



## **Aviation Fuels with Improved Fire Safety: A Proceedings**

Committee on Aviation Fuels with Improved Fire Safety,  
Commission on Engineering and Technical Systems,  
National Research Council

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# Aviation Fuels with Improved Fire Safety

## A Proceedings

Committee on Aviation Fuels with Improved Fire Safety  
National Materials Advisory Board  
Commission on Engineering and Technical Systems  
Board on Chemical Sciences and Technology  
Commission on Physical Sciences, Mathematics, and Applications  
National Research Council

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The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competencies and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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## PREFACE

Fire hazards associated with aircraft fuels have been a major concern of the military services, the Federal Aviation Administration, aircraft manufacturers, and aircraft operators. Current approaches to reduce the likelihood of fuel ignition emphasize design criteria for the routing of electrical wiring and fluid lines, fuel tank venting, engine fire walls, fire detection and suppression systems, and material fire resistance, as well as procedural rules regarding the storage, handling, and dispensing of fuel. However, as described in the 1996 National Research Council publication *Fire-and Smoke-Resistant Interior Materials for Commercial Transport Aircraft*: "Fuel flammability can overwhelm post-crash fire scenarios." Thus the reduction of the fire hazard of fuel is most critical for improving survivability for impact-survivable accidents.

The purpose of the Workshop on Aviation Fuels with Improved Fire Safety, held on November 19–20, 1996, at the National Research Council's Georgetown Facility, Washington, D.C., was to review the current state of development, technological needs, and promising technology for the future development of aviation fuels that are more resistant to ignition during a crash.

The organizing committee, which included recognized experts in aviation fuels, propulsion systems, combustion and flammability, additive materials, and analysis methods, developed the workshop format and agenda and identified potential participants. The committee felt that the most effective way to address this multidisciplinary topic was to include a series of invited presentations to provide background and perspective for workshop discussions and to introduce information on state-of-the-art technological developments. The invited speakers prepared summary papers, which are included in this proceedings (Parts II–IV). The workshop summary presented in Part I of this proceedings describes the subsequent workshop discussions and presents ideas for research and development that workshop participants felt were needed to develop fuels with improved fire safety.

This workshop provided a unique opportunity for participants representing a diverse range of technical backgrounds and experiences to get together to discuss a very difficult and important problem. The importance of the problem was impressed on the participants by a tragic accident that occurred at Baldwin Municipal Airport outside Quincy, Illinois, on the first evening of the meeting (November 19). The accident, as reported by the Chicago Tribune (November 20, 1996), involved a collision, on the ground, of a commuter aircraft with a private aircraft. The subsequent fuel fire, which resulted in 13 fatalities, was so intense that rescue personnel could not intervene.

This proceedings provides a summary of the results of the workshop and represents the views and opinions of the participants. The objective of the workshop was to identify technical issues and develop ideas for investigation and further development in an important area that has been essentially neglected for more than a decade. The committee hopes that the results of this effort catalyze further assessments by government and industrial organizations that will lead to real improvements in aviation fuel fire safety for both military and commercial operations.

Comments and suggestions can be sent via Internet electronic mail to [nmab@nas.edu](mailto:nmab@nas.edu) or by FAX to the NMAB (202) 334-3718.

JOHN J. WISE, CHAIR

COMMITTEE ON AVIATION FUELS WITH IMPROVED FIRE SAFETY



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The committee on Aviation Fuels with improved fire safety acknowledges the hard work of the invited speakers, who prepared outstanding presentations that provided important background for workshop discussions and excellent papers for inclusion in this proceedings. The committee would also like to thank all of the workshop participants for contributing their time and energy to the workshop discussions.

The committee would also like to thank Douglas Mearns of the Naval Air Systems Command and Robert Morris of the Naval Research Laboratory for their help in planning the workshop. The committee is particularly grateful to Thor I. Eklund, whose vision helped to initiate this effort and whose perseverance and expertise helped to complete the proceedings.

Finally, the committee gratefully acknowledges the support of Thomas Munns, National Materials Advisory Board (NMAB) senior program officer, Aida C. Neel, NMAB senior project assistant, and Jack Hughes (until August, 1996) and Bonnie Scarborough, NMAB research associates.

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# I

## Summary of Workshop

The National Research Council (NRC) Workshop on Aviation Fuels with Improved Fire Safety, held on November 19 and 20, 1996, in Washington, D.C., presented a rare opportunity for individuals familiar with different scientific and technical aspects of the fuel fire-safety problem to discuss opportunities for long-term research and development (see [Appendix A](#)). Invited papers covered a broad range of relevant topics to provide background for workshop discussions. Workshop discussions were devoted to the history of fuel fire-safety research, issues of fundamental fuel science, fuel system implementation issues, the technical status of analytical tools and materials, and recent advances in technical capabilities.

[Part I](#) of this proceedings presents a summary of the discussion that occurred at the workshop, as well as background information and technical and design issues associated with the fuel fire-safety problem prepared by the workshop planning committee and NRC staff. [Chapter 1](#) provides information on the history of fuel fire-safety research and practices, and places the problem in a policy context. [Chapter 2](#) presents workshop discussions on fuel and additive technologies, aircraft fuel system requirements, the characterization of fuel fires, and fuel fire-safety strategies. The most relevant technological advances and the most promising opportunities for research identified by workshop participants are summarized in [Chapter 3](#). Workshop papers are included in [Parts II, III, and IV](#) for aircraft fuel system requirements, fuel and additive technology, and fuel fire characterization, respectively.

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# 1

## Background and Historical Perspective

The fear of fire has influenced aviation practices throughout the history of flight. The dangers posed by the combination of flight and uncontrolled fire have been etched into the public's consciousness by film footage of wartime aviation, the Hindenberg conflagration, and tragedies in the Apollo and space shuttle programs. Media coverage of commercial airplane accidents typically includes grim photographs of the aftermath.

Fire can be defined, in these instances, as the uncontrolled release of energy through the combustion of flammable materials, with destructive consequences. However, it is precisely the release of energy through fire, or combustion, that makes flight a viable means of transportation. Significant mechanical force is required to lift an aircraft and payload off the ground and move it through the atmosphere. The energy for this motive force comes from fuel. Jet engines provide for the controlled release of energy from fuel, which is used for aircraft propulsion. Hence, although the controlled release of energy through the combustion of flammable materials makes flight possible, the uncontrolled combustion of the same materials has potentially destructive consequences.

### AIRCRAFT FIRE SAFETY

Throughout the history of aviation, preventing and mitigating fire has been a major consideration in all aspects of aviation design. Current designers of commercial and military aircraft incorporate a broad array of fire safety features, such as firewalls, shrouded and break-away fuel lines, flame arrestors, fuel-line isolation, explosion-proof electromechanical equipment, detectors and extinguishing systems, and fire-resistant materials, into their designs. In the last decade, a range of new requirements have imposed stringent fire safety standards on civil aircraft. These requirements include the use of low-heat-release-rate materials for cabin linings, floor-level emergency escape lighting, heat-resistant evacuation slides, fire-resistant liners for cargo compartments, improved hand-held fire extinguishers, and fire-resistant seat cushions. The Companion Report to the Aviation Safety Research Act of 1988 (Public Law 100-591) defined the goal of a "totally non-combustible aircraft cabin." In 1995, the National Research Council (NRC) published a study, commissioned by the Federal Aviation Administration (FAA), that defined research that could lead to the development of materials to meet that goal (NRC, 1995a, 1995b).

Design features alone, however, cannot protect an aircraft against the danger of fire. Although the NRC reports acknowledged the importance of research on fire- and smoke-resistant materials, they also noted that burning fuel has dominated most post-crash fire scenarios and causes even the most fire-resistant materials to burn readily. Therefore, "the reduction of the fire hazard of fuel is critical in improving survivability in post-crash fires" (NRC, 1995b, 41).

To appreciate the contribution of aviation fuel to the total aircraft fire load, consider that fuels comprise a substantial portion of an aircraft's weight. For example, one version of the Boeing 747-400 holds up to 57,285 gallons of fuel; this constitutes approximately 195 tons, or 45 percent of the maximum takeoff weight of the aircraft. Currently there are no regulations requiring that commercial airlines use low volatility fuels (e.g., Jet A). In fact, insurance industry classifications have had the effect of increasing the volatility of the aircraft fuels used because they separate flammable fluids into two categories using a minimum flash point temperature of 100°F as the divider. In the mid-1970s, the Jet A specification for minimum flash point temperature, which had been set at 110°F, was lowered to 100°F to correspond with these classifications.

