	Unable to stabilize a spray flame, having an SFP of 20 x 10^4, or less.
<u>Group 2</u>	Less flammable than mineral oil fluids, but may stabilize a spray flame under certain conditions, having an SFP greater than 20, but less than 40 x 10^4.
<u>Group 3</u>	Flammability approximating that of mineral oil fluids, having an SFP greater than 40 x 10^4.

The approach of classifying fluids will allow users to weigh flammability against other properties when selecting fluids and, thus, make more cost-effective purchasing decisions. In these decisions, the cost of containment, auxiliary extinguishing systems, or other "hardening" of the installation which may be required by the authority having jurisdiction must also be factored into the decision based upon total installed and operating costs.

It should also be noted that the assignment of fluids into classes, rather than publishing actual SFPs, attempts to avoid misleading purchasers into giving consideration to the functionally trivial differences between the values assigned to two different fluids within the same class. Some laboratories involved in strict rating, rather than classification, programs have been besieged by manufacturers pursuing incremental improvements in their product's rating. Classification is a reasonable strategy to avoid a laboratory's becoming involved in such marketing wars.

Obviously, the measurement of SFP currently requires the use of the FMRC Fire Products Collector [4], or an equivalent apparatus not generally available. This could result in scheduling delays for manufacturers seeking Approval of new fluids, as this apparatus is used for a variety of other research and testing programs. Further, implementation of the revised standard would require that all fluids currently Approved be classified per the SFP methodology within one year of the effective date of the new standard. This could also result in delays and additional expense for the affected manufacturers if their submittals are not timely. Similarly, if a manufacturer were to encounter unforseen undesirable performance, the turnaround time for reformulation and retest might be burdensome. In an attempt to at least partially address this problem, a screening algorithm has been developed]. This algorithm attempts to minimize the number of Fire Products Collector tests that will be required to assess a fluid's flammability.

SCREENING ALGORITHM

Figure 1 is a flow chart of the evaluation process, which incorporates the screening algorithm. The logic is based on the following:

SFP is defined by Equation 1,

$$SFP = Q_{ch} / (d_s^2 \times q''_{CR}) \qquad (1)$$

where Q_{ch} is the chemical heat release rate determined from Fire Products Collector testing and expressed in units of kW,

q''_{CR} is the critical heat flux for ignition determined per the piloted ignition test described in Reference 1 and expressed in units of kW/m^2, and

d_s is the equivalent diameter of the nozzle, expressed in units of meters. (Nozzle exit diameter is multiplied by the ratio of the square root of the fluid density at the test temperature to the ambient air density to obtain equivalent diameter. Ambient air density is taken as 1.2 kg/m^3 and density of the fluid must be measured at ambient temperature and expressed in the same units for this calculation.)

However, Khan [4] has shown that SFP can also be expressed as follows:

$$SFP = \chi_{ch} \times \Delta H_T \times \rho_a \times u_0 / (\alpha \times \sigma \times T^4_f), \qquad (2)$$

where χ_{ch} is the (dimensionless) efficiency of combustion;

ΔH_T is the net heat of complete combustion, measured per the ASTM Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (D 240), and expressed in units of kJ/g;

ρ_a is the ambient air density, expressed in units of g/m^3;

u_0 is the fluid exit velocity, in units of m/s;

α is the fluid surface absorptivity, assumed to be unity;

σ is the Stefan-Boltzman constant (5.67×10^{-11} kW/m^{2}K^4); and

T_f is the fire point temperature measured per ANSI/ASTM Standard Test method for Flash and Fire Points by Cleveland Open Cup (D 92), in units of K.

Further, it is possible to calculate u_0 as follows:

$$u_0 = C_d \times (2 \times \Delta P/\rho_f)^{1/2}, \qquad (3)$$

where C_d is the discharge coefficient of the nozzle,

ΔP is the pressure differential across the nozzle in units of kPa, and

ρ_f is the ambient fluid density in units of g/m^3.

Since ρ_a, α, σ, C_d and ΔP are constants, and ρ_f can be easily measured, Equations 2 and 3 can be combined to yield a simplified relationship:

$$SFP = (\text{a constant for a given fluid}) \times \chi_{ch} \times \Delta H_T / T^4_f \qquad (4)$$

If χ_{ch} is assumed = 1, a conservative assumption, since combustion efficiency will always be less than 1, the relation can be further simplified to:

$$SFP_1 = (\text{a constant for a given fluid}) \times \Delta H_T / T^4_f \qquad (5)$$

This leads to the starting point of Figure 1.

If ΔH_T and T_f are both known, one moves from box 1, through box 3, directly to box 7 to make a first order estimate of SFP.

On the other hand, if this is a new fluid and one or the other of the two variables is not known, they must be measured by the appropriate test method, taking the appropriate routes through boxes 2, 4, and 5. Further, if the fluid is not single phase, it is difficult to measure a true fire point, because the phases are preferentially evaporated. If, as with many hydraulic fluids, one of the phases is water, then ignition cannot occur until nearly all of the water has been evaporated. Therefore, for these fluids, the FMRC piloted ignition method must be used to determine the critical heat flux for ignition, as indicated by the path through box 6. In this latter situation, SFP is approximated as follows:

$$SFP_1 = \Delta H_T \times \rho_a \times u_0 / q''_{CR} \qquad (6)$$

From Appendix G of Reference 3, it can be seen that combustion efficiencies for organic esters average in the high 90 percent range for the proposed standard's 6.9 MPa discharge test pressure. Therefore, it may be reasonable to assume χ_{ch} = 0.95 for the second order approximation of SFP for these fluids (box 9). This value and those for fluids of other chemistries will be further refined as additional test data become available.

If this estimate is not satisfactory at the decision box 10, then it will be necessary to conduct Fire Products Collector testing to measure Q_{ch} accurately and calculate a true SFP, per Equation 1. This takes one through boxes 11 and 12.

At box 13, the final decision is made. If the SFP thus obtained permits classification in the range desired one comes to the desirable conclusion at box 14. Conversely, if SFP is still not in the desired range, then the only option is indicated at box 15. The fluid must be modified and reenter the screening process and proceed via the appropriate path once again.

CONCLUSIONS

1. A revised test methodology was required to make hydraulic fluid flammability evaluations more accurate, fair, and universally applicable.

2. SFP addresses these goals by measuring two components of flammability,

ignitability and heat release in a non-scenarion specific configuration, and combining them in a dimensionless single parameter.

3. The change from a pass-fail evaluation to a classification scheme mirrors the classification of fluids with regard to other properties, such as viscosity. As such, it provides the user with information that would otherwise not be available for knowledgable selection of the most acceptable tradeoff in fluid properties.

4. For fluids with well-defined fire points and a known net heat of combustion, it will not always be necessary to use the unique Fire Products Collector apparatus to assign hydraulic fluids to the appropriate SFP class.

5. A screening algorithm has been portrayed in a flow chart to clarify the alternatives to Fire Products Collector testing.

REFERENCES

1. Approval Standard: Class 1 Insulated Wall or Wall & Roof Ceiling Panels, Plastic Interior Finish Materials, Plastic Exterior Building Panels, Wall/Ceiling Coating Systems, Interior or Exterior Finish Systems, Class Number 4880, Factory Mutual Research Corporation, Norwood, MA. August 1994.

2. Approval Standard: Less Hazardous Hydraulic Fluids, Class Number 6930. Factory Mutual Research Corporation, Norwood, MA. February 7, 1975.

3. Khan, M.M., "Spray Flammability of Hydraulic Fluids and Development of a Test Method", Technical Report, FMRC JI 0T0W3.RC, Factory Mutual Research Corp., Norwood, MA, May 1991.

4. Khan, M.M., "Spray Flammability of Hydraulic Fluids", <u>Fire Resistance of Industrial Fluids ASTM STP 1284</u>, George E. Totten, Jürgen Reichel, Eds, American Society for Testing and Materials, Philadelphia, 1995.

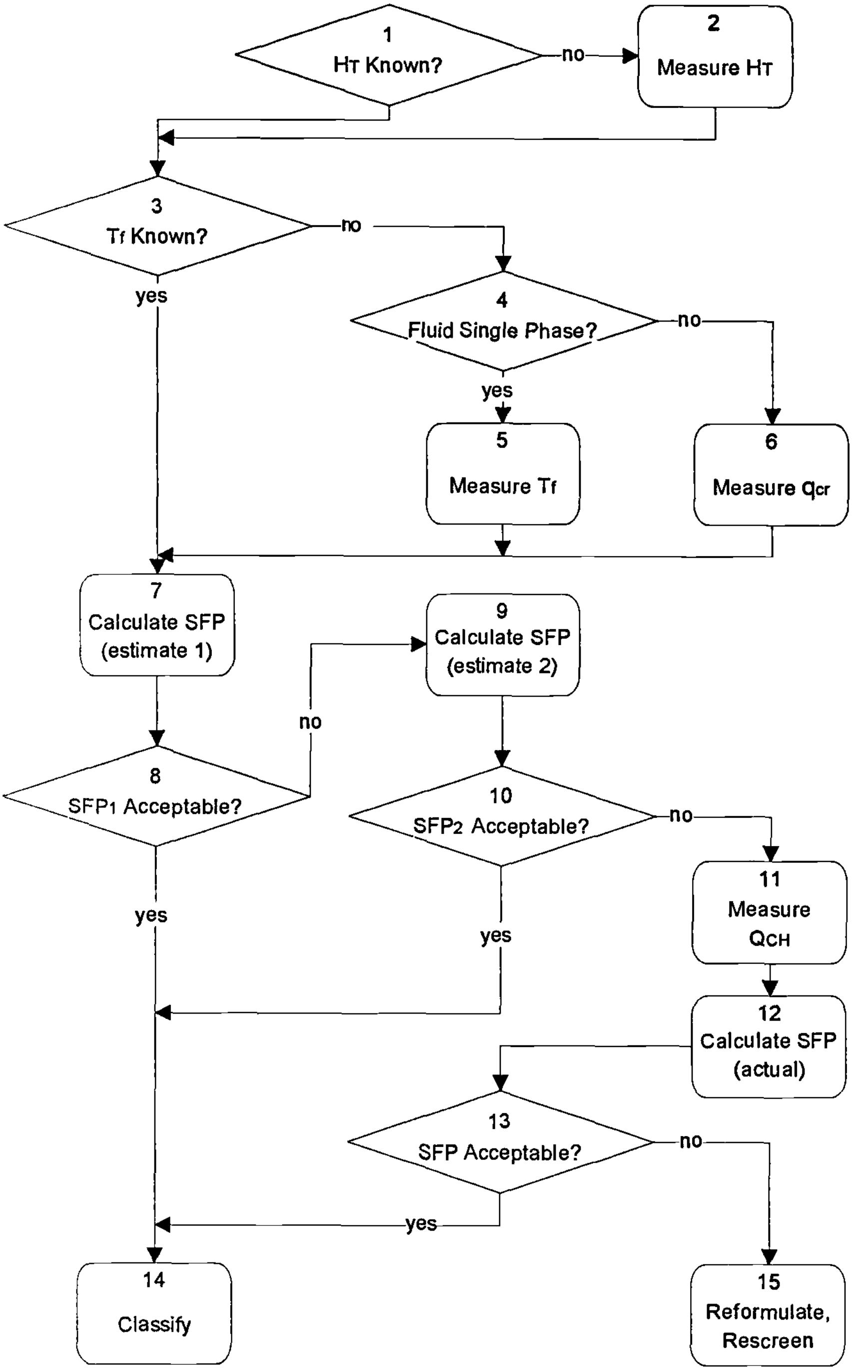


Figure 1. Flow Chart for Evaluation Process for Hydraulic Fluids Flammability Classification

Arthur F. Grand[1] and Javier O. Trevino[2]

FLAMMABILITY SCREENING AND FIRE HAZARD OF INDUSTRIAL FLUIDS USING THE CONE CALORIMETER

Reference: Grand, A. F. and Trevino, J. O., **"Flammability Screening, And Fire Hazard Of Industrial Fluids Using The Cone Calorimeter,"** Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

Abstract: There are numerous qualitative test methods to evaluate the flammability characteristics of industrial fluids (e.g., hydraulic fluids). These methods generally are based on potentially hazardous scenarios such as ignition of fluid droplets by a hot manifold or fluid sprays by an open flame. However, there is a need for a reproducible, quantitative, bench-scale test for screening the potential flammability of industrial fluids in such a way that good engineering data are also obtained. Preliminary laboratory evaluations were conducted using the "cone calorimeter," according to ASTM E1354, to assess the feasibility of this technique as a standard test method for industrial fluids. Specimens ranging in volume up to 28 mL in pans up to 100 mm diameter were evaluated, although most testing was conducted using 14 mL in 77 mm diameter pans. The specimens were exposed to external radiant heat fluxes of 25 to 50 kW/m^2. Measured parameters included ignition time, heat release rate, mass loss, effective heat of combustion, and smoke evolution. The seven fluids evaluated had a broad range of flammability and smoke properties. Limited large scale comparison tests were conducted with 0.9 m diameter pool fires. The versatility, reliability and accuracy of the cone calorimeter applied to industrial fluids make it a viable candidate for consideration as a standard test method for screening and fire hazard analysis.