Several defense agencies have already taken steps to prevent or mitigate the danger of aviation fires, including switching to lower volatility fuels, inerting fuel tanks, and working to develop an antimisting additive for the fuel. In two instances, military aircraft have switched to lower volatility fuels to increase fire safety. For the past 40 years, the U.S. Navy has used a special low volatility aviation kerosene (JP-5) to ensure fire safety on aircraft carriers. Although JP-5 is costly, it has also been shown to reduce the vulnerability of aircraft fuel tanks to ignition by gunfire. The U.S. Air Force has recently completed a 20-year transition from the more easily produced JP-4 fuel to the less volatile JP-8 fuel (comparable to the commercial Jet A fuel). The conversion involved the entire Air Force fleet, as well as U.S. Army aircraft, and was an effort to reduce combat losses from fuel tank ignition caused by gunfire.

The U.S. Air Force has pioneered many safety innovations in fuel systems, including the installation of porous foams in fuel tanks and dry bays, the inerting of fuel tanks with nitrogen and halogenated compounds, and the use of bladder

fuel tanks in helicopters. With the exception of bladder fuel tanks, these innovations were designed to improve fire safety in combat, rather than to improve fire protection in the event of release of fuel during an airplane crash.

The Army has devoted substantial resources to improving fire safety for tracked vehicles (e.g., tanks) that use diesel fuel. Antimisting agents, water and fuel emulsions, and halons for inerting fuel tanks have all been evaluated. Many of the Army's fuel safety concepts were reported in the findings of a 1984 *ad hoc* committee that explored possible research approaches to fuel fire safety (see [Appendix B](#)). Similarities between diesel fuel and low-volatility aviation kerosenes have created a synergism between fire safety research on Army tanks and research on aircraft fuel safety. However, military aircraft fuel has different requirements than civil aircraft fuel. In military aircraft, the fuel is used as a heat sink and exposed to higher temperatures (up to 300°F) for longer periods of time under certain operational conditions.

### FEDERAL AVIATION ADMINISTRATION RESEARCH ON FUEL FIRE SAFETY

The transition from piston-powered to turbine-powered aircraft enabled the replacement of highly volatile gasoline with much less volatile aviation kerosenes. This transition resulted in a reduction in fuel fire hazards in both combat situations and aircraft crashes. But the need for improvement remained. In the case of aviation kerosenes with flash points higher than ambient temperatures (e.g., Jet A and JP-5), the main post-crash fire hazard was associated with misting of the kerosene as it spilled from ruptured fuel tanks. Kerosene mist is far more susceptible to ignition than kerosene in bulk form. The flammability of mist, as well as its susceptibility to being ingested and ignited by a turbine engine, was documented in the 1950s by Pinkel et al. (1958). Research was undertaken to find fuel additives that could prevent the formation of fine mist.

#### Gelled Fuel Program

The first additive considered by the Federal Aviation Administration (FAA) for preventing the formation of fine mist was CAB-O-SIL<sup>®</sup>, a fumed silica formulation studied in the early 1960s. CAB-O-SIL was suspended in the fuel to increase viscosity and reduce the misting propensity. This early additive was soon followed by a range of gel and emulsion formulations, causing the FAA's fuel safety research program to be dubbed the "gelled fuel" program. Candidate additive packages were screened by shooting plastic bags of modified fuel from a compressed air gun into a coarse screen and ignition flame. Rudimentary testing for fuel system compatibility was also undertaken using engine combustor rigs and fuel pumps. Despite enormous problems with fuel system compatibility, the gelled fuel program proceeded to a full-scale-crash phase involving an RB-66 jet aircraft at the Navy jet track facility in Lakehurst, New Jersey. The program was terminated after the unexpected post-crash fuel fire of a test aircraft in 1972.

#### Antimisting Kerosene (AMK) Program

Although the major focus of the FAA fuel safety program was on gels and emulsions, a number of long-chain polymers used to improve the viscosity index were also tested. These polymers, in fact, represented the direction that additive manufacturers would take in the future.

The British Civil Aeronautics Administration (CAA) had been supporting the development of additive packages that were derivatives of the early long-chain polymer candidates. The CAA finally decided that FM-9, an additive package from Imperial Chemical Industries (ICI), was the best candidate for large-scale testing and evaluation. FM-9 consists of long-chain polymers (tertiary butyl styrene) that remain coiled in kerosene until the fuel is subjected to a certain level of shear force. The molecules then extend and interact with one another to inhibit the formation of mist. As long as the polymers remain coiled, the flow behavior of the modified fuel is close to the flow behavior of neat fuel. A British research report states that "FM-9 fuel has no measurable viscoelastic properties under the particular experimental conditions studied" (Coomer et al., 1977). However, problems with the solubility of the additive in kerosene necessitate the addition of surfactants as well.

In 1976, the FAA subjected FM-9 to extensive intermediate-scale fire tests at the Naval Weapons Center at China Lake, California. Based on the promising results of these tests, the FAA entered into negotiations with the CAA to define a joint research program focused on the FM-9 additive package. These negotiations resulted in a Memorandum of Understanding specifying responsibilities for each of the signatories (Churchill, 1982). The research program to develop and evaluate FM-9 came to be known as the antimisting kerosene (AMK) program.

In 1980, antimisting kerosene was considered "the concept that has the greatest potential for reducing post-crash fire risk" by a Special Aviation Fire and Explosion Reduction (SAFER) Advisory Committee (FAA, 1980). The new AMK program was much more broadly based than the earlier gelled fuel program. The AMK program involved aircraft component and engine manufacturers, as well as airframe manufacturers, government and nonprofit laboratories, and universities. Fuel system compatibility studies were undertaken, including flight testing of a Convair 880 jet with one engine operating on fuel with FM-9 added. A special in-line degrader was developed for this test so that the viscosity of the fuel with

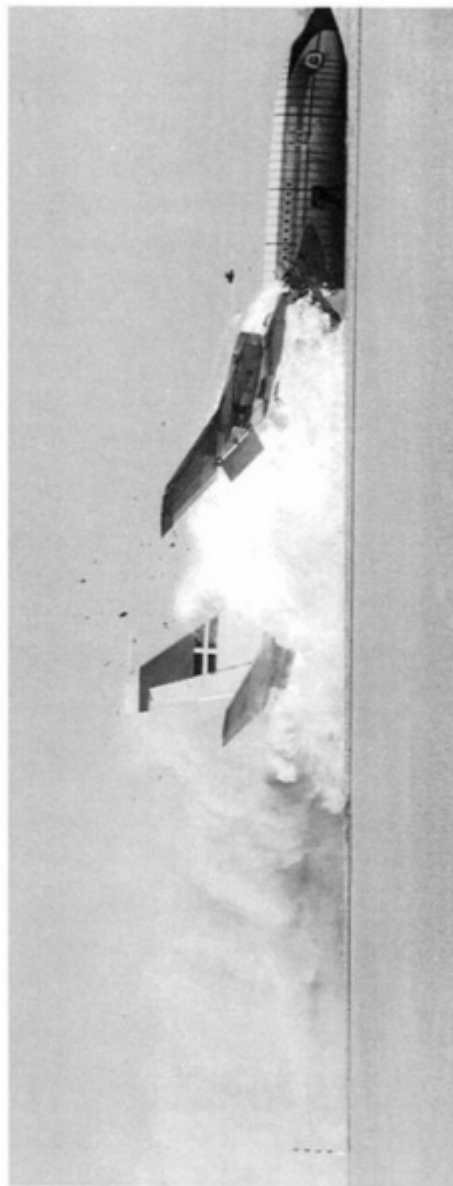


FIGURE 1-1 Controlled impact demonstration (CID) at Edwards Air Force Base, December 1984.

FM-9 additive could be mechanically reduced prior to pumping it into the engine.

Several defense agencies were involved to various degrees in the AMK program. Both the Navy and the Air Force explored the fire safety effectiveness of long-chain polymer fuel additives in tests with live gunfire. The Navy, however, had reservations about using FM-9 because of its known affinity for water and the Navy's need to keep water out of its fuel supplies.

The AMK program culminated in December 1984 with a joint FAA and National Aeronautics and Space Administration (NASA) "controlled impact demonstration" (CID). The CID involved a remotely piloted flight and "crash" of a surplus FAA B720 aircraft using only FM-9 fuel and equipped with degraders on all four engine cases. As part of the demonstration, undertaken at Edwards Air Force Base, the plane moved through stationary wing cutters on the ground. In an unanticipated event, one engine was damaged by these cutters. The CID resulted in a destructive fire caused by the massive ignition of fuel spray by the disintegrating engine (see [Figure 1-1](#)). The role played in this ignition by fuel that had already gone through the degrader (and that was therefore no longer antimisting) has been the subject of discussion. Although the AMK program produced a large number of research and engineering reports, many of which are discussed in a final summary report (Yaffee, 1986), the CID marked the end of substantive fuel safety research by the FAA.