Keywords: cone calorimeter, heat release, heat of combustion, smoke obscuration, calorimetry, heat flux, hydraulic fluids, pool fire

---

[1] Director of Research, Omega Point Laboratories, Inc. Elmendorf, TX 78112

[2] Fire Test Technologist, Omega Point Laboratories, Inc. Elmendorf, TX 78112

INTRODUCTION

Industrial fluids are used in numerous applications requiring specific properties. These properties include viscosity, heat capacity, density, lubricity, color, chemical resistance, biodegradability, toxicity, and flammability. The fluids range in composition from mostly water (e.g., some water-glycol mixtures), hydrocarbons (e.g., mineral oils), and numerous other compositions (e.g. phosphate esters and polyol esters). Some properties of these fluids, including flammability, are measured using qualitative or quantitative test methods.

Currently available fluid tests are designed to evaluate the "flammability" of the fluid being tested using "pass/fail" criteria. These criteria often include the ignitability of the fluid under certain test conditions. Other tests are designed to measure specific properties of the fluid, such as heat of combustion, ignition temperature, flame propagation, and heat release rate. Comparisons among the results of these different test methods are not currently available. Thus, a result from one test may not necessarily reflect the behavior of a material in another test procedure (e.g., the ignitability of a fluid in the "Hot Manifold Test" may not necessarily correlate to its ignitability in a spray ignition test). In order to fully evaluate the flammability properties of a fluid, one must subject that fluid to a battery of procedures. Although most of the methods available today are laboratory scale tests, some of the more widely accepted methods involve large apparatuses that consequently result in relatively high testing costs.

There is a need for a laboratory scale technique for screening the potential flammability of industrial fluids and for gathering engineering data that can be applied to ~~an~~ realistically estimate potential fire hazard. A standard test apparatus, the "cone calorimeter," has the potential for satisfying the needs both for a screening test and an engineering test for fire hazard analysis. This device is described in ASTM E1354 Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter. International recognition of this apparatus is also very important, since many of the fluid flammability tests have been developed and/or conducted in European countries. Therefore, although we will generally refer to the cone calorimeter in this paper as ASTM E1354, the reader should note that the same apparatus is described in the International Organization for Standardization method ISO 5660.

In this paper, preliminary results of tests on various industrial fluids using the cone calorimeter are presented. These results and the slightly modified procedures we developed are the basis for a recommended test protocol. A correlation among data gathered using the cone calorimeter and the other fluid flammability tests has not been established. However, the breadth and quantity of data obtainable with the cone calorimeter should be useful in relating fluid flammability properties to other test methods.

Current Test Methods

As previously noted, there exists a wide array of test methods which measure specific flammability parameters. These parameters include auto ignition temperature, flame spread, ignitability, flash point, fire point, heat of combustion, heating rate, heat release rate, and spray flammability parameter. The more common flammability test methods employed today are outlined in Table I (this information was taken in part from [1]). The table includes the generic test designation, the principle of the method, and the parameter(s) being measured.

TABLE 1 -- Outline of common flammability tests for fluids

Test Designation	Test Method	Parameter(s) Measured
Open Cup Flash and Fire Point (ASTM D-92)	Open cup flame exposure	Vapor ignition temperature and sustained ignition temperature
Linear Flame Propagation	Soaked string flame exposure	Flame spread velocity
Auto Ignition Temperature (ASTM D-2155 replaced w/ ASTM E659)	Open flask heat exposure	Auto ignition temperature
Heat of Combustion (ASTM D-240)	Bomb calorimeter	Heat of Combustion
Heating Rate	Immersion heated fluid filled flask	Fluid temperature increase rate
"Monsanto" Molten Metal Test	Fluid stream exposure to molten metal	Ignition (Pass/Fail)
Hot Manifold Test	Dripping fluid onto hot metal tube	Ignition on tube and/or after dripping from tube (Pass/Fail)
FM Hot Channel Ignition Test	Fluid spray exposure to inclined hot surface	Sustained ignition (Pass/Fail)
Spray Ignition Flammability Test	Low/high pressure spray exposure to open flame/ rotating torch	Visual flame properties/ sustained ignition (Pass/Fail)
FM High Pressure Spray Flammability Test	Vertical high pressure spray exposure to external heat (flaming source), convective flow collection hood	Spray Flammability Parameter based on chemical heat release rate and minimum external heat flux for ignition
Buxton Test Method	Horizontal high pressure spray exposure to flame into exhaust duct	Heat output, oxygen depletion, smoke number (1-10) based on optical density measurements
Flame Propagation (Wick) Tests	Soaked wick exposure to open flame (fixed wick/ rotating wick)	Burning time/ignitability based on no. of exposures required to ignite wick
Soaked Cube Flammability Test	Fluid filled cavity exposure to muffle furnace	Ignition temperature

APPARATUS AND TEST PROCEDURES

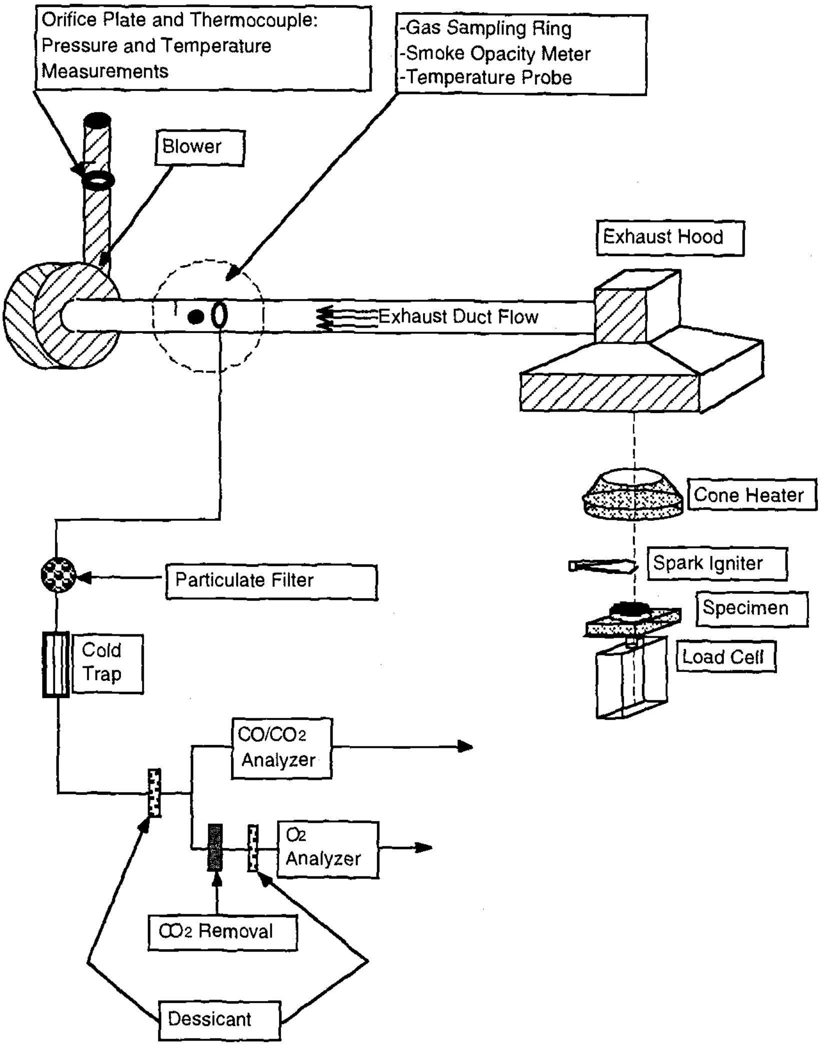


FIGURE 1--Schematic drawing of the cone calorimeter (ASTM E1354)

The Cone Calorimeter

A schematic drawing of the cone calorimeter (ASTM E1354) is shown in Figure 1. The method is based on the principle of "oxygen consumption calorimetry." The net heat of combustion of most organic materials is directly related to the amount of oxygen consumed during combustion. The value used is 13.1 MJ of heat released per kg of oxygen consumed. The standard procedure involves exposing samples measuring 100 mm x 100 mm (3.9 in. x 3.9 in.) x up to 50 mm (2 in.) thick to an external radiant heat flux of up to 100 kW/m^2, generally in the presence of a spark ignition source. The sample is exposed in a horizontal orientation (with vertical exposure as an option) and rests on a load cell for continuous measurement of mass loss. Smoke,-including gaseous products, are collected in a forced-flow collection system. Oxygen, carbon monoxide, and carbon dioxide are sampled from the exhaust duct, treated to remove moisture, and analyzed by instruments specific to those gases. The oxygen concentration in the duct along with the temperature and flow rate of the exhaust gases (monitored by an orifice plate and pressure transducer system) are used to calculate the heat release rate of the specimen undergoing combustion. Data are collected using a computer data acquisition system.

The results are generally expressed as time to sustained ignition (4 s or more not requiring the presence of the igniter); peak and average heat release rates, total heat released; total mass loss and mass loss rate; effective heat of combustion; smoke evolution (as extinction coefficient and specific extinction area); and concentrations and yields of carbon monoxide and carbon dioxide. These parameters are listed in Table 2, with the usual units and whether or not these are reported in the summary tables of results.

TABLE 2 -- Features of the cone calorimeter

Parameter	**Units**	**Reported Herein**
applied heat flux	kW/m^2	Y
time to sustained ignition	s	Y (a)
peak heat release rate	kW/m^2	Y
average heat release rate	kW/m^2	Y (60 s avg.)
total heat released	kJ	Y
total mass loss	g	N (b)
mass loss rate	g/s	N (c)
effective heat of combustion	MJ/kg	Y
smoke obscuration (extinction coefficient)	m^{-1}	N (d)
specific extinction area	m^2/kg	Y (avg.)
CO and CO_2 concentrations in duct	ppm, %	N (e)
CO and CO_2 yields	kg/kg	N (e)

Notes:
a) Both "flash" ignition and sustained ignition are reported.
b) Total mass loss was 100 percent for these fluids and test conditions; therefore, it is not reported in the tables.
c) Mass loss rate is directly proportional to heat release rate and is not presented herein as an independent value.
d) Smoke obscuration is reported for one run, as an example.
e) Gas concentrations are not reported herein; however, these data were obtained.

Specific Extinction Area (SEA), one of the items shown above, is somewhat harder to understand than heat release rate and many of the other parameters derived from the cone calorimeter. This value is derived from the extinction coefficient (similar to "optical density") of the smoke in the exhaust duct, normalized to duct flow rate and specimen mass loss.

Cone calorimeter data can be obtained over a range of external heat fluxes (whereas a single heat flux is usually specified in a standard testing protocol). These results are very useful for research and development purposes because they may be used to calculate other fire-related parameters such as heat of gasification and a thermal response parameter.

Cone Calorimeter Test Procedure

The standard test procedure specifies that the cone-shaped electric heater is positioned 25 mm (1 in.) from the top of the specimen and that the spark ignition source is positioned midway between the specimen and the cone heater (see Figure 1). The products of combustion from the burning specimen pass through the truncated-cone heater and are collected in an exhaust duct. Important events (e.g., times to ignition) are noted and the test is terminated after all flames have ceased. For these tests, a scan rate of two seconds was used.

For testing fluids, the only procedure that had to be modified was the specimen preparation. A 20 ga. stainless steel pan measuring 77 mm (approximately 3 in.) in diameter x 13 mm (1/2 in.) deep was used in most experiments to contain the fluid. A disposable syringe was used to deliver a precise quantity of the fluid into the pan, which was then placed on a 100 mm square x 12 mm thick piece of calcium silicate board (nominal density of 700 kg/m^3) on top of the metal specimen holder described in the E1354 method. In our test procedure, the specimen was shielded from the heat (by a "shutter" immediately beneath the cone heater) during positioning on the load cell, which was accomplished in less than 10s. Upon exposure to the heat flux, the specimen heated up, pyrolyzed, and subsequently ignited. For these materials, "flashing," or non-sustained ignition, was often observed and is noted in the data summaries.

Large Scale Test Procedure

In the large scale test procedure, we used the same basic principles as in the cone calorimeter method. The setup is described in ASTM E 1537 and consists of a "furniture calorimeter" used to measure heat release, smoke release, and mass loss of a large item. The same oxygen consumption principle is used to compute heat release rate. The main difference between the small scale and large scale procedures was the manner of generating the external heat flux and ignition, due to the large size of the test specimen. A 16 ga. stainless steel pan measuring approximately 0.91 m (36 in.) diameter by 50 mm (2 in.) deep was placed on a gypsum-lined load cell platform underneath a 3 m x 3 m (10 ft x 10 ft) collection hood. The fluid was pumped (monitored by volume) into the pan until the desired fluid depth was achieved. A propane grid burner measuring 0.63 m x 0.63 m (approximately 25 in. x 25 in.) was designed so that a flat plane of flames was present over the surface of the fluid. The burner was placed approximately 25 mm (1 in.) above the surface and ignited to create an external heat flux of approximately 13 kw/m^2 normalized across the area of the fluid (approximately 21 kW/m^2 immediately underneath the burner). Upon ignition of the fluid, the burner flames were removed, allowing the fluid to burn freely under its own heat feedback. All heat, smoke, and mass loss data were recorded by computer while observational data were recorded by the test engineer.

SAMPLES TESTED

The seven fluids used in this study are described briefly below. The fluid identification is coded to correlate with the data presented in later sections of this paper.

Code	Fluid Type
A	Hydraulic Oil
B	Phosphate Ester
C	Water Glycol #1 (40% Water)
D	Diol Ester
E	Polyol Ester
F	TMP (trimethylol propane) Ester
G	Water Glycol #2 (40% Water)

All fluids were kept at room temperature prior to testing.

RESULTS AND DISCUSSION

Several variations in the test procedure were studied to establish the suitability of the cone calorimeter method for application to industrial fluids. These variations included the specimen pan support, specimen pan diameter, fluid volume (depth) and external heat flux. Examination of these variations resulted in the establishment of several parameters for subsequent tests. These parameters are noted below.

- A 77 mm diameter stainless steel pan was selected over a 100 mm pan because it permitted less fluid to be used for testing, produced a smaller flame that was more controlled within the confines of the cone heating element, and produced essentially the same results as the other pan when normalized to an equivalent surface area.

- A fluid volume of 14 mL was selected for most testing, which produced a depth in the 77 mm diameter pan of approximately 3 mm. The relationship of the results of testing 1 mm, 3 mm and 6 mm depths are reported below. It was deemed important to use a uniform volume for all fluids in comparable tests and a minimum depth of 3 mm in order to obtain reliable results.

- Calcium silicate board, on top of the metal specimen holder that is described in the E1354 method, was selected as the support for the sample pan. This offered two advantages over the ceramic fiber insulating blanket recommended in the standard procedure. First, the board was a more stable and more level platform for the liquids than the compressible blanket material. Second, the higher density of the board provided a modest heat sink (as opposed to the blanket that absorbs very little heat), permitting the specimen to behave in a more "thermally thick" manner. Use of the blanket in place of the board caused the liquids to overheat near the end of the test, spilling pyrolysis products out of the pan and producing unusually high peak heat release rates. In a few tests, we wrapped the board in aluminum foil, producing no change in the pattern of heat release rate vs. time, but providing a more repeatable test protocol and helping to keep the board free of contamination.

- External applied heat fluxes of 25, 35 and 50 kW/m^2 were evaluated (details and results are given below). Most of the testing was performed at 25 kW/m^2 because all of the fluids ignited at that level and the lower heat flux was less prone to problems with overheating.

It was important that the results of this study establish that the proposed test procedure could differentiate among the results of different materials. These results are summarized in Table 3. The data reflect averages from replicate tests (two, in most cases). A large quantity of data is obtainable from the cone calorimeter test procedure, as demonstrated by the "summary" of results in the table. Therefore, serious consideration must be given to the manner and the detail in which these data are used to evaluate the performance of any given specimen.

TABLE 3 -- Summary of results of tests of various industrial fluids in the cone calorimeter at 25 kW/m^2 external heat flux

Pan diameter = 77 mm, Volume of fluid = 14 mL

Fluid	Flash Ign. (s)	Sust. Ign. (s)	Peak HRR (kW/m^2)	Avg. HRR 60s (kW/m^2)	THR (kJ)	Flame Out (s)	Eff. Hc (MJ/kg)	Avg. SEA (m^2/kg)	Initial Mass (g)
A	72	84	579	166	486	376	40.2	730	12.1
B	89	146	334	153	233	363	14.8	2180	15.8
C	...	202	289	139	178	417	12.0	7	14.8
D	77	122	778	119	459	402	35.9	520	12.8
E	126	143	735	118	454	398	34.8	600	13.1
F	193	202	913	136	469	419	36.1	510	13.0
G	...	167	404	185	208	355	13.7	1	15.2

Notes and Abbreviations:
All data are averages of at least two tests
Flash Ign. – Onset of periodic ignition of vapors (flashing)
Sust. Ign. – Sustained ignition for at least 4 s that did not require the presence of the spark igniter
Peak HRR – Maximum Heat Release Rate for the duration of the run
Avg. HRR – Average Heat Release Rate for 60s following sustained ignition
THR – Total Heat Released
Eff. Hc – Effective Heat of Combustion
SEA – Specific Extinction Area (smoke)

From the data in Table 3 and the plots in Figures 2a and 2b, it is apparent that the seven fluids produced results that were substantially different from one another. This includes the pattern of the heat release rate (HRR) curves vs. time (figures), and the values for times to ignition, peak and average HRR values, effective heats of combustion, smoke, etc. Figure 3 is an example of the relationship of HRR to mass loss and smoke evolution for a single specimen. Mass loss, a commonly-reported parameter, is not shown in the tables because it was found that these fluids burned with essentially no residue under these test conditions. Therefore, it did not seem necessary to report the mass loss in the tables.

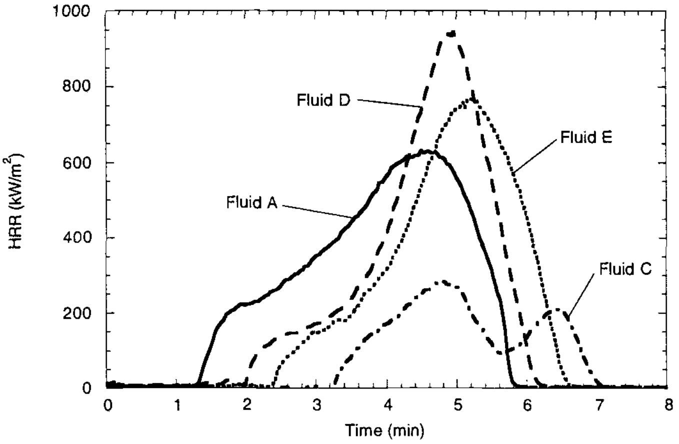


FIGURE 2a--Heat release rate curves for several industrial fluids at an external heat flux of 25 kW/m^2

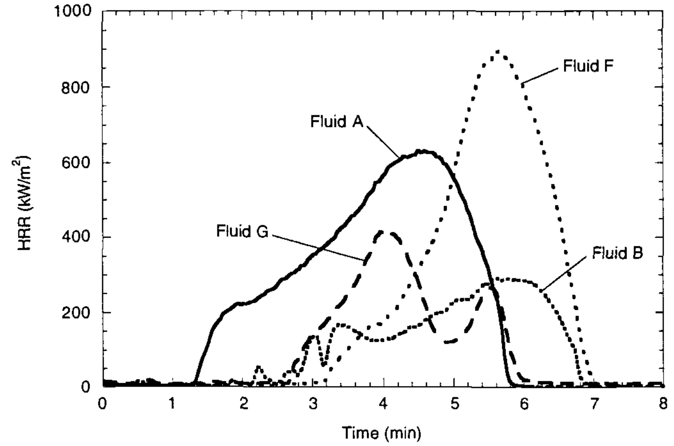


FIGURE 2b--Heat release rate curves for several industrial fluids at an external heat flux of 25 kW/m^2

The reasons for the different appearances of the HRR-time curves (Figure 2) have not been established. Peaks in HRR data near the end of a test (for solids as well as liquids) are sometimes due to an increased burning rate associated with vaporization of the remainder of the specimen, causing a peak in the heat release rate. In the case of the water-glycol mixtures (Fluids C and G), the flames had very different appearances corresponding to the two peaks. For these solutions, it is possible that the first peak represents the burning of a glycol-water azeotrope, while the second peak represents the burning of the residual glycol after all of the water is gone.

Some of the fluids tested developed more than one peak HRR value, although we only reported the highest peak in the summary table. The issue of multiple peaks will have to be resolved prior to the establishment of a standard test protocol. It is likely that an "average" HRR value (e.g., for the 60 s period following sustained ignition) as shown in Table 3, may be more useful for these materials than the peak HRR. In any event, caution is advised when interpreting the heat release rate data from these tests.

Compared to mineral oil (Fluid A), most of the other fluids tested had delayed ignition and lower effective heats of combustion, both of which are associated with lower flammability. However, the other properties were less consistent. Thus, Fluids B, C and G had lower peak HRR values than A, but not necessarily significantly lower Avg. HRR numbers. The lowest values for the Avg. HRR were Fluids D and E, which had high peaks (however, keep in mind that the peak values for fluids may not be the best factor for comparison). As an interesting note, the times to "sustained ignition" for Fluids B and E (organics) were similar to Fluid G (a water-glycol), and Fluid F (another organic) was similar to Fluid C (another water-glycol). However, the organic fluids all began to "flash" earlier in the test (from 9 to nearly 60 seconds prior to "sustained ignition"), while the water-glycol solutions were presumably evaporating water and showed no flashing ignition.

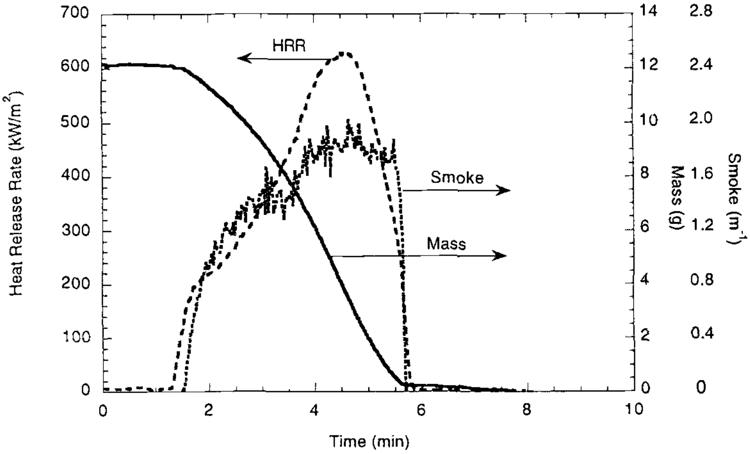


FIGURE 3--Heat release rate, mass loss and smoke for a single fluid (Fluid A)

The water-glycol fluids (C and G) produced very little smoke (i.e., the SEA values), while Fluid B produced a great deal of smoke. The other organic fluids were between these two extremes and were similar to one another. Generally, reduction in burning due to action of a fire retardant (e.g., the phosphate content of Fluid B) often creates more smoke.

Fire properties are often not as easy to replicate as other physical and chemical processes. This may be due to the dependence of ignitability and burning rate on various physical and chemical properties of the materials (e.g., absorption of radiant energy, density, thermal conductivity of the specimen, and ease of chemical bond cleavage). In addition, the heat released by the specimen during burning may affect the burning rate. Thus, a 10 percent variation between results of replicate fire tests is often considered to be acceptable. The repeatability of four tests on a single fluid (Fluid A, a mineral oil) under the same test conditions are reported in Table 4. The table contains results from the four tests conducted for this fluid, including average values and plus and minus deviations, expressed as percents, from the average (statistical analysis would not be meaningful here).