### POLICY CONTEXT

In 1980, the SAFER Advisory Committee report stated, "The overall safety record of U.S. scheduled air carrier aircraft shows a continuing reduction in the fire-involved accident rate since the advent of jet transport service in 1958" (FAA, 1980). However, since that time, the FAA administrator, the NASA administrator, and industry spokespersons have all recognized that both the total accident rate and the fire-involved accident rate have stabilized since 1980 and that the stabilized rates, combined with continued growth in air traffic, will mean more frequent accidents and more passenger fatalities in the coming years (Murray, 1995; FAA, 1991). Passenger fatalities can be decreased both by lowering the accident rate and by improving crash survivability. Improved aviation fuel fire safety could prevent or lower the number of fatalities in survivable accidents.

The Aviation Safety Research Act of 1988 required that the FAA undertake research on low-flammability aircraft fuels. In his 1988 congressional testimony on fuel safety, then FAA Administrator T. Allan McArtor characterized the agency as "idea-limited" for fuel fire safety improvements (McArtor, 1988). Although research plans were developed for fuel safety (FAA, 1993), no substantive work in this area was undertaken. The NRC's Workshop on Aviation Fuels with Improved Fire Safety described in this proceedings was convened in November 1996 for the purpose of discussing the current state of development, technological needs, and promising technologies for the development of aviation fuels with improved fire safety.

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## 2

# Workshop Discussions

The NRC Workshop on Aviation Fuels with Improved Fire Safety was held on November 19 and 20, 1996, in Washington, D.C. Participants included representatives of engine manufacturers, airframe manufacturers, petroleum refiners, government agencies, national laboratories, and academia (see participant list in [Appendix A](#)). The objectives of the workshop were to summarize the state of current technical efforts that could lead to the development of fuels with improved fire safety, to discuss performance goals for the development of more fire-safe fuels, to forecast future activities for commercializing fire-safe fuels, and to identify promising research topics and key issues.

Invited speakers presented papers outlining a broad range of basic, but relevant, technologies. Topics included fuel chemistry and rheology, new fuel additives, airframe and fuel system design, post-crash fuel dispersal, and modeling post-crash scenarios. Papers provided background and perspective for the workshop discussions and presented information on state-of-the-art technological developments. The papers (Parts [II](#), [III](#) and [IV](#) of this report) are divided into three general categories: aircraft fuel system requirements, fuel and additive technologies, and fuel fire characterization. [Part II](#) includes five workshop papers dealing with fuel and additive technologies by Becher, Clodfelter, Khan et al., Taylor, and Wright. [Part III](#) includes the three workshop papers related to aircraft fuel system requirements by Eder, Griffis, and Mehta and Peacock. [Part IV](#) includes three papers covering the characterization of fuel fires by Faeth, Sirignano, and Tieszen.

The development of a fuel with improved fire-safety is generally considered to be a challenging, high risk research objective. For one thing, the concept of a "fire-safe" fuel appears to be an oxymoron (see Becher)<sup>1</sup> because the goal is to prevent the burning of a material that is developed specifically to be burnt for its combustion energy. Second, the burning of fuel must be prevented under conditions involving the dissipation of enormous amounts of mechanical energy (crashes and impacting or exploding weapons), situations that provide ample opportunity for ignition. Finally, the fuel requirements that must be met to ensure the reliability and safety of normal aircraft operations severely limit changes that can be made in fuel characteristics.

The workshop presented a rare opportunity for individuals familiar with different aspects of the fuel fire-safety problem to combine their expertise in an effort to clarify the obstacles to and possibilities for progress in this field. Portions of the workshop were devoted to outlining issues of fundamental science, describing aircraft design and performance requirements for fuel systems, identifying the current technical status of analytic tools and materials, and describing recent advances in technical capabilities. Workshop discussions are summarized in this chapter according to topic—fuel and additive technologies, requirements for aircraft fuel systems, the characterization of fuel fires, and fire inerting and suppression technologies.

### FUEL AND ADDITIVE TECHNOLOGIES

Aviation kerosene consists mostly of hydrocarbon molecules with eight to sixteen carbon atoms arranged in various molecular configurations. It is produced primarily through the straight-run distillation of crude oil. Depending on the composition of the raw crude and other petroleum stock used for production, aviation kerosene typically undergoes further processing to reduce the sulfur and acid content either by chemical treatment or by more severe processing. More severe processing methods include hydrotreating and hydrocracking. These processes can remove heteroatoms, enhance fuel hydrogen content, and change distillation characteristics (see Taylor).

The actual composition of aviation kerosene can be affected by overall market demands for petroleum. For example, refineries often produce a single product suitable for either Jet A fuel or for blending into home heating oil. Because the flash point temperature for home heating oil must be at least 120°F to meet local building safety codes (Blake, 1982), the flash point temperature for aviation kerosene is usually between 125°F and 135°F, even though the specification minimum is 100°F. The portion of crude available for aviation kerosene represents a trade-off against the demand for other petroleum products, such as gasoline and diesel fuel. Other circumstances, such as wartime contingencies, political instability, or petroleum embargoes, can also necessitate the use of off-specification fuel. Because less than 10 percent of

<sup>1</sup> Workshop papers included in Parts [II](#), [III](#), and [IV](#) will be cited by author only, e.g., (see Becher), to distinguish them from citations in the reference list, which are listed by author and year, e.g., (Blake, 1982).



the refineries in the U.S. produce virtually all of the aviation kerosene (Karlick, 1980), disruptions from accidents and natural disasters could also impact fuel characteristics.

The past 15 years have seen extensive modernization and automation of U.S. refineries, as well as a shake-out of unprofitable plant capacity. New processing techniques have become available to fuel refiners, and refinery methodologies have become more widely known (see Taylor). New technologies and more flexibility in processing have enhanced refiners' ability to produce fuels from a wider range of raw stock.

Approaches to reducing fuel flammability, including the FAA's gelled fuel and antimisting kerosene (AMK) programs, generally involve the use of additives to change fuel characteristics and decrease the likelihood of unwanted ignition. Workshop participants discussed barriers to implementing additive programs in general, as well as relevant advancements in the development of polymers and surfactants and improvements rheology, measuring equipment, and analytical methods.

Fuel hydrocarbons, by themselves, tend to be resistant to reactions; but the dissolved oxygen and additives inevitably present in fuel are more reactive. Efforts are made, therefore, during refining, transportation, and storage, to minimize the presence of chemicals and impurities that could react adversely with these materials, and also to remove any particulate and water contamination. Several workshop participants pointed out that the need to minimize contaminants directly affects the viability of safety fuels. Fire-safe fuel additives must not be adversely reactive either with existing aircraft fuels or with additives already in use, such as antistatic compounds, antioxidants, corrosion inhibitors, and metal deactivators. A viable fire safety additive has to be an integral chemical component of the kerosene formulation and must have predictable, measurable, and consistent characteristics.

Polymers and surfactants may be useful for reducing fuel flammability, according to several workshop speakers and participants. Because of the emphasis on evaluating FM-9 during the AMK program, many other polymers in existence at the time were never investigated for potential antimisting capabilities. Today, even more polymers and surfactants are available (see Becher; Hall, 1996). In addition, more powerful computational capabilities offer possibilities for molecular modeling and polymer design that were not available at the time of the FM-9 program. With molecular design, in principle, a polymer fuel additive could be developed that would self-degrade thermally prior to injection into the combustor. This would obviate the need for a mechanical degrader to restore acceptable fuel flow characteristics, as was necessary with the FM-9 additive (Hall, 1996).

A parallel situation exists with surface active agents, or surfactants. Thousands of surfactant molecules are available for use in safety fuel formulations (see Becher). The U.S. Army has extensively tested fire-safe candidate fuels that employ surfactants to make emulsions of water and fuel. Participants noted that the FM-9 formulation required surfactants to enable the styrene-based polymer to swell enough to prevent mist formation. A number of workshop participants felt that future fire-safe fuel additive packages might include both high molecular weight polymers and surfactants. It was suggested that recent developments in microemulsion technology could be of interest in developing such formulations.

In addition to the increased technical sophistication of the petroleum industry and the broad array of polymers and surfactants available, fire-safe fuel research is now facilitated by advances in the rheology of polymer solvent systems. With dynamic rheological measurements, polymer-solvent interactions can now be characterized at the microstructural level. For example, with steady-flow rheology, changes in microstructure caused by fluid flow can now be quantified in simple fluid systems. In addition, with advanced techniques for measuring extensional viscosity, composition effects for very dilute polymer systems and for solutions of associative polymers (typically water-soluble polymers that also possess hydrophobic groups) can now be identified. Rheological methods to characterize non-Newtonian flow behavior have also become more firmly established (see Khan et al.). These advances in rheological tools have enhanced the capacity for designing effective fuel additives.

The availability of large numbers of polymer compounds and surfactants, coupled with the complexity of kerosene composition, means an unmanageable array of candidate additive packages is available for investigation. However, workshop participants felt that progress in analytical methods, including molecular computation and measurement technology, could alleviate this problem. The past 15 years have yielded increasingly automated, technically sophisticated equipment for process monitoring and quality assurance testing. With chromatography, mass spectrometry, and infrared spectrometry, more detailed and quicker chemical analyses than were available during previous programs can be done.

Given the advances in materials and tools described above, participants with expertise in the area of chemical additives felt that an effective fire-safe fuel additive package could probably either be selected or designed, provided that fuel performance requirements were identified in advance. Participants also felt that modernization and new technology have provided today's refineries with more flexibility to compensate for changes in fuel properties caused by additives.

### AIRCRAFT FUEL SYSTEM REQUIREMENTS

The overall issues of concern regarding the properties of aviation fuels have not changed much since they were

originally documented in the 1950s (Barnett and Hibbard, 1956; Sharp, 1951). Requirements for aircraft fuel systems are continually evolving in response to experience, scientific advances, practicality, and best judgment. Fuel system requirements include fuel properties for safe and efficient operation along with characteristics of aircraft systems that enable the use of fuel with specified properties. Many of the barriers that must be overcome to implement a fire-safe fuel involve fuel performance and requirements for fuel properties. Altering fuels to add fire safety features for the case of an aircraft crash may very well cause problems with fuel performance during normal operation. Workshop participants discussed barriers to the implementation of fire-safe fuels and additives presented by interrelations among fuel specifications, fuel system requirements, and the operational requirements of existing aircraft.

Fuel properties are specified to ensure safe and efficient aircraft operation. Performance specifications for aviation fuel for the commercial aviation kerosene Jet A are identified in ASTM specification D1655; for JP-8, they are identified in military specification MIL-T-83133A; and for JP-5, they are identified in military specification MIL-T-5624L. These specifications ensure that fuels meet requirements in the following areas:

- *Combustion performance.* Requirements are set to ensure that aviation fuels have adequate altitude relight capability, that radiative heat transfer to the combustor liner not be excessive, that the level of emissions is acceptable, and that temperature patterns at the combustor exit are acceptable.
- *Fuel thermal behavior.* Specifications for commercial transport are primarily associated with gum deposits that can form on hot surfaces traversed by the fuel as it is pumped to the combustor nozzles. Fuel thermal stability is more crucial in military aircraft because of the high operating temperatures in the fuel system and the thermal effects on fuel circulated for cooling purposes. Fuel temperatures at the engine inlet can run as high as 250°F, and the fuel is then heated as it passes through as many as three additional pumping stages and is used as a fluid to power thrust control actuators (see Eder). A new additive package has recently been demonstrated to enhance the thermal heat sink capabilities of both Jet A and JP-8 (Heneghan et al., 1996).
- *Flow characteristics.* Requirements specify allowable pressure drops across small orifices in the engine fuel controls, as well as allowable low temperature viscosities, freeze point temperatures, and performance criteria in fuel tank boost pumps. Fuel flow requirements for military aircraft are extremely complex because fuel is increasingly used by the military as a lubricant for accessories and as a surrogate hydraulic fluid (see Eder).
- *Materials compatibility.* Problems associated with wear and tear on components caused by flowing fuel, with the integrity of seals and sealants, and with the sensitivity of thermal barrier coatings on turbine blades to fuel constituents have been identified.

If fuel properties are changed to improve fire safety, other performance specifications might not be met. For example, decreasing the volatility of a fuel by raising the flash point temperature might interfere with engine relight capability.

Aircraft systems design criteria are established for the safe and effective utilization of specified fuels. For commercial aircraft, these criteria are established in FAA advisory circulars, certification requirements, and industry design practices. For military aircraft, design considerations have been codified in formal specifications, such as MIL-F-87168 for the Air Force (see Clodfelter). There are also specifications for aircraft materials that are exposed to fuels. These materials are selected on the basis of minimal adverse effects on performance and minimal aging as a result of exposure to fuels, and for not, themselves, degrading fuel quality. Satisfactory metals for pumps, lines, and accessories are aluminum, certain stainless steel compositions, some nickel-steel alloys, Monel, carbon molybdenum steel, and chrome-molybdenum steel. Bronze, nickel, copper, zinc, cadmium, and brass do not have satisfactory properties. Similarly, depending on the temperature, polymeric materials suitable for seals and gaskets include nylon, polyethylene, fluoropolymer resins (e.g., Teflon<sup>®</sup>), and fluoroelastomers (e.g., Fluorel<sup>®</sup> and Viton<sup>®</sup>) (CRC, 1983). Several workshop participants pointed out that fuels altered to improve fire safety could require major changes in design and materials specifications for many aircraft system components.

Workshop participants pointed out that operators of both military and commercial aircraft will continue to depend on existing and derivative aircraft in both the nearterm (up to 5 years) and the midterm (up to 10 years) future. The U.S. military fleet contains a large number of older aircraft (20 to 35 or more years), with minimal replacements (e.g., C-17 transport, F-22 fighter, and Joint Strike Fighter) planned in the next 25 years (NRC, 1997). Also, no new civil aircraft designs are anticipated in the near-to mid-term because the industry's focus has been on derivative aircraft models (NRC, 1996a). Hence, fuels with improved fire safety must be evaluated for current airplane models.

If current aircraft have to be retrofitted, fuel performance in existing engines could be a significant barrier to implementation. Engine designs have been developed based on the availability of a known, specified fuel. These designs have been tested to demonstrate that they meet safety and performance criteria and have been certified based on using that fuel (Blake, 1982). Because the effects of changing fuel properties on engine performance are not known, extensive testing and requalification would be required.

Participants knowledgeable about engine design and manufacturing stated that this would significantly affect manufacturers of engines and components who provide warranties on their products, because the off-specification fuels might degrade safety and performance.

Past experience provides some information on the time and cost that would be involved in the development of a fuel modification and subsequent retrofitting. Participants pointed out that the qualification of the Stadis 450<sup>®</sup> antistatic additive used in Jet A-1 fuel took seven years; the Air Force transition from JP-4 to JP-8 took 20 years. The Air Force transition could also provide a basis for estimating the costs of changing fuel specifications for a broad spectrum of aircraft and aircraft systems (see Clodfelter). Problems likely to be caused by the tremendous variation in age and system characteristics of aircraft in both the civil and military fleets have not been estimated. There could be major differences in the compatibility of the new fuel with various aircraft.

Finally, workshop participants discussed the wide variety of existing aircraft design features that already minimize the likelihood of fuel ignition. Most of these design features are compatible with any type of fluid and, therefore, do not present barriers to the implementation of a fire-safe fuel. A number of features are designed specifically to prevent the ignition of fuel vapors by electrical sources (see Mehta):

- Engine accessories are electrically bonded to the engine case, which in turn is bonded to the airframe, to prevent discharges of static electricity, as well as discharges induced by circuitry and electromagnetic fields.
- Explosion-proof electromechanical equipment is used wherever there may be contact with fuel liquids or vapors.
- Fuel tank capacity and sensor circuits are designed with electrical power requirements an order of magnitude lower than the minimum spark ignition energy of 0.2 mJ.
- Fuel vent ports from aircraft surge tanks are located inboard of the lightning strike zone, and tank structure is designed to prevent internal sparking in case of a lightning strike.

Additional fire safety design features include the strategic placement of fuel drain masts, shrouded fuel lines within the aircraft pressure hull, flame arrestors in vent lines, fireproof hose assemblies in engine nacelles, the separation of fuel lines from electrical wiring, and the ventilation of compartments and bays where fuel vapor can accumulate. Fuel leaks are prevented by measures such as fuel line stretch flexibility, fuel shutoff capability outside the engine fire zone, and duplicate wiring to the shutoff valve actuator. Finally, aircraft power-plant technology now has on-board computers capable of controlling fuel utilization and monitoring performance discrepancies.