The information in Table 4 illustrates both the good and not-so-good features of the cone calorimeter for evaluating industrial fluids. The best results are those taken for the entire course of the run, i.e., the total heat released and the effective heat of combustion. The repeatability of these values were within ± 5 percent. On the other hand, the peak and average HRR values were in the range of 10 – 20 percent. These data reflect the variability, for these specimens, in the pattern of heat release rate vs. time. For practical purposes, this means that some parts of the heat release rate data may be more meaningful and more repeatable than others. The variability in the times to ignition are acceptable (10 percent or less), especially considering that these specimens tended to "flash" for up to 20 s prior to sustained ignition. The smoke values (SEA) would seem to be outside the limits of "acceptability" (10 – 15 percent); however, they are not unreasonable, considering the difficulties in characterizing smoke particulates, and the additional errors due to normalization of the smoke values to duct flow rate and mass loss. The initial masses are shown in this table to affirm that similar volume and mass specimens were being tested in repeat runs.

TABLE 4 -- Replicate tests on Fluid A at 25 kW/m^2

Pan diameter = 77 mm, Volume of fluid = 14 mL

Test No.	Flash Ign. (s)	Sust. Ign. (s)	Peak HRR (kW/m^2)	Avg. HRR 60s (kW/m^2)	THR (kJ)	Flame Out (s)	Eff. Hc (MJ/kg)	Avg. SEA (m^2/kg)	Initial Mass (g)
A-05	64	86	507	138	465	402	39.4	732	11.8
A-16	76	80	653	154	510	361	41.5	832	12.3
A-55	70	79	631	176	479	343	39.6	650	12.1
A-56	78	92	525	197	489	396	40.4	712	12.1
Avg.	**72**	**84**	**579**	**166**	**486**	**376**	**40.2**	**731**	**12.1**
+ dev. (%)	8	10	13	17	4	7	3	14	2
- dev. (%)	11	6	12	19	5	9	2	11	2

Notes and Abbreviations (see Table 3)

TABLE 5 -- Results on Fluid A at multiple heat fluxes and different depths

Heat Flux (kW/m^2)	Fluid Depth (mm)	Flash Ign. (s)	Sust. Ign. (s)	Peak HRR (kW/m^2)	Avg. HRR 60s (kW/m^2)	THR (kJ)	Flame Out (s)	Eff. Hc (MJ/kg)	Avg. SEA (m^2/kg)	Initial Mass (g)
25 (a)	3	72	84	579	166	486	376	40.2	731	12.1
35 (a)	3	53	55	806	178	488	281	40.3	698	12.1
50 (a)	3	21	28	1465	295	498	262	40.7	612	12.2
25	1	...	86	259	123	165	273	38.4	776	4.3
25 (a)	3	72	84	579	166	486	376	40.2	731	12.1
25	6	87	88	750	156	924	544	39.0	723	23.7

Notes:
a) Data are averages of multiple tests
Notes and Abbreviations (see Table 3)

Studies on Fluid A were also conducted at several external heat fluxes, 25, 35 and 50 kW/m^2. The results of these tests are presented in Table 5, and certain values are plotted in Figures 4 and 5. These illustrate the typical behavior of specimens subjected to increasing external heat fluxes: decreasing times to ignition, decreasing times to the peak heat release, and increasing peak heat release rates. The areas under the curves (total heat release), however, are very similar. The one value in the table that is somewhat out of line is the unusually high peak HRR value for the data at 50 kW/m^2, relative to the other heat fluxes.

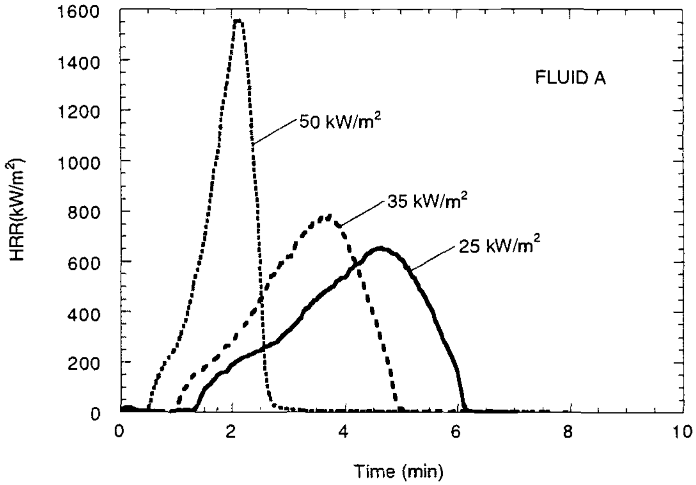


FIGURE 4--Heat release rate vs. time at three external heat flux levels

This was caused by excess pyrolysis products "spilling out" of the pan near the end of the test, due in part to the higher heat flux, and resulting in a faster rate of burning. The Avg. HRR values are more consistent with the changes in heat flux.

In Figure 4, typical HRR-time plots are shown. In Figure 5, the average times to ignition are plotted as the reciprocal of the square root of the ignition delay time vs. external heat flux. The consistency of these data as a function of heat flux data is evident by this plot. Data obtained at several heat fluxes provides the opportunity to calculate other parameters not measurable using a single test. For example, a plot of $1/(t_{ig})^{1/2}$ vs. external heat flux (Figure 5) permits calculation of a term known as the thermal response parameter, kρc, which is the product of the material's thermal conductivity, density, and heat capacity. The thermal response parameter may be useful in ranking a material's thermal inertia or flammability resistance. With sufficient data at several heat fluxes, one can extrapolate times to ignition at other heat flux levels and make a determination of the ease of continued burning once the applied heat flux is removed. The formula below describes how time to ignition and external heat flux are related.

$$t_{ig} = \frac{\pi k\rho c}{4}\left[\frac{\Delta T}{\dot{Q}''_{ext}}\right]^2 \qquad (1)$$

where

$k\rho c$: Thermal response parameter $((kW/m^2\text{-}K)^2\text{-}s)$

ΔT : Ignition temperature minus ambient temperature (K)

$\dot{Q}''_{ext}$: Applied external heat flux (kW/m^2)

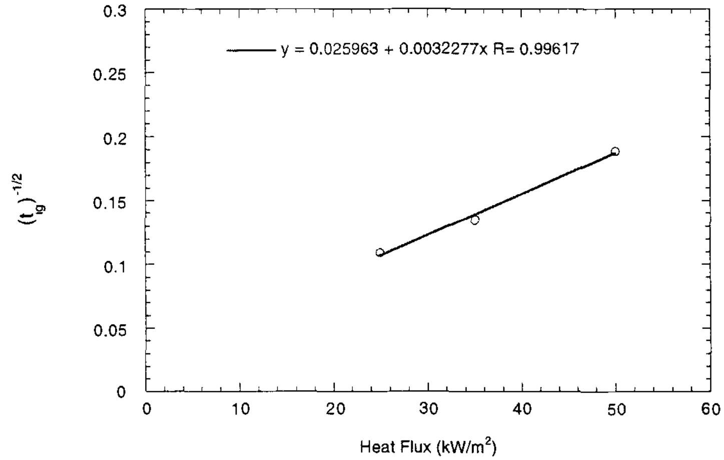


FIGURE 5--Relationship of ignition delay time and external heat flux for Fluid A

Inverting equation 1 and taking the square root, the relationship is the following:

$$\frac{1}{\sqrt{t_{ig}}} = \sqrt{\frac{4}{\pi k \rho c}}\, \frac{\dot{Q}''_{ext}}{\Delta T} \tag{2}$$

where the slope of the line (S) includes $k\rho c$:

$$S = \sqrt{\frac{4}{\pi k \rho c}}\, \frac{1}{\Delta T}. \tag{3}$$

From Tewarson [2], the reciprocal of the slope is his "TRP," which is proportional to $k\rho c$. This value was estimated from our data to be 310 for Fluid A (equation shown in Figure 5). From other data obtained on Fluids B and C over the same heat flux range, TRPs of 300 and 800, respectively, were calculated. These results indicate that the thermal response parameter (i.e., response as a function of increasing heat flux) for Fluids A and B are similar, while that for Fluid C is substantially higher.

The depth of the fluid and the diameter of the pan were not crucial factors in the test procedure. Results of tests on Fluid A at three different depths are given in the second part of Table 5. The peak HRR would be expected to change with the quantity of specimen [3], while time to ignition and effective heat of combustion should not. These results, then, are consistent with what one should expect as a function of depth of a fluid. The HRR curves for three selected runs at different specimen depths are presented in Figure 6. It is evident from these plots that the burning behavior for the initial period of the tests was reasonably repeatable.

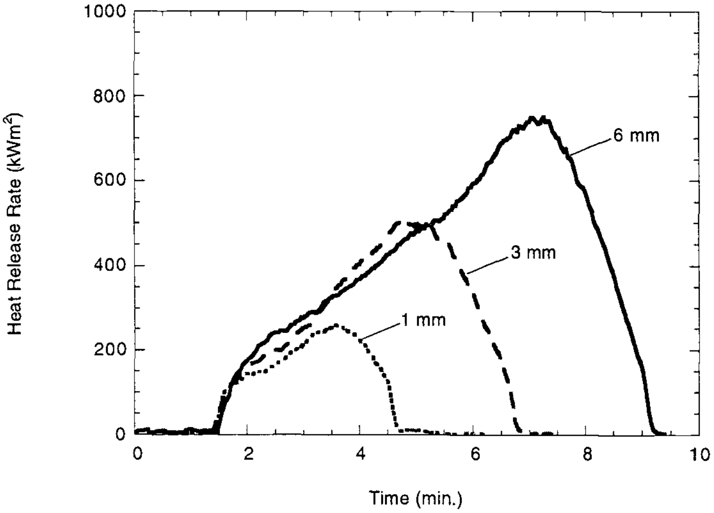


FIGURE 6. Heat release rate for Fluid A at several depths in the test pan (external heat flux of 25 kW/m^2)

The results of the limited larger scale testing (0.9 m diameter pan), performed on Fluids A, B and C, were inconclusive. In Figure 7, a plot of heat release rate, normalized to specimen surface area, is presented for the large scale test for comparison with two of the cone calorimeter tests on Fluid A. Considering the somewhat different protocol (for the large scale, the heat flux was removed after the specimen showed sustained ignition), the curves are similar. The continuing heat release from the large scale test indicates that the sample flame was producing its own heat flux back onto the surface of the fluid producing sustained burning. The heat release rate pattern in the cone calorimeter test that corresponds to a similar pattern in the large scale test was obtained with an external heat flux of 35 kW/m^2. This suggests that the fluid in the large scale test may have been experiencing a heat flux from its own burning of approximately that level. The ignition delay in the large scale test occurred later than at 25 kW/m^2 in the small scale, as expected from the lower heat flux exposure. These data support the likelihood that small scale test data on fluids in the cone calorimeter will have some relevance to larger scale processes. The tests on Fluids B and C were less conclusive, partly because they were not easily self-sustaining.

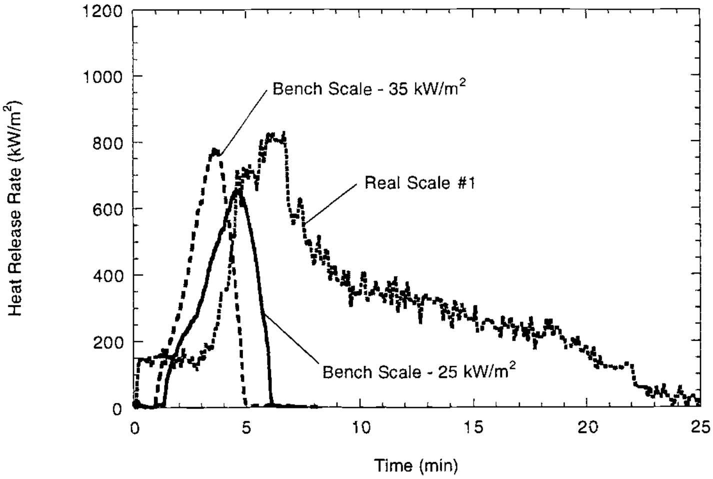


FIGURE 7. Comparison of heat release rate curves (normalized to surface area) for bench scale and real scale fire test procedures

The results obtained from cone calorimeter studies on industrial fluids may be useful in several ways. An obvious application is to support research and development efforts on products intended to have reduced flammability and smoke characteristics. A second application is for bench scale "screening" of fluids that are required to pass a larger scale test procedure, for example the spray flammability test method proposed by Factory Mutual [4]. The results of this particular large scale method have some similarities to the cone calorimeter test method, including the reporting of heat release rates as a function of external heat flux.