### CHARACTERIZING FUEL FIRES

The literature applicable to post-crash aircraft fires is abundant. However, most past studies have focused on ignitability, based on small quantities of fuel, and the burning of large fuel pools and have been intended to provide information either for fire-fighting tests or for the effects of fire exposure on materials and structures. The overall development of a fire during an airplane crash is still not well understood.

To disrupt the processes of fire development, it is necessary to have a clear understanding of them. For aircraft crashes where spilled fuel burns, it is important to understand how the fuel is released, how it is dispersed, how it is ignited, and how the fire is spread. The process is different for each crash scenario, and the changes from one scenario to another must be ascertained. The effectiveness of fire safety measures must be gauged for the full range of possible accident scenarios. Advances in analyzing risk and vulnerability have enabled far more comprehensive and reliable systems analyses of proposed fuel candidates than was possible prior to the CID crash in 1984 (see Griffis).

Workshop speakers and participants discussed recent developments in analytical techniques that could be used to analyze fire development processes in crash scenarios. Important developments have occurred in computational approaches to the prediction of fuel dispersal and in the modeling of fluid dynamic and combustion phenomena.

A recent study of post-crash fuel dispersal has demonstrated the complexity of the fuel release, atomization, and dispersal processes (see Tieszen). This study recommends using a computational approach involving smooth particle hydrodynamics to investigate fuel release on impact in certain very high energy crash modes. Detailed modeling of the atomization of fuel after release is currently computationally impossible partly because there is a four-order-of-magnitude difference in scale between fuel droplet size and wing cross section. However, the post-atomization dispersal process becomes more tractable as the overall concentration of liquid fuel in air decreases.

Workshop participants pointed out complexities associated with the aerodynamic flow field that develops around a crashing aircraft that is moving in a direction other than along the fuselage center line. The flowfields undoubtedly include regions of strong vorticity, recirculation, and local acceleration.

The modeling of fluid dynamic and combustion phenomena relevant to post-crash fires has improved dramatically in the last 10 years, and some impressive tools are now available for analyzing turbulent combustion, spray formation, and spray burning (see Faeth). Notable advances include the use of universal functions to analyze turbulent diffusion flames, the development of stochastic separated flow (SSF) models for prediction of droplet life histories in fuel sprays, and the clarification of the role of vorticity in the breakup of liquid

jets. Although the most extensive efforts at computational and experimental verification have been directed toward axisymmetric jets and wall jets, the same methods could have a significant impact on the characterization of post-crash fires if applied to the release of aviation fuel during a crash.

These computational tools were presented to the workshop as cohesive engineering framework based on laminar diffusion flamelet concepts and classical turbulence models. Universal state relationships can be used to correlate various fluid properties with the degree of mixing predicted by turbulence models. Laminar flamelet concepts can then be used in conjunction with turbulence models, and their effectiveness is a key feature of the success achieved in modeling turbulent flames.

The locally-homogeneous flow approximations and state relationships used for gaseous fuels have been used to analyze turbulent burning sprays. Although these analyses are not accurate in predicting the changes undergone by the spray over time, they have revealed an extremely important physical fact about burning sprays, that combustion occurs only in regions of relatively low mixture fraction. Once this is understood, much of the process of spray formation can be analyzed without including combustion effects.

With new analytical methods, a more accurate method for predicting flame radiation is now available. Stochastic techniques allow turbulent fluctuations in temperature to be factored into the radiation transfer equations, thereby rectifying the underestimation of radiation flux, which was characteristic when averaged thermal properties were used. However, major inaccuracies in the prediction of overall fire development remain, primarily because of the difficulty of characterizing the size, distribution, and evolution of soot in turbulent fires.

With newly developed SSF methods, handling phenomena with droplet turbulence interaction is now computationally tractable. SSF methods can successfully predict droplet life histories in a burning spray. The accuracy of SSF methods suffers most from uncertainties concerning initial spray characteristics. Although recent studies have clarified the role of vorticity and turbulence in the primary breakup of liquid jets and sheets and have demonstrated that the breakup leads to universal normal distributions of droplet size, the rate of breakup processes has not been predicted by any generalized method. Droplet sizes in primary breakup are limited by surface tension; however, viscosity affects droplet sizes in secondary breakup. According to workshop participants, methods for predicting secondary breakup accurately will also require further investigation of the rate processes.

Workshop participants pointed out that, to be applicable to safety fuels, existing computational (or modeling) techniques for spray combustion would have to be modified to include rheological effects. In particular, the analysis of the primary and secondary breakup of fuel jets would have to include the effects of shear-rate-dependent viscosity, normal stresses, and elongational viscosity. The time dependence of changes in the elastic and viscous fluid properties would most likely also be important. Direct application of current turbulent spray combustion models to the analysis of incendiary ignition of fuel in tanks appears to be more difficult. However, if adequate descriptions of the turbulent flow variables can be developed, some concepts, such as the universal state relationships, may be useful.

### FIRE INERTING AND SUPPRESSION TECHNOLOGIES

Strategies discussed thus far have been aimed at disrupting or eliminating aspects of the fire development process. Fuel additives are primarily aimed at preventing fuel spray ignition, while aircraft design features enhance the fire resistance of the aircraft structure. Workshop participants drew a distinction between fire-safe fuels, which they classified as a preventive strategy, and other ameliorative strategies. Fuel-fire inerting and suppression emerged as an area of interest in both the workshop discussions and invited papers (see Clodfelter; see Wright).

Strategies were discussed for increasing the chances of survival and rescue of passengers via suppression of fire around crashed aircraft. Approaches to fire suppression depend on the aircraft itself deploying countermeasures and on the means of deployment remaining effective after the crash. Halon fire extinguishing agents have been the agents of choice for aircraft engine and cargo compartment fires, but the production of halon agents, as well as certain other chlorofluorocarbons, has been terminated because they contribute to the depletion of stratospheric ozone. The search for alternatives has driven researchers toward other technologies, such as pyrotechnically generated aerosols, water mist systems, and low volatility agents (see Wright). The four concepts proposed by workshop participants for fire suppression are:

- *Surface enhancement of halons.* A surfactant or other substance would be used to concentrate halon or halon replacement agents at the surface of a burning pool.
- *Low volatility technology.* A chemical compound would be deployed that would thermally decompose into one or more extinguishing agents when passing through a fire plume.
- *Propellant generated solid aerosols.* Solid generators would burn to release agents, such as potassium compounds, that could extinguish a fire.
- *Micro-encapsulation.* Capsules would degrade to a dry chemical fire suppressant, releasing their contents, which would be another liquid or gaseous extinguishing agent.

Advancements since the 1980s relevant for deployment mechanisms include the development of air bag gas generator



technologies by which a variety of suppression agents could be generated *in situ* from various reacting solids.

Exclusive focus on suppression around crashed aircraft may prevent fire safety approaches from being applied to other fire scenarios, such as fuel tank ignition by incendiary projectiles. If the focus is on ignition and flame spread, then processes like fire spread on liquids, hot projectile boundary-layer ignition, and spray combustion become the phenomena of interest (see Sirignano). Concepts arising from this perspective in workshop discussions were:

- *Pressure sensitive fuel*. This fuel would burn well in the engine combustor but very poorly upon release into the atmosphere.
- *Two fuel combination*. This fuel system would comprise two separate components that would burn poorly when unmixed but would burn efficiently when blended and injected into the engine.

Workshop discussions also identified potential technologies for fuselage hardening involving intumescent coatings and fire-resistant carbon fiber or polymer foam aircraft insulation. Hardening technologies can increase escape times by enhancing the resistance of the aircraft fuselage to burn-through from external fuel fire.

### COST CONSIDERATIONS

Workshop participants discussed significant changes in the technical landscape since the CID crash in 1984. Changes in the corporate culture, driven by international competition, have significantly reduced private sector investment in long-term scientific and engineering research. The government's debt-driven budgetary pressures have resulted in an overall reduction in federal research funding of approximately 30 percent (NRC, 1996b). The end of the Cold War has resulted in a downsized aerospace industry, and the longer-term effects of deregulation have resulted in a more cost conscious and conservative outlook by airlines and commercial aircraft manufacturers.

Some participants felt that the type of fuel safety research done in the past could not be contemplated in today's climate because the private sector would be unlikely to invest resources in a long-term fuel safety research program without government support, and the government would be unlikely to commit large resources for an engineering demonstration of an industry sample product without a substantial systems analysis of the costs, benefits, and likelihood of success. Hence, for economic reasons, as well as for technical reasons, a future fuel safety research program will have to be grounded in fundamental research and subscribed to by all stakeholders. Participants felt, however, that technical difficulties transcend issues of cost and that the technical difficulties place safety fuel development squarely in the realm of long-range research.

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### 3

## Summary of Progress and Opportunities

Developing a safer fuel has always been considered an unusually challenging, or high risk, research objective. First, the concept of preventing the burning of a substance used specifically for its combustion energy appears to be an oxymoron. Second, the conditions under which fire must be prevented are precisely the conditions that involve the dissipation of enormous amounts of mechanical energy, such as crashes and impacting or exploding weapons. Third, present day requirements for fuel performance severely limit the kinds of changes in fuel characteristics that can be made.

In this chapter, the ideas and observations of individual workshop participants are summarized. The industries and technologies represented by workshop participants rarely come together in a common endeavor. Consequently, a portion of the workshop was devoted to outlining fundamental aircraft design and fuel performance requirements, identifying the current technical status of relevant technologies, and describing advances in technical capabilities. Opportunities are identified for each major area—fuels and additives, fuel systems, and the characterization of fuel fires.

### FUEL AND ADDITIVE TECHNOLOGIES

Aviation kerosene is produced primarily from the straight-run distillation of crude oil. The portion of crude oil available for aviation kerosene represents a trade-off against the demand for other petroleum products, such as gasoline and diesel fuel. Two advances in fuel production that could have a positive effect on the development of improved fuel formulations were discussed. First, extensive modernization and automation, with new technologies and more flexible processing, has increased the ability of U.S. refineries to produce fuels from a wider range of raw stock and to tailor the properties of fuels. Second, with the development of automated and technically sophisticated measurement equipment and techniques (e.g., chromatography, mass spectrometry, and infrared spectrometry), more rapid and detailed chemical analyses of fuel formulations can be made.

Many of the workshop participants believe that fuel additive packages are likely to include both high molecular weight polymers and surfactants. There are literally thousands of potential polymer and surfactant additives, many of which either did not exist fifteen years ago or have not been investigated as fuel additives. Along with improved fire performance, fire-safe fuel additive packages will have to be nonreactive with the base kerosene as well as with additives presently used during fuel handling, storage, and service in aircraft tanks and components.

Advances in the understanding of polymer rheology complement the technical advances in the petroleum industry described above. Workshop participants discussed several advances that could help in the development of fuel additives, including:

- molecular modeling techniques that allow for designing and tailoring polymer and surfactant systems with specified characteristics at the microstructural level
- advances in measuring extensional viscosity that can identify composition effects for very dilute polymer systems and for solutions of association polymers
- techniques for making dynamic rheological measurements that can characterize polymer-solvent interaction at the microstructural level
- rheological modeling methods that provide means for relating non-Newtonian flow behavior to the micro-structure of polymer systems

In principle, the capability exists of employing rheological methods and molecular design techniques to develop polymer and surfactant additives that would thermally self-degrade prior to injection into the combustor, rather than requiring a mechanical degrader to restore acceptable fuel flow characteristics. The availability of large numbers of polymer compounds and surfactants, coupled with the complexity of kerosene composition, make for a huge number of potential fire-safe fuel packages. New analytical methods, molecular computation, and measurement technology have made it feasible to select likely candidate packages for investigation, although many of these techniques would need to be specifically tailored to the complex rheology expected to be present in antimisting kerosene. Several workshop participants suggested that, once fuel performance requirements have been identified, an additive package could be either selected or designed. However, the full power of state-of-the-art molecular design and analysis capabilities cannot be effectively used until safety fuel performance requirements have been identified and appropriate small scale flammability screening tests to evaluate additive packages have been developed.

## AIRCRAFT FUEL SYSTEM REQUIREMENTS

Aircraft fuel system requirements are based on experience, science, practicality, and engineering judgment. Fuel system requirements include the fuel properties needed for safe and efficient operation of the aircraft, along with the characteristics of aircraft systems that enable the use of fuel with specified properties. Fuel performance specifications have evolved in the areas of combustion performance, fuel thermal behavior, flow characteristics, and materials compatibility.

The workshop participants discussed several fire-safe design features already used in aircraft systems:

- preventing the ignition of fuel vapor by electrical sources using several methods including electrical bonding of components to the airframe to prevent discharges of static electricity and discharges induced by electromagnetic fields, the use of explosion-proof electromechanical equipment, the use of low power fuel tank capacity and sensor circuits, locating fuel vent ports from aircraft surge tanks inboard of the lightning strike zone, and designing the tank structure to prevent internal sparking during a lightning strike
- the strategic placement of fuel drain masts
- shrouded fuel lines within the aircraft pressure hull
- flame arrestors in vent lines
- fireproof hose assemblies in engine nacelles
- separating fuel lines from electrical wiring
- ventilating compartments and bays where fuel vapor can accumulate
- preventing fuel leaks by fuel line stretch flexibility, fuel shutoff capability outside the engine fire zone, and duplicate wiring to the shutoff valve actuator

Military and civil aircraft vary widely in terms of age and technologies. Each engine model has been subjected to certification testing to demonstrate safety and performance with a particular fuel. The effects of changing individual fuel properties are largely unknown. However, because engines are developed, validated, and warranted based on the performance of a specified fuel and because changing fuel specifications requires extensive validation tests, several workshop participants pointed out that the impetus is to maintain the status quo. For example, the transition from JP-4 to JP-8 fuel by the Air Force took 20 years. Many of the workshop participants felt that neither producers nor users of aircraft would be likely to accept fuel modifications that require substantial changes to existing fuel systems without a total fleet systems analysis. Safety fuel additive packages would have to be shown to be nonreactive with the base kerosene, as well as additives presently used during fuel handling, storage, and service in aircraft tanks and components.

## CHARACTERIZING FUEL FIRES

Although a great deal of research has been done on aircraft post-crash fires and ballistic ignition of aircraft dry bays and fuel tanks, understanding of the overall development of aircraft fuel fires is still conjectural. How the fuel is released, how it is dispersed, how it ignites, and how the fire spreads are still open questions. Finding ways to disrupt fire development requires a clear understanding of these processes. Workshop participants identified promising technical approaches to analyzing fire processes, but these approaches have not been validated for aircraft fuel fires.

In last 10 years, some impressive new tools for analyzing turbulent combustion, spray formation, and spray burning have been developed. Some workshop participants suggested that the application of these tools to aviation fuel release during a crash could have a significant impact on the characterization of post-crash fires. Recent advances that could lead to a cohesive engineering framework based on laminar diffusion flamelet concepts and classical turbulence models include:

- using universal state relationships to correlate fluid properties with the degree of mixing predicted by turbulence models
- the development of stochastic techniques for factoring turbulent fluctuations in temperature into the radiation transfer equations, rectifying any underestimation of radiation flux caused by the use of average thermal properties
- using locally-homogeneous flow approximations and state relationships to analyze salient features of turbulent burning sprays
- using stochastic separated flow methods to compute droplet life history in burning sprays

Barriers to development of numerical representations to model post-crash fire processes include:

- computational complexity resulting from the need to consider size scales over four orders of magnitude—from drop size to wing cross-section size—in modeling fuel atomization after fuel release
- incomplete understanding of fuel release and primary breakup processes
- incomplete understanding of soot characteristics, including size, distribution, and evolution in a crash fire
- incomplete characterization of the initial ignition mechanism

Workshop participants discussed a number of opportunities for advancing the fundamental understanding of fuel

fires. First, the complexities associated with the aerodynamic flow field around a crashing aircraft moving in a direction other than along the fuselage center-line have not been investigated. Strong vorticity, recirculating flows, and locally accelerated flows can significantly influence the breakup of fuel streams and subsequent fire behavior. Although recent studies have clarified the role of vorticity and turbulence in the primary breakup of liquid jets and sheets, the rate of these breakup processes cannot be predicted by any generalized method. Second, although it is known that surface tension limits the size of drops resulting from primary breakup processes and that viscosity limits the size of drops in secondary breakup processes, methods for making accurate predictions of secondary breakup depend on the rate processes involved, which are still not well understood. Third, to be applicable to fire-safe fuels, methods for analyzing turbulent combusting sprays need to be modified to accommodate non-Newtonian fluid properties. In particular, an analysis of fuel jet primary and secondary breakup would have to include the effects of time- and shear-rate-dependent viscosity, normal stresses, and elongational viscosity. Finally, applying methods for analyzing turbulent spray combustion, including some concepts like universal state relationships, directly to the analysis of the incendiary ignition of fuel in tanks could improve the understanding of these complex processes.