A further application of the results from the cone calorimeter is in the assessment of the potential fire hazard of a material. Many hydraulic fluids are used in large quantities in places where fire is a potential problem. Thus, ignition of the fluid, the tendency for the fluid to continue to burn, the rate at which it will burn under any of several different applied heat fluxes and the smoke evolution are all important parameters. Fire hazard is very dependent on the scenario, so it is virtually impossible to test the flammability of a product under all possible real-scale situations. The only reasonable way to assess hazard is to develop data that can be applied to scenarios other than the one specifically tested. This is the guiding principle behind the development and application of the cone calorimeter method.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions from Experimental Results

- After experimenting with several options for exposing fluids to the conditions of the cone calorimeter (ASTM E1354), it was decided to concentrate on testing 14 mL of fluid in a 77 mm diameter pan at 25 kW/m^2 external heat flux. Seven different fluids were tested under these conditions.

- Heat release rate data over selected time periods (e.g., for 60 s following sustained ignition) will be very useful for screening and for fire hazard analysis calculations. The "peak" heat release rate may not be the best measure of the flammability of fluids. Time to ignition, effective heat of combustion, total heat release and smoke evolution are all useful parameters to consider for the assessment of industrial fluids. Also, these values were less subject to experimental uncertainties, such as more rapid burning at the end of a test, and thus were more repeatable in multiple tests.

- Testing of different fluids produced results in the cone calorimeter test procedure that were different from one another. Thus, it is likely that this method will permit the development of data that will be useful for characterizing the flammability properties of industrial fluids.

- A wide range of results were evident from the evaluation of different fluids in the cone calorimeter at 25 kW/m^2. Times to ignition ranged from 84 to 202 seconds, total heat release ranged from 178 to 486 kJ, effective heats of combustion ranged from 12 to 40 MJ/kg, and smoke extinction areas ranged from nearly zero to over 2000 m^2/kg.

- The dependence of the test results on different external heat fluxes, ranging from 25 to 50 kW/m^2, were shown to be similar to that expected from solid polymeric materials. These data may have particular use in extrapolation to larger scale testing, in research and development activities and in the assessment of potential fire hazard.

- Limited larger scale testing (0.9 m diameter pan) on one fluid demonstrated that the results could be compared to those from the cone calorimeter.

- The cone calorimeter appears to be a suitable bench scale apparatus for evaluating the flammability properties of industrial fluids, either as a screening protocol or a research tool.

Recommendations for a Standard Test Protocol

- Use the standard equipment described in ASTM E1354, with a modified sample pan.

- Use the standard protocol (E1354), and the calculations prescribed.

- Select a volume of fluid that fills a nominal 77 mm diameter pan to at least a 3 mm depth. We found that using 14 mL of fluid in a 77 mm diameter pan (resulting in a fluid depth of approximately 3 mm) provided good data.

- Select a heat flux that will ignite most fluids without causing pyrolysis products to spill over the edge of the pan. We found that an external heat flux of 25 kW/m^2 ignited all of the fluids tested without overheating the pan (which results in pyrolysis spillover). This heat flux also provided good repeatability and comparability among the various fluids.

- Select from among the parameters listed in the E1354 standard (e.g., time to ignition, average heat release rate, total heat released, effective heat of combustion, smoke extinction area, etc.) to evaluate a fluid. Peak heat release rate probably should not be a primary criterion for characterizing fluids using this procedure.

Acknowledgment

The authors gratefully acknowledge the following companies who provided samples for our evaluation, without which this study could not have been conducted: Houghton International (Ross Holgado); Union Carbide Corporation (George E. Totten); and Quaker Chemical (Robert Hopkins).

REFERENCES

1. G.E. Totten and G. M. Webster, "Review of Testing Methods For Hydraulic Fluid Flammability" SAE Technical Paper Series # 932436 1993 International Off-Highway & Powerplant Congress & Exposition

2. A. Tewarson, "Flammability Parameters of Materials: Ignition, Combustion, and Fire Propagation," J. Fire Sciences, v. 12, July/August 1994, pp 329-356.

3. R. H. Whiteley, M. D. Sawyer, and M. J. McLoughlin, "Cone Calorimeter Studies of the Flame Retardant Effects of Decabromodiphenyl Ether and Antimony Trioxide in Cross-linked Polyethylene," Flame Retardants '94, Interscience Communications Ltd., London, 1994.

4. M. M. Khan, "Spray Flammability of Hydraulic Fluids and Development of a Test Method," Technical Report No. FMRC J.I.OTOW3.RC, Factory Mutual Research, Norwood MA, May 1991.

Gordon L. Nelson[1]

EASE OF EXTINCTION - AN ALTERNATIVE APPROACH TO LIQUID FLAMMABILITY

REFERENCE: Nelson, G. L., ''**Ease of Extinction—An Alternative Approach to Liquid Flammability,**'' Fire Resistance of Industrial Fluids, ASTM STP 1284, George E. Totten and Jürgen Reichel, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: Traditionally fluid fire resistance testing has focused on ignitability under specific test conditions. It is well known, however, that fluids of similar flashpoint can differ substantially in their abilities to sustain fire. One technique which has been used extensively to measure ease of extinction of solid plastic strips is oxygen index. This simple test has also been applied to 1000 compounds including hydraulic fluids, lubricating oils, and silicone fluids. This paper reviews data on fluids and powders and discusses how oxygen index can be used to provide additional insight into the flammability behavior of fluids.

KEYWORDS: flammability, oxygen index, ease of extinction, liquids, fluids

Every so often interest in the flammability of liquids and fluids comes to the fore. Usually the focus is on specific applications, such as hydraulic fluids or insulating oils (transformer or capacitor) (1-3). Questions usually concern the meaning of flammability or fire resistance, methods of assessment, and the relation of test data to actual hazards. Assessment techniques have included flammability limits, flash point (lower and upper), fire point, autogenous ignition temperature, spray flammability tests, hot metal tests, molten metal tests,rate of heat release, heat of combustion, electric arc tests, wick tests, as well as large scale application tests, to name a few. (4)

---

[1] Dean, College of Science and Liberal Arts, Florida Institute of Technology, Melbourne, FL 32901

The flammability of any material is not a single property, but rather a combination or series of properties: ignition, flame spread, heat release, ease of extinction, smoke, toxicity. These depend both on the material and on environments or conditions. Practical fluid flammability is perhaps more complex than that of a solid in that the volatility of the fluid plays a key role in its flammability performance. Indeed flash point is very much related to volatility.(5) Figure 1 shows a plot of flash point versus boiling point for a large number of compounds. Part of the scatter is due to the fact that data from several flash point apparatus were used. Concentrations of a fuel in the vapor space above a liquid will depend on the free space above the fuel and thus affect the result. For mixtures the relative amounts of constituents will also be affected. (6) Flash point data are by far the most frequently reported data for the flammability of fluids. Both flash point and fire point have associated issues. (7)

Heat release rate testing of fluids has involved both laboratory and larger scale assessment. (8) In more recent approaches results have been reported on the use of the cone calorimeter to assess liquid flammability. The cone heater has been used to assess the ignitability of hexadecane and crude oils (9). Full rate of heat release data have been reported for silicones (10) and for pesticides. Heat release data for hydrocarbons are of the order of 1600 kW/m^2 at 60 kW/m^2 external flux, similar to low heat, non-flame retardant polymers. Silicones above a degree of polymerization of 15 are one-tenth that figure. Short chain silicones however had RHR of over 2000 kW/m^2. Other efforts with heat release rate calorimetry are reported in this volume.

One test which has also been used by 50-100 laboratories for fluids is that of oxygen index. Oxygen index, of course, has been used extensively for solid polymer samples (ASTM D2863): molded polymers, fabrics, cellular plastics, and thin films. For a review see (11).

OXYGEN INDEX

Oxygen index is a measure of ease of extinction. While a characteristic of a material, it is a flammability limit and as such is dependent upon oxidizer flow (oxidants other than oxygen may be used), fuel geometry, and test configuration as well as temperature and pressure. The oxygen index is the percentage of oxygen in an oxygen/nitrogen atmosphere which will just sustain combustion of a material.

The concept of oxygen index derives from work on gases and liquids. For example, Simmons and Wolfhard studied the burning of fuels at the surface of a porous hemispherical burner, fuels ranging from hydrogen, carbon monoxide, low molecular weight hydrocarbons, alcohols, and benzene. (12) Data have also been reported for liquids using a glass wick technique (to study organophosphorus liquids) (13) By far the largest amount of data on liquids has been reported utilizing a small ceramic reservoir containing liquids or fusible solids replacing the usual polymer sample in a standard oxygen index test apparatus. (14-15). See Figure 2.

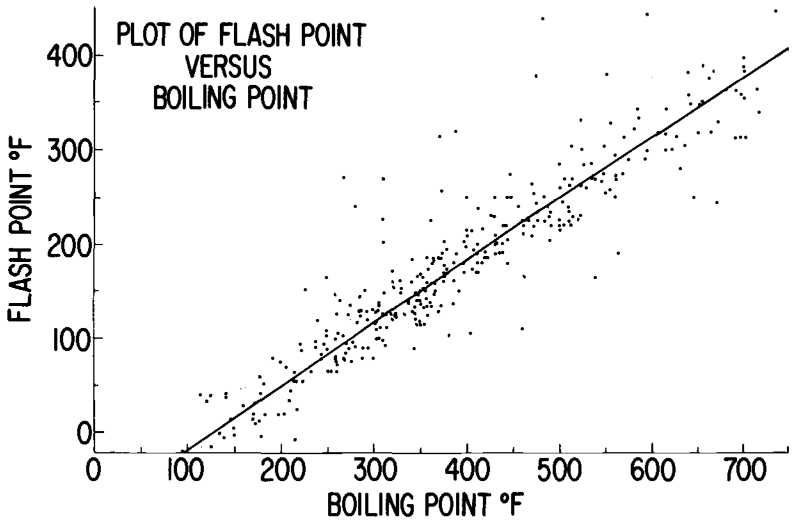


FIG. 1--Plot of flash point versus boiling point for a large number of compounds. Data from several flash point apparatus are used. **REF** [11]

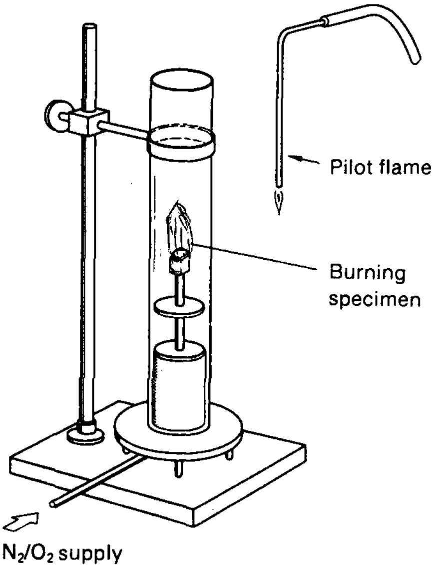


FIG. 2--Oxygen index test apparatus modified for use with liquids and powders. N_2/O_2 supply provides N_2/O_2 mixtures of precise concentrations and is discussed in ASTM D2863. The oxygen index is the minimum percent of oxygen in the oxygen nitrogen mixture which will just sustain combustion.

The technique is: a sample is placed in a ceramic reservoir in the test chamber. Prior to ignition, the % oxygen flowing through the OI cylinder is adjusted to a level higher than that expected for combustion of the test sample. After ignition with a hydrogen or propane flame, the sample is allowed to burn for 10-20 seconds to achieve a steady state. With the flame burning in a smooth motionless state the % O_2 is slowly reduced until the flame begins to wave or oscillate. The onset of unsteadiness is a useful signal and usually occurs within one oxygen index unit of the end point. The end point is the final % O_2 which just barely supports combustion. This percentage is the oxygen index. It is precise and reproducible. Sample size and geometry of the reservoir were found to have little practical effect for most materials. The technique has been applied to some 1000 simple organic compounds. Data for some 600 liquids and fuseable solids are listed in the Appendix to this paper. A plot of oxygen index versus number of compounds at each value is given in Figure 3.

Mixtures give variable results depending upon the total time to determination of end point. This is to be expected as the gaseous fuel composition will vary as the more volatile component is depleted from the reservoir. Experiments such as addition of Sb_2O_3 to bromocyclohexane show no change in oxygen index. Temperatures reached in the cup are no higher than the boiling point of the material being tested.