### GENERAL CONCEPTS

The subject of fuel fire inerting and suppression emerged as an area of interest in both the invited papers and in workshop discussions. The workshop participants discussed five concepts of fire suppression as alternatives to fuel modification. The assumption was that controlling post-crash fires around the aircraft to increase the chance of the survival and rescue of passengers could be as effective as modifying the fuel. Fire inerting and fire suppression are predicated on sensing fire and effectively deploying countermeasures (and that the means of deployment remain effective after a crash). The concepts discussed included:

- *Surface enhancement of halons.* A surfactant or other substance would concentrate halon, or halon replacement, agents at the surface of a burning pool.
- *Low volatility technology.* A chemical compound would thermally decompose into one or more extinguishing agents when passing through a fire plume.
- *Propellant generated solid aerosols.* Solid generators would be burned to release agents, such as potassium compounds, that could extinguish the fire.
- *Suppression gas generation.* Gas generator technology used in automotive air bags could be used to generate gaseous suppression agents from reacting solids.
- *Micro-encapsulation.* Microcapsules, which would degrade in a fire, would release a liquid or gaseous extinguishing agent.

Some workshop participants warned that focusing exclusively on suppression in the area around a crashed aircraft could keep fire safety approaches from being applied to other fire scenarios, such as fuel tank ignition by incendiary projectiles. Others noted that focusing on ignition and flame spread would lead to emphasizing processes like fire spread on liquids, hot projectile boundary-layer ignition, and spray combustion. The concepts that would arise from this perspective include:

- *Pressure sensitive fuel.* This fuel would burn well in the engine combustor but very poorly when released into the atmosphere.
- *Two component fuel.* This fuel would have two separate components that burn poorly individually but that burn efficiently when blended and injected into the engine.

In addition, fuel tank inerting technologies offer ways to protect fuel tanks and dry bays from ignition by electrical sources and incendiary devices.

One of the concepts discussed at the workshop that could improve the chances of survival in the event of an external fuel fire is aircraft fire-hardening. Intumescent coatings and fire resistant aircraft insulation (e.g., carbon fiber and new technology foam insulation) can delay aircraft fuselage burn-through as a result of external fuel fires.

### RESEARCH OPPORTUNITIES

Workshop participants discussed six primary areas of opportunity for long-term research to establish performance goals, evaluate potential fuel additives and modifications, and develop fundamental capabilities to model the complex phenomena that need to be considered in the development of fuels with improved fire safety. The primary areas include:

- evaluating the effectiveness of various strategies for improving fire safety (e.g., fuel safety additives, inerting, fire suppression) in various scenarios (e.g., incendiary devices, post-crash fires, electrical ignition)
- estimating costs and benefits of proposed fuel safety additive packages on fleet safety and operations
- characterizing the aerodynamics, fuel release and dispersion, ignition, and burning phenomena for a range of aircraft crash scenarios
- investigating the rheology and interfacial phenomena of polymer and surfactant systems in aviation kerosene solvents, as distinguished from the single component solvents commonly used in academic research



- investigating the operational effects of changes in fuel specification parameters individually and in combination
- extending methods for analyzing the atomization and combustion of fuel sprays to fuel systems with non-Newtonian flow characteristics

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## II

### Presented Papers Fuel and Additive Technologies

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4

## Potential Surfactant Additives: The Search for the Oxymoron

Paul Becher

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According to the program, I am expected to discuss potential surfactant additives. This is a difficult problem, because prior to hearing the talks at this meeting, it was impossible to determine what these additives were, in fact, to be added to. I may say that this problem has not become much easier, but I shall return to that point a little later.

Let me concentrate instead on the subtitle of my presentation, namely, "The Search for the Oxymoron." Since this is an educated audience, I will assume that everyone knows what an oxymoron is. However, on the statistically small chance that some member of the audience has not come across this word, I give you the following definition (American Heritage Dictionary, 1996):

**ox·y·mo·ron** ( *ók'sē-mōr 'ōn, -mōr 'ē* ) *n.*, *pl.* **ox·y·mo·ra** ( *-mōr 'ə, -mōr 'ə* ) or **ox·y·mo·rons**. A rhetorical figure in which incongruous or contradictory terms are combined, as in *a deafening silence* and *a mournful optimist*. [Greek *οξύμωρον*, from neuter of *οξύμωρος*, pointedly foolish: *oxus*, sharp; see OXYGEN + *μῶρος*, foolish, dull.] —**ox·y·mo·ron 'ic** ( *-mə-rōn 'ik* ) *adj.*—**ox·y·mo·ron'i·cal·ly** *adv.*

However, the oxymoron for which we are searching is (as you might guess) "nonflammable fuel." You will at once assure me that what we are seeking is actually "reduced flammability," and I will agree. But the further target is, at least, worth thinking about.

The oxymoron in question is not particularly new. I recall using it in, I believe, 1945. At that time, I was serving as an enlisted research chemist in the Air Force laboratories at Wright Field, Dayton, Ohio. My general area of activity was work on petroleum products used in military aircraft, including fuels, lubricants, and hydraulic fluids. A principal target was the development of a nonflammable hydraulic fluid.

We did, in fact, succeed in developing a usable fluid, and I share in a patent (U.S. Patent 2,470,792) which, to the best of my knowledge, has never actually been tested, much less used, by the Air Force (or for that matter, anyone else). I am not too unhappy about this result because I have since developed some doubts about the toxicity of the principal ingredient. Nonetheless, I may perhaps be able to claim priority in this area over most attendees to this workshop. I should point out that even in 1945 we recognized that the term nonflammable fuel was an oxymoron. However, we also understood that it was, in principle, obtainable and, perhaps, important.

While teaching in the Georgia University system, I did a small amount of research into the synthesis of the principal ingredient of our patented hydraulic fluid. This resulted in my one and only citation in the Beilstein Handbook of Organic Chemistry. However, subsequent employment by the Colgate-Palmolive Company and the Atlas Powder Company, which I followed through its various name changes finally to ICI Americas, shifted my interest to surface-active materials. So I allowed this particular oxymoron to fall into disuse.

Although my research interests have changed, my fate seems to be involved in this problem. About 20 years ago, I was invited to participate in a study by a Bureau of Ships committee to consider the problem of the flammability of hydraulic fluids in submarines. Flammability, as anyone who has ever been inside a submarine knows, is an even greater hazard in a submarine than in aircraft. Nowhere in a submarine is one more than a few feet from a hydraulic line. In addition, one has the option of parachuting from an airplane, but the same option does not present itself in a submerged vessel. The committee met here in Washington, D.C. to consider the problem. Although the Navy's not unreasonable lack of interest in retrofitting the entire submarine fleet limited our options rather severely, a report was issued. As far as I know, none of the recommendations was ever implemented.

My final experience with this problem actually completed my tour of the military services, as well as resurrecting, at last, the oxymoron. I was called to join a committee at the U.S. Army Fuels & Lubricants Laboratory in San Antonio, Texas, to consider problems involving fuel fires in military vehicles. This is a substantial problem because many military vehicles, tanks and the Bradley vehicle, for example, are run by diesel engines where the fuel doubles as engine coolant. Thus, at any time there may be as many as 400 gallons of diesel fuel sloshing about the vehicle.

The Army also proved to be unwilling to retrofit, and other restrictions seriously reduced the possible solutions to the problem. Nonetheless, a report was issued. To the best of my knowledge, the recommendations for further study were not implemented.

It will be noted that I have qualified the results of my tour of the services by saying in each case, "to the best of my knowledge" or "as far as I know." The reason for the qualification is obviously the possibility of "military secrecy" (another oxymoron?). The fact that we are here today suggests, however, that no great measure of success has been achieved in the intervening years.

Now, to return to my principal theme: in what way can surface-active agents, new or old, contribute to progress in this area? The obvious answer is as stabilizers in multiphase systems. Some form of emulsion seems an obvious approach. The limitation that no water be included in the formulation has been imposed. It should be noted that hydrocarbon-water systems have been used extensively as fuels, notably in diesel engines. Generally, these have been water-in-oil systems and have been investigated with a view to reducing emissions and costs, rather than to reducing flammability. An interesting review of some research in this area was recently given by Thompson (Thompson, 1990). In addition, some work has been done on using oil-in-water emulsions as heating or power-plant fuel, namely using emulsions of heavy crude, as exemplified by Orimulsion fuel (Briceno et al., 1990; Marcano et al., 1991).