For materials which char or ash on burning, some workers have shown a substantive dependence of oxygen index on reservoir (cup) diameter, with larger cups giving lower oxygen indicies. Plots of extinction time versus % O_2 in the atmosphere allow extrapolation of the oxygen index (16). Similar behavior has been observed in heat release tests (17).

Volatility has limited impact on oxygen index values. Simple hydrocarbons are in a range of 15-17 whether pentane, petroleum hydraulic fluid, jet fuel, mineral oil, or polypropylene.

Using this technique one can learn much of the chemistry of flame retardancy of organic structures (11,18). And oxygen index can be used to evaluate materials in a variety of environments. (19,20)

A very detailed theoretical treatment of oxygen index has been performed by A. Murty Kanury (21). Oxygen index is dependent upon the expected physicochemical properties of the system, that is of a small pool fire. Others have developed empirical relationships to estimate oxygen indicies for liquids. (22)

OXYGEN INDEX VERSUS SPRAY FLAMMABILITY

It is interesting that the earliest utilization of the concept of oxygen index is a study of the flammability of oil mists, which was reported by Sullivan, Wolfe, and Zisman in 1947. (23) The parameter measured was called the "spray flammability limit." The test measured the minimum percentage of oxygen required to allow propagation of a flame in an oil mist in a closed chamber after ignition by an electrical arc. The flammability of lubricating and hydraulic oils for aircraft were of particular interest in their study. Table 1 (14,15,23) gives selected results for the limiting oxygen concentrations as measured by their

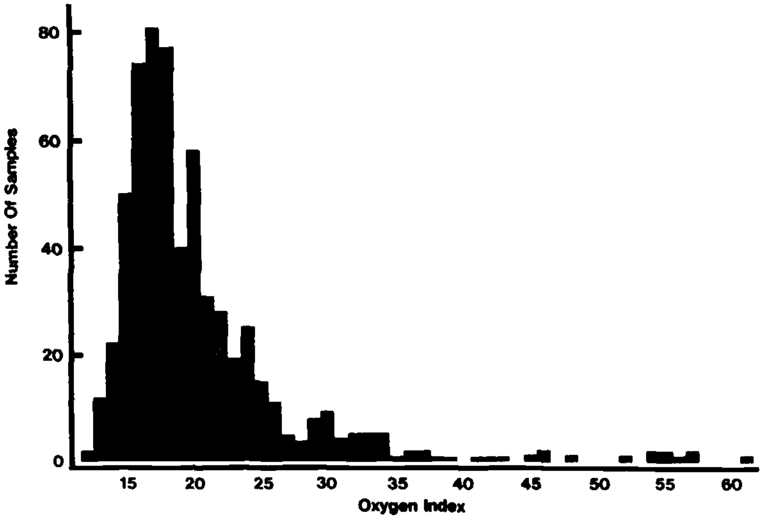


FIG. 3--Plot of oxygen index versus number of compounds at each value for 600 fluids and powders listed in appendix.

TABLE--1 Oxygen Indicies and Spray Flammability Limits for Selected Compounds

Compound	Spray Flammability Limit	Oxygen Index
1. Diethyl ether	11	16.5
2. Benzene	12	15.9
3. Cumene	12	15.2
4. n-Hexadecane	12	15.5
5. B-Methoxymethoxyethanol	12	13.3
6. Trioctylphosphate	13	18.6
7. Aniline	14	16.3
8. Chlorobenzene	14	19.2
9. Tricresyl phosphate	19	22.0
10. Ω-Chloronaphthalene	27	19.8
11. Tributyl phosphate	27	20.1
12. o-Dichlorobenzene	29	23.1
13. Dichlorodiphenylether	33	21.2
14. Ethylene glycol	40	14.8
15. Diethylene glycol	42	13.6
16. 1,2,4-Trichlorobenzene	44	30.1
17. Aroclor 1242	45	33.1
18. Trimethyl phosphate	47	23.7
19. Aroclor 1248	64	36.5
20. Hexachlorobutadiene	77	54.4

technique compared with oxygen indicies as measured for the same materials by Nelson and Webb (14,15). Figure 4 shows a plot of oxygen index versus the spray flammability limit for each material listed. While there is some curvature, there is considerable correlation between the two techniques. Compounds 14 and 15, the glycols seem to be out of place, however, since they do burn readily. Estimated errors in the Naval Research Laboratory work were reported to be ± 1% in the lower ranges and ± 2% in the higher ranges. Comparison of their results with incendiary fire experiments (bullets) showed that fluids having a value of over 45-50 in the spray test showed no incidence of fire in the incendiary tests. As can be seen in Figure 4, this corresponds to an oxygen index of 29-32, similar to the values of about 27 taken for marginal fire retardance in the case of polymers.

SUMMARY

In summary, measurement of the oxygen index of liquids provides a different view of liquid flammability. Unlike the flash-point test, the oxygen index is not a direct function of volatility nor is it a measure of ease of ignition; but rather an extinction-related phenomenon. The oxygen index of liquids has been used to evaluate and compare a number of industrially important fluids such as hydraulic fluids, lubricating oils, silicone fluids, and others. With oxygen index of liquids as a tool, the elucidation of chemical structure-flammability relationships, is made easy. Given the ease with which the oxygen index of liquids can be measured, its use and comparison with other techniques is to be encouraged.

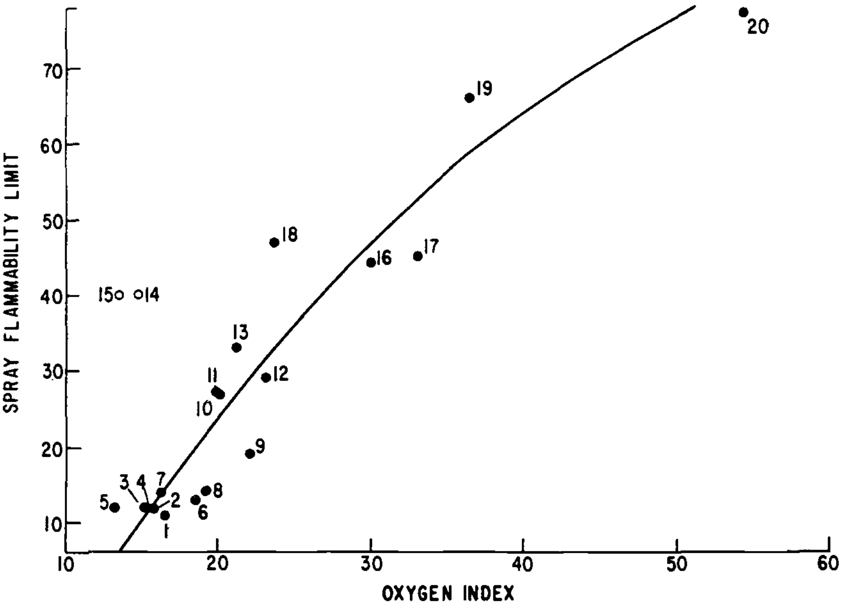


FIG. 4--Plot of oxygen index versus spray flammability limit values for materials listed in Table 1. **REFERENCE** [11]

REFERENCES

[1] "Fire Resistance of Hydraulic Fluids," ASTM STP 408, American Society for Testing and Materials, Philadelphia, PA. 1966, 194pp.

[2] Miller, D. B. et al., "An Appraisal of Tests and Standards for the Evaluation of Electrical Insulating Fluids," *NBSIR*, 76-1054, U.S. Department of Commerce, Washington, DC, July 1976, 122pp.

[3] Orsbeck, T. "New Principles of Fire Hazard Assessment for Fluid-Filled Electrical Equipment," *Proceedings Ninth International Conference of Fire Safety*, Milbrae, CA, January 16-20, 1984, Product Safety Corporation, *9*, 1984, pp. 101-125.

[4] Early, C. L. and Hatton, R. E., "Industrial and ASTM Fluid Fire-Test Programs," in ASTM STP 408, American Society for Testing and Materials, Philadelphia, PA, 1966, pp. 105-134.

[5] Li, C. C. and Moore, J. B., "Estimating Flash Points of Organic Compounds," *Journal of Fire and Flammability*, *8*, 1977, pp. 30-40.

[6] Affens, W. A. and Carhart, H. W., "The Effect of Ullage on the Flash Point and Lower Flammability Limit Temperatures of JP-5 Jet Fuels, NRL Memorandum Report 1735, Naval Research Laboratory, Washington, DC, November, 1996, 10pp.

[7] Ishida, H. and Iwama, A., "Some Critical Discussions on Flash and Fire Points of Liquid Fuels," Fire Safety Science, *Proceedings of the First International Symposium*, C. E. Grant and P. J. Pagni, eds., Hemisphere Publishing Corporation, Washington, DC,. 1986, pp. 217-226

[8] Lipowitz, J., "Fire Safety Properties of Some Transformer Dielectric Liquids," *Journal of Fire and Flammability*, *15*, 1982, pp. 39-55.

[9] Elam, S. K. et al., "Cone Heater Ignition Tests of Liquid Fuels," *Fire Safety Journal*, *16*, 1990, pp. 65-84.

[10] Buch, R. R., "Rates of Heat Release and Related Fire Parameters for Silicones," *Fire Safety Journal*, *17*, 1991, pp. 1-12.

[11] Nelson, G. L. and Webb, J. L., "Oxygen Index, Flammability and Materials." In Advances in Fire Retardant Textiles (Advances in Fire Retardants Part 3), Progress in Fire Retardancy Series 5, ed. V. J. Bhatnagar, Technomic Publishing Co., Westport CT, 1975.

[12] Simmons, R. F. and Wolfhard, H. G., *Combustion and Flame*, *1*, 1957, p.155.

[13] Arney, W. C., Jr., and Kuryla, W. C., "Structure-Property Relationships in Flame Retardant Systems," *Journal of Fire and Flammability*, *3*, 1972, pp. 183-191.

[14] Nelson, G. L. and Webb, J. L., "Oxygen Index of Liquids-Technique and Applications," Journal of Fire and Flammability, 4, 1973, pp. 210-226.

[15] Nelson, G. L. and Webb, J. L., "Oxygen Index of Liquids: Halogen Compounds," Journal of Fire and Flammability, 4, 1973, pp. 325-343.

[16] Lipowitz, J.and Ziemelis, M. J., "Flammability of Poly(dimethylsiloxanes). II. Flammability and Fire Hazard Properties," Journal of Fire and Flammability, 7, 1976, pp. 504-529.

[17] Sundin, D., "Heat Release Rates of Dielectric Fluids: A Guide to Method Selection." Seventeenth International Fire Safety Conference, Product Safety Corporation, Milbrae, CA, January 13-17, 1992.

[18] Nelson, G. L., "Flammability and Oxygen Index, International Polymer Journal, 7, (3-4), 1979, 127-145pp.

[19] Ikeda, G. K., "Oxygen Index Tests to Evaluate the Suitability of a Given Material for Oxygen Service," Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres, ASTM STP 812, B. L. Wesley, ed., American Society for Testing and Materials, 1983, pp. 56-57.

[20] Benning, M. A., "Measurement of Oxygen Index at Elevated Pressures," Flammability and Sensitivity of Material in Oxygen-Enriched Atmospheres, ASTM STP 812, B. L. Wesley, Ed., American Society for Testing and Materials, 1983, pp. 68-83.

[21] Kanury, A. M., "Theoretical Analyses of Fire and Flammability Tests: III. The Limiting Oxygen Index Test, "International Symposium-Fire Safety of Combustible Materials, University of Edinburg Center for Industrial Consultancy and Liaison, Edinburgh, UK, 1975, pp. 187-198.

[22] Kishore, K. and Mohandas, K., "A New Parameter for the Flammability of Combustible Materials," Journal of Hazardous Materials, 3, 1980, pp. 349-356.

[23] Sullivan, M. V., Wolfe, J. K., and Zisman, W. A., Ind. Eng. Chem, 39, 1947, p. 1607.

APPENDIX (OXYGEN INDEX OF LIQUIDS AND POWDERS)

Compound	Oxygen Index
Acetic acid	20.7
Acetone	16.0
Acetophenone	16.5
n-Acetyl-n′(4,5-dimethyl-oxazol-2) sulfanilamide	18.5
Acetyl ferrocene	15.6
Acetylsalicylic acid	17.7
Acridine	18.3
Allylacetate	16.7
1-Allyl-2-thiourea	16.8
Allyl urea	12.8
o-Aminobenzenesulfonic acid	20.5
p-Aminobenzenesulfonylamide	17.7
m-Aminobenzoic acid	18.5
p-Aminobenzoic acid	17.7
p-Aminodiphenyl	17.3
2-Amino-4-methylthiazole	18.1
1-Amino-2-naphthol-4-sulfonic acid	26.5
4-Amino-1.8-naphthol-p-xenylimide	25.4
4-Aminophenyl disulfide	20.1
2-(p-aminophenyl)-6-methylbenzothiazole	18.8
m-Aminophenyl sulfone	22.7
3-Aminophthalic anhydride	19.1
α-Aminopropyl triethoxysilane	14.0
2-Aminopyridine	17.4
3-Aminopyridine	18.4
Amyl bromide	20.9
Amyl stearate	15.5
Aniline	16.3
Aniline hydrochloride	19.2
Aniline-2-sulfonic acid	20.5
Anthracene	17.1
Anthranilic acid	17.4
Anthraquinone	19.5
Aroclor 1016	31.3
Aroclor 1221	20.5
Aroclor 1232	23.1
Aroclor 1242	33.1
Aroclor 1248	36.5
Aroclor 1262	45.7
Aroclor 1269	55.5
Aroclor 1819	20.5
Aroclor 5460	61.0
DL-aspartic acid	30.4
Azobenzene	15.9
Barbital	17.4
Barbituric acid	25.1
Benzalazine	15.2
Benzaldehyde dibenzylmercaptal	16.5
Benzamide	17.4
Benzene	15.7
Benzene boronic acid	16.7
m-Benzenedisulfonyl chloride	46.2
Benzenesulfonamide	18.1
Benzenesulfonic acid	19.4
1,3,5-Benzenetrisulfonyl chloride	55.0
p-Benzimidazol-2 benzenesulfonic acid	20.4
(2-Benzimidazolylmethylthio) acetic acid	18.1
2,3-Benzo-diphenyleneoxide	17.7
Benzoguanamide	18.1
Benzoic acid	15.1
Benzonitrile	15.3
Benzophenone dicarboxylic acid	18.8
2,1,3-Benzothiadiazole	16.8
2-Benzothiazoyl disulfide	18.1
Benzotrifluoride	18.2
Benzyl disulfide	16.8
2-Benzyl-2-thiopseudourea hydrochloride	18.1
Biphenyl	17.7
4-Biphenylcarboxylic acid	17.4
Bis(p-acetoxyphenyl) dichloroethylene	22.0
Bis(chloroethyl)vinyl phosphate	21.4
Bis(p-chlorophenyl)sulfone	21.4
Bis(3,5 dimethyl-4-hydroxyphenyl)sulfone	20.4
1,1-Bis(p-diphenylether) ethylene	20.2
Bis-(hexadecafluoro-nonyl) terephthalate	16.5
Bis-b-hydroxy ethylisophthalate	15.9
4,4-Bis(4-hydroxyphenyl) pentanoic acid	19.0
Bis-phenol-A	18.9
1,4-Bis(trichloromethyl) benzene	52.0
Borneol	15.5
White bread (dry)	21.0
1-Bromoadamantane	20.4
o-Bromoaniline	24.7
o-Bromoanisole	21.6
m-Bromoanisole	23.8
p-Bromoanisole	21.1
Bromobenzene	23.3
m-Bromobenzotrifluoride	33.1
4-Bromobiphenyl	23.5

Compound	Oxygen Index
1-Bromobutane (n-butylbromide)	21.5
Bromocyclohexane	21.4
1-Bromodecane	18.5
p-Bromodiphenylether	26.4
5-Bromoisatin	25.8
1-Bromohexane	20.0
1-Bromooctane	19.1
p-Bromophenyl ferrocene	39.0
p-Bromophenyl phenylether	21.3
p-Bromophenyl trimethoxysilane	17.7
1-Bromopropane	24.7
Bromostyrene	21.8
α-Bromotoluene	28.8
o-Bromotoluene	24.5
m-Bromotoluene	26.0
p-Bromotoluene	23.6
5-Bromovaleronitrile	20.4
Brown corn syrup	20.2
Butadiene sulfone	16.5
1,4-Butanediol	16.5
n-Butylbenzene sulfonamide	16.5
n-Butylbromide (1-bromobutane)	21.5
n-Butyl ferrocene	14.1
n-Butyl iodide	20.9
tert-Butyl iodide	21.8
n-Butylbenzenesulfonamide	15.5
Caffeine	15.9
d-Camphor sulfonic acid	17.5
Carbon black	37.2
Carbowax 1000	18.7
Castor oil	22.9
Chalcone	17.0
Chloroacetic acid	18.1
o-Chloroaniline	19.4
m-Chloroaniline	20.6
p-Chloroaniline	20.4
Chlorobenzene	19.2
p-Chlorobenzoicacid	19.2
o-Chlorobenzoic acid	19.8
p-Chlorobiphenyl	19.9
2-Chloroethylbenzoate	17.8
b-chloroethyl-p-toluene sulfonate	13.6
bis-b-Chloroethylvinyl phosphonate	21.7
1-Chloroheptane	15.3
1-Chlorohexane	15.7
α-Chloro-α-hydroxy-o-toluenesulfonic acid	21.2
m-chloroiodobenzene	24.2
3-Chloro-6-methoxypyridazine	15.6
α-Chloronaphthalene	19.8

Compound	Oxygen Index
2-chloro-4-nitrobenzamide	19.3
1-chloro-2-nitrobenzene	18.2
4-Chloro-3-nitrobenzene sulfonamide	23.4
2-Chloro-4-nitrobenzoic acid	21.5
2-Chloro-5-nitrobenzoic acid	22.3
4-Chloro-3-nitrobenzoic acid	22.6
1-Chlorooctane	15.2
1-Chloropentane	15.9
o-Chlorophenol	20.1
p-Chlorophenol	21.0
Chlorophenyl ferrocene	24.0
4-Chloro-n-phenylphthalimide	21.1
1-Chloropropane	17.9
o-Chlorotoluene	19.2
m-Chlorotoluene	19.7
p-Chlorotoluene	19.1
Chlorotriphenylmethane	19.6
2-Chloro-p-xylene	18.6
Cinnamyl acetophenone	15.5
o-Cresyl-p-toluenesulfinate	16.4
Cumene(isopropylbenzene)	15.2
p-Cyanobenzenesulfonamide	19.2
4-Cyanobenzoic acid	17.7
Cyclohexane	16.4
Cyclohexanone oxime	15.9
3-Cyclohexene-1-carbonitrile	16.5
Decamethylene glycol	12.0
1-Decene	16.3
Delrin polyacetal	14.0
Dextrose	18.5
Diacetoacetylethylenediamine	18.5
Diacetone acrylamide	17.4
4,4-Diamino-stilbene-2,2-disulfonic acid	29.6
Dibenzalacetone	15.6
Dibenzothiophene sulfone	17.4
1,1-Dibenzoylferrocene	24.3
p-Dibromobenzene	30.8
1,4-Dibromobutane	28.6
1,10-Dibromodecane	21.3
Dibromodiphenyl ether	30.0
1,12-Dibromododecane	19.6
1,2-Dibromoethane	33.6
1,6-Dibromohexane	24.6
Dibromoneopentyl alcohol	29.0
1,8-Dibromooctane	23.7
1,5-Dibromopentane	27.5
1,3-Dibromopropane	32.6
Dibutyldiphenyl tin	18.1
Dibutylsebacate	15.6
Di-t-butylterephthalate	17.4
1,3-Di-n-butylthiourea	17.4
Dibutyltin diacetate	16.8
p-p′-Dicarboxydiphenyl ether	22.2

Compound	Oxygen Index
3,5-Dicarboxymethylbenzene sulfonic acid	38.4
o-Dichlorobenzene	23.1
m-Dichlorobenzene	25.8
p-Dichlorobenzene	22.5
Dichlorodiphenyl ether	21.2
p,p′-Dichlorodiphenylsulfone	20.0
1,4-Dichlorophthalizine	23.0
2,3-Dichloro-1-propene	24.0
g-g′-Dichloropropylcarbonate	17.4
2,5-Dichloro-p-xylene	24.8
n-n′-Dicyclohexylcarbodimide	15.9
1,2-Di(2,4-dichlorophenoxy) ethane	32.2
4-4′-Dicyanobiphenyl	17.4
Diethylbenzylphosphate	20.6
Diethylbenzenephosphonate	20.0
Diethylbenzylphosphonate	20.3
Ferrous diethyldithiocarbamate	18.5
Diethyl-n-ethylcarbamylphosphonate	20.8
Diethylethylphosphonate	20.9
Di-2-ethylhexylphthalate	15.8
Diethylphosphorosuccinimidate	20.0
4,4-Difluorobiphenyl	16.6
2,4-Dihydroxybenzoic acid	17.7
2,5-Dihydroxybenzoic acid	17.7
p,p′-Dihydroxydiphenylsulfone	18.1
1,8-Dihydroxynaphthalene-3,6-disulfonic acid	32.3
4,5-Dihydroxy-2,7-naphthalenedisulfonic acid	33.0
4,4′-Dihydroxytolan	40.9
p-Diiodobenzene	27.6
Dimethylaminoacetaldehydediethylacetal	15.2
n,n-Dimethylbenzamide	16.8
2,6-Dimethyl-4-iodophenol	25.2
1,4-Dimethoxybenzene	15.5
Dimethylketene dimer	16.5
Dimethyl oxalate	15.6
4,5-Dimethyl-2-oxo-1,3,2-dioxathiolane	16.8
Dimethylphosphonoacetamide	20.7
2,6-Dimethyl piperidine	17.0
Dimethyl sulfoxide	15.3
Dimethyltin chloride	22.2
Diphenic acid	17.4
Diphenolic acid	19.0
1,2-Diphenoxyethane	17.4
Diphenylacetylene	16.8
Diphenylbenzene phosphonate	23.5
Diphenylcarbamyl chloride	19.5
Diphenyl carbonate	17.1
Diphenyl ether	16.5
2,5-Diphenyl furan	16.6
3,3-Diphenyl-1,1,1,5,5,5-hexamethyltrisiloxane	15.8
Diphenylhexynediol	14.8
Diphenyliodonium bromide	23.1
Diphenylmethane	15.3
Diphenylmethylphosphate	21.2
2,3-Diphenylquinoxaline	17.8
Diphenylsulfide	17.4
Diphenylsulfone	17.2
Diphenylsulfoxide	17.4
5-Diphenylthiourea	15.5
Dipropyldiglycolate	16.5
2,2′-Dithiobis(benzothiazole)	18.1
Di-p-tolyl disulfide	16.3
Divinyl sulfone	14.3
Dodecane-1,12-diol	16.8
Dodecahydrotriphenylene	16.9
Dodecylbenzenealkylate-2,3-ol	15.2
Durene(1,2,4,5-tetramethylbenzene)	16.7
Epiphenlin	15.2
Ethanesulfonic acid	19.7
Ethylamine hydrobromide	26.0
Ethyl benzoate	15.0
Ethyl bromide	25.0
Ethyl carbanilate	15.9
Ethyl-A-A′-dibromosuccinate	22.8
(Ethylenedinitrilo) tetra-acetic acid	20.2
Ethylene glycol	14.8
Ethylene oxalate	20.0
Ethyl iodide	24.0
Ethyl isocyanatoacetate	15.9
Ethyl-octyl phosphoric acid	20.4
4-Ethylpyridine	17.2
Ferrocene	12.2
Ferrocene carboxylic acid	19.9
Fluorene	18.1
Fluorescein	27.2
p-Fluorobenzonitrile	19.7
p-Fluorochlorobenzene	21.1
1-Fluoro-4-nitrobenzene	13.5
4-Fluorophenylsulfone	17.0
2-Fluoropyridine	19.7
Fluorosilicone fluid	16.8
Fumaric acid	16.0
Furoic acid	12.8
Furylacrylic acid	15.5
Fyrquel 150 (Stauffer Chemical)	25.5
Fyrquel 220 (Stauffer Chemical)	25.9

Compound	Oxygen Index
Glucono-a-lactone	18.1
Glucose	18.5
Glucose phenylosazone	18.5
d-Glycuronolactone	18.5
Glutaric acid	18.1
Glycerine carbonate	15.6
Glyccolic acid	23.8
Heptane	15.2
Hexachlorobutadiene	54.1
Hexadecane	15.5
Hexafluoroacetylacetonedihydrate	18.5
Hexamethyldisiloxane	15.0
Hexamethylphosphoramide	20.4
Hexane	15.4
Hexaphenyl ditin	17.4
sec-Hexyl iodide	20.3
Houghto Safe 1120 (EF Houghton Co)	22.1
Houghto Safe P C F G 15	24.0
Hydantoin	25.0
Hydraulic fluid MIL-H-83282	17.7
Hydraulic fluid MIL-H-5606B	16.0
m-Hydroxybenzoic acid	17.0
p-Hydroxybenzoic acid	17.4
b-Hydroxyethylbenzoate	15.9
p-Hydroxyphenol dimethylsulfoniumchloride	15.7
n-Hydroxyphthalimide	16.0
4-Hydroxystilbene	16.5
Indanedione	15.9
3-Indolepropionic acid	19.3
p-Iodoaniline	24.8
Iodobenzene	20.2
m-Iodobenzoic acid	23.6
p-Iodobenzoic acid	23.3
Iodocyclohexane	20.1
1-Iodohexadecane	18.2
1-Iodohexane	19.7
7-Iodo-8-hydroxyquinoline-5-sulfonic acid	56.8
Iodomethane	29.6
b-Iodonaphthalene	16.5
1-Iodooctane	19.2
1-Iodopentane	20.1
2-Iodopropane	22.4
p-Iodotoluene	21.1
Isatoic anhydride	32.0
d-Isoascorbic acid	22.2
JP-5-MIL-T-5624 fuel	15.1
JP-4-MIL-T-5624 (wide cut) fuel	15.1
Lactic acid	17.7
Lauric acid	15.6
Lucite R (polymethylmethacrylate	18.1
Maleic acid	17.7
Malonic acid	24.0
Marlex R 5002 (polyethylene)	18.2
2-Mesitylenesulfonic acid dihydrate	16.8
Metanilic acid	30.0
Methacrylamide	17.4
Methanesulfonic acid	30.0
Methoxy-methoxyethanol	13.3
Methyl benzenesulfonate	15.5
n-Methylbutylamine	15.0
Methylene dianiline	19.1
Methylene di-b-oxy-naphthoic acid	18.8
Methyl iodide	29.0
4-Methyl-1-pentene	16.5
2-Methyl piperazine	17.0
2-Methylpyrazine	17.1
5-Methyl-2-pyrrolidone	17.7
5-methylsalicyclic acid	15.9
Methyl p-toluenesulfonate	15.3
4-Methyl uracil	20.4
MIL-F-24376A type B	15.3
MIL-H-5606B hydraulic fluid	16.0
MIL-H-83282 hydraulic fluid fluorocarbon	17.7
MIL-L-23699B Stauffer Jet-II lubricant	16.1
MIL-L-7808G Esso 2389 (0-67-7)	17.0
Mineral oil USP	16.1
Mineral oil 5314A - Socony Mobil Co	15.2
Monsanto MCS 293	18.1
Monsanto MCS 354 lubricant	18.6
Monsanto MCS 1122	22.1
Monsanto MCS 1284 lubricant	16.6
Monsanto MCS-1238	15.4
Naphthalene	15.9
1-Naphthaleneacetic acid	17.7
2,7-Naphthalenediol	15.9
Naphthalene-1,5-disulfonic acid	30.6
Naphthalene-2,7-disulfonic acid	37.0
Sodium naphthalene-2,7-disulfonate	31.6
b-Naphthalene sulfonic acid	29.1
1,4,5,8-Naphthalene tetracarboxylicdiimide	25.4
Naphthalic anhydride	17.7
a-Naphthoic acid	16.2
b-Naphthioc acid	15.6

Compound	Oxygen Index
1-Naphthol-4-sulfonic acid	27.9
1-Naphthylisocyanate	18.2
Nicotine	17.1
Nitrilotriacetic acid	21.7
Nitrilotriacetonitrile	15.9
4-Nitro-2-aminophenol	25.7
o-Nitroaniline	13.6
m-Nitroaniline	13.6
p-Nitroaniline	13.6
o-Nitroanisole	13.2
m-Nitroanisole	13.1
p-Nitroanisole	13.4
Nitrobenzene	13.2
m-Nitrobenzene sulfonic acid	31.2
o-Nitrobenzoic acid	14.6
m-Nitrobenzoic acid	14.0
p-Nitrobenzoic acid	14.3
o-Nitrobisphenol-A	15.6
3-Nitro-4-chlorobenzotrifluoride	24.0
2-Nitroisobutyl phosphate	18.5
p-Nitromethylbenzoate	13.4
p-Nitrophenylbenzoate	14.5
o-Nitrophenol	14.1
m-Nitrophenol	13.8
p-Nitrophenol	13.8
4-Nitro-o-phenylenediamine	18.5
p-Nitrophenylisocyanate	15.2
p-Nitrophenylphenyl ether	15.2
3-Nitro-n-phenylphthalimide	16.5
4-Nitro-n-phenylphthalimide	17.4
o-Nitrotoluene	13.6
m-Nitrotoluene	14.0
Octamethyltetrasiloxane	15.7
2-Octanethiol	15.2
Isooctylphosphite	16.9
Olive oil	16.6
2,2′-Oxydiethanol (diethylene glycol)	13.6
b,b′-Oxydipropionitrile	15.5
Parabanic acid	28.0
Paraffin oil, mineral oil (white-heavy)	16.4
Paraffin wax	17.3
Pentachlorophenol	57.5
Pentane	15.6
Penton	20.0
Phenanthrenequinone	19.1
Phenol	17.0
Phenolphthalein	21.4
p-Phenolsulfonic acid	34.7
Phenoxyacetic acid	13.6
b-Phenoxyethyl-levulinate	16.5
diPhenoxy phenol	17.7
Phenoxypropylene oxide	15.2
Phenyl acetate	15.7

Compound	Oxygen Index
dl-Phenylalanine	17.4
2-Phenyl-1,3,2-benzodiazaborole	18.1
Phenyl biguanide hydrochloride	20.0
Phenyl butynol	15.5
a-Phenyl-p-cresol	16.8
Phenyl disulfide	17.0
Phenyl-iso-thiocyanate	15.2
1-Phenyl-3-methyl-5-pyrazolone	15.5
n-Phenyl-2-naphthylamine	17.0
2-Phenyloxybiphenyl	16.4
4-Phenyloxybiphenyl	16.2
n-Phenyl-p-phenylenediamine	17.7
Phenyl phosphinic acid	18.1
Phenylphosphonic dichloride	21.5
n-Phenylphthalimide	18.1
n-Phenylsulfonyl benzenesulfonamide	21.1
Phenylsulfoxide	15.9
Phenyl-p-toluenesulfonate	14.5
Phosphonitrilic chloride-trimer	56.0
Phosphorus tetranilide	18.1
Phthalic anhydride	17.4
Phthalimide	17.4
Picolinic acid	16.2
Polyacrylamide	23.0
Polybutadiene	14.4
Polydichlorostyrene	29.0
Polyethylene	18.4
Polyethylenimine	17.5
Poly-l-glutamic acid	33.6
Poly-(methylvinylether) maleic anhydride	18.5
Polyphenyl	32.0
Polyphenyleneoxide	24.0
Polypropylene	17.0
Polystyrene	17.5
Vinyl acetate polymer	19.6
Polyvinyl alcohol	18.8
Polyvinylcarbazole	19.2
Polyvinyl chloride	33.0
Polyvinyl hydrogen phthalate	18.8
Polyvinylpyrrolidone	25.2
1-Propanediol	14.9
Isopropylbenzene (cumene)	15.2
p-Iso-propyl benzoic acid	15.5
Propyl iodide	22.3
Propyl methacrylate	17.7
Isopropyl phenyl carbamate	17.4
Pyridine	16.4
Pyromellitic acid	19.7
p-Quaterphenyl	26.0
Quinoxaline	17.0

Compound	Oxygen Index
Salicylamide	19.2
Salicylic acid	16.8
Sebacyl dihydrazide	18.5
Silicone fluid viscasil 60,000	20.0
DF1040-GE Silicone	17.6
SF81-50-GE Silicone fluid	21.1
SF96(50)-GE Silicone fluid	21.4
SF96(100) GE Silicone fluid	22.4
SF96(350)-GE Silicone fluid	27.3
SF1029-GE Silicone fluid	23.0
SF1093(100)-GE Silicone fluid	23.6
SF1128-GE Silicone fluid	16.0
SF1147-GE Silicone fluid	19.8
SF1153-GE Silicone fluid	24.0
SF1154-GE Silicone fluid	22.0
XF1050-GE Silicone fluid	13.3
Versalube F50-GE Silicone	21.6
Skydrol 500 Monsanto hydraulic fluid	18.9
Skylube 600 (MCS354) Monsanto	18.6
Skylube 450 lubricant polyol ester type-2	19.2
d-Sorbitol	17.4
Stearic acid	16.5
Succinic acid	19.6
Sucrose	22.0
Sucrose octaacetate	17.4
Sulfolane	17.4
Sulfolene	17.2
Sulfonyl diacetic acid	26.0
5-Sulfosalicylic acid	34.2
Sulfur	13.6
Terephthaldehyde	15.2
Terephthalonitrile	16.3
m-Terphenyl	18.4
p-Terphenyl (14-diphenyl benzene)	18.6
1,2,4,5-Tetra-bromobenzene	42.9
Tetrabromotetramethyl-biphenol	34.5
1,2,4,5-Tetrachlorobenzene	47.9
Tetrachloro-bis-phenol-A	24.0
2,3,5,6-Tetrachloro-p-xylene	31.7
1,2,4,5-Tetramethyl benzene	16.7
Tetramethyl hydroquinone	17.4
1,3,6,8-Tetraphenylpyrene	22.2
Tetraphenyl tin	17.4
Tetraisopropyl titanate	15.5
Therminol 66	16.1
Thiamine hydrochoride	20.4
Thianaphthene	17.4
1-Thiazolidine-4-carboxylic acid	20.4

Compound	Oxygen Index
Thioacetamide	18.5
Thioanisole	15.5
2-Thio-barbituric acid	45.0
Thiocarbanilide	17.4
Thioglycolic acid	13.6
Thiomalic acid	20.4
Thiophene	16.6
Toluene	16.6
p-Toluene sulfonamide	16.9
p-Toluenesulfonic acid	21.8
o-Toluic acid	16.2
m-Toluic acid	18.1
p-Toluic acid	16.7
10C Transformer oil	15.6
Triamyl borate	16.3
Tribenzyl borate	15.9
1,2,4-Tribromobenzene	41.8
Tri-t-butyl-p-phenylphenol	17.7
Tri-n-butylphosphate	20.1
Tributylphosphine	20.0
1,2,4-Trichlorobenzene	30.1
1,3,5-Trichlorobenzene	30.1
Trichlorobiphenyl	36.0
2,2,3-Trichlorobutyric acid	20.0
Tri(2-chlorophenyl)phosphate	21.8
Tricyclohexyl borate	13.6
2,4,6-Trichloro-1,3,5-triphenylborazine	20.4
Tri-p-cresylphosphate	22.0
Triethanolamine borate	12.8
Triethyl borate	16.6
Triethyl phosphate	20.3
Triethyl phosphite	19.5
Trifluoroacetaldehyde hydrate	18.1
Trifluoroacetophenone	16.8
Trifluoromethylphenyl acetate	17.4
a,a,a-Trifluorotoluene	18.2
2,4,6-Triiodophenol	54.5
Trimethylphosphate	23.7
Trimethylphosphite	20.4
Trimethylsulfonium iodide	20.3
Trimethyl tin chloride	18.8
Trioctyl phosphate	18.6
2,4,6-Triphenoxy-s-triazine	18.1
Triphenyl phosphate	22.5
Triphenyylphosphine	20.4
Triphenyl phosphine oxide	24.9
Triphenylphosphite	21.0
Triphenyl phosphonium bromide	24.0
Triphenyl stibine	19.2
Triphenyl stibine dichloride	21.8
Triphenyl thiophosphate	19.2
Triphenyltin chloride	20.0
Tripropylamine	16.3
Tripropylene glycol	17.7
Vegetable oil	19.

Compound	Oxygen Index
Versamid 711	21.9
Versamid 900	22.3
Versamid 930	23.2
Versamid 940	23.6
Versamid 950	21.4
White corn syrup	21.8
o-Xylene	17.6
m-Xylene	17.6
p-Xylenebis(triphenylphosphonium chloride)	17.7
p-Xylenesulfonic acid	19.5

ISBN 0-8031-2041-9