These studies reveal that fuel emulsions can indeed burn. Unfortunately, I have not been able to determine if studies on the *prevention* or *limitation* of burning have been carried out. I have identified a suggestive paper by Kitamura and coworkers dealing with water-in-oil emulsions (Kitamura et al, 1991). This paper suggests that the flash point decreases with increasing surface area per unit volume of the emulsion. Since the utility of the emulsion as a fuel depends on its ability to burn, it is obvious that this clue must be employed with some caution.

All of the papers I consulted in preparing this presentation on the use of surface-active agents have included very conventional surfactants in the formulations. This is not surprising because there are literally thousands of surface-active materials available to the investigator or formulator. The laws of thermodynamics being what they are, one may expect that all of these materials will act in pretty much the same way. For any given system, these thousands of surfactants may shrink to a few suitable ones. The methods of determining the appropriate ones are well known and are described in a number of places, including in my own work.

In conclusion, new approaches to this problem may be rather limited. Although it may be that no current product meets the needs of a new system subjected to, for example, environmental extremes, the synthesizer of new materials will be guided by the wealth of previous experience, as well as by the laws of thermodynamics.

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5

# Fire Safety in Military Aircraft Fuel Systems

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## INTRODUCTION

Because of the large quantity and dispersed storage of fuel on board aircraft, there is a high probability that aircraft accidents will involve fire in one way or another. The probability of fire is increased by the aircraft design requirement for lightweight structures for fuel containment. Fire could result from a fuel explosion in a fuel tank, fuel leakage into dry bays, cabin areas, cargo bays, or engine compartments, or from a fuel release on impact. Whether the fire or explosion is caused by the initial event or by a secondary cause, the result is often catastrophic.

One way to reduce the aircraft fire problem is to develop a fuel that is less susceptible to combustion in locations other than the engine. This is a challenging technical and economic goal, especially considering the requirements of aircraft operation and fuel availability. Candidate "fire-safe" fuels should have the availability, reasonable cost, and suitable physical and chemical properties for direct utilization in operational aircraft without extensive fuel system modifications or serious degradation of aircraft performance. Because of these stringent requirements, most of the successful efforts to reduce the aircraft fire hazard have been improvement in prevention and protection areas rather than development of fire-safe fuel. This paper uses the term fire-safe in the broad sense, i.e., any change in fuel that improves fire safety.

The Air Force's recent conversion from JP-4 (which has Jet B as its commercial equivalent) to JP-8 fuel is a step in the right direction from the standpoint of fire safety. Army aircraft use the same fuel as the Air Force. The Navy has used JP-5 fuel for many years for fire safety reasons. Properties of these military fuels and commercial fuels (Jet A and Jet A-1) are given in Table 5-1. The production of these fuels is illustrated in Figure 5-1 as a percentage obtained by simple distillation of an average crude oil. By using refinery techniques, such as hydrocracking, hydrotreating, and reforming, these percentages can be adjusted on demand. However, fewer added refinery costs are associated with converting heavy bottom fuels to high vapor pressure fuels (low flash point temperature) than vice versa.

The use of JP-5 and JP-8 was implemented to reduce the availability of fuel vapors for ignition and to reduce the amount of fuel vapor which could support a reaction. The use of antistatic additives in aircraft fuels (a specification requirement for JP-4 and JP-8 but not for Jet A or Jet A-1) is helpful for minimizing static as a potential ignition source. The lack of an antistatic additive may have been a contributing factor in the recent TWA 800 accident (17 July 1996). Other

TABLE 5-1 Comparison of the Properties of Aviation Fuels

|                          | JP-4               | JP-8               | Jet A-1 | Jet A   | JP-5               |
|--------------------------|--------------------|--------------------|---------|---------|--------------------|
| Minimum Flash Point, °F  | -20                | 100                | 100     | 100     | 100                |
| Maximum Freeze Point, °F | -72                | -53                | -53     | -40     | -51                |
| Lbs/gal                  | 6.3                | 6.7                | 6.7     | 6.8     | 6.8                |
| BTUs/gal                 | 118,900            | 124,500            | 124,500 | 125,700 | 126,000            |
| Vapor Pressure, psi      | 2-3                |                    |         |         |                    |
| Viscosity, cSt@-4°F      | 2.4                | 4.2                | 4.2     | 5.5     | 5.5                |
| Acid NR, mg KOH/g        | 0.015 <sup>a</sup> | 0.015 <sup>a</sup> | 0.1     | 0.1     | 0.015 <sup>a</sup> |

<sup>a</sup> Allow up to 0.022.

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attempts to make fuels more fire safe have included developing modified fuels, such as gels, emulsions, and antimisting kerosene (AMK). Tests on modified fuels have demonstrated potential reductions in ignition and flame propagation by the mists and sprays normally associated with "neat" fuels in the event of a crash landing and structural failure. All of the currently known modified fuels, however, have serious operational and logistical problems mainly associated with fuel transfer, storage, and engine performance. Many of the proposed solutions for these problems have inherent negative safety factors and present new design challenges. Needless to say, modified fuels have only been used in test programs and not operational service.

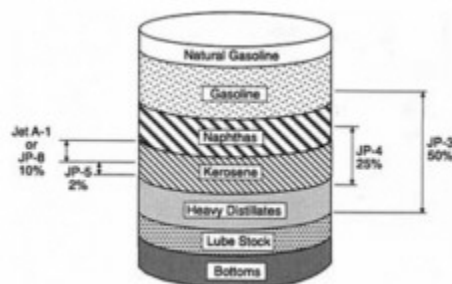


FIGURE 5-1 Availability of distillate fuels.

The search for a less hazardous fuel has taken two fundamental approaches. The first entails reducing the availability of fuel vapors for ignition and limiting their availability for feeding the combustion process. This may be accomplished by increasing the flash point temperature of the fuel (lowering the vapor pressure), a fuel property that can be easily measured. Fuels with a wide range of flash point temperatures are currently available. Gasoline has a flash point temperature of about -60°F, whereas aviation jet fuels have flash points in the 100<sup>l</sup> to 150°F range (with the exception of JP-4 [Jet B] which has a flash point near 0°F). Unfortunately, increasing the flash point temperature of a fuel has negative operational and performance effects, such as increased viscosity, increased freeze point temperature, and problems with engine starting and engine relight at altitude. These problems can be minimized by refinery techniques and design or procedural changes with some increase in fuel cost and operational inconvenience.

The second approach to the search for fire-safe fuel involves modifying the fuel to reduce the ignition and flame propagation of mists and sprays normally associated with neat fuels in a crash situation. This approach has few fire safety benefits for neat fuels with high vapor pressures, i.e., for low flash point fuels (Gandee and Clodfelter, 1974). This is one reason the Air Force showed limited interest in the many modified fuel programs that were being conducted in the U.S. and United Kingdom in the 1960s, 1970s, and into the 1980s. The Air Force was using JP-4, a high vapor pressure fuel, during this time and had many other concerns to address associated with their planned conversion from JP-4 to JP-8. This conversion was completed, at all but a few locations, in 1995. Since the changeover to JP-8 fuel, the Air Force and commercial airlines are using fuel with the same vapor pressure. The Air Force fuel (JP-8), however, contains several additives, some of which are not required in the commercial fuel (Jet A and Jet A-1). See Table 5-2.

Based on the experience of the Air Force during their conversion to JP-8, operational fuel changes are very complex and time-consuming in addition to being expensive. In 1967, when the Air Force initiated efforts to evaluate the combat benefits of JP-8, commercial airlines had more than 15 years of operational experience with Jet A and Jet A-1, the commercial equivalent of JP-8. Even with this long-term experience, the first JP-8 conversions at NATO bases didn't occur until 1978.

A study team of the Coordinating Research Council (CRC) reviewed the JP-8 (Jet A and Jet A-1) and JP-4 (Jet B) accident experience from 1952 to 1974 (CRC, 1975). The study team reported that:

TABLE 5-2 Characteristics of Current Military Fuel Additives

| Fuel Additive                            | Comments   |
|--|--|
| Antioxidants                             | Reduces or prevents formation of gums and peroxides<br>Key ingredient in JP-8+100  |
| Metal Deactivator                        | Deactivates trace metals<br>Maintains thermal oxidate stability  |
| Corrosion Inhibitors/Lubricity Enhancers | Originally required to protect pipelines<br>Removal from fuel caused significant wear problems<br>Minimum adjusted to protect F-111<br>NATO, ASCC investigating potential of lowering minimums   |
| FSII                                     | Water in fuel caused crashes<br>Prevents biological growth   |
| Static Dissipator                        | Allows A/C and ground storage sumps to be drained in winter<br>1960s USAF experienced 1 or 2 static-initiated fires per year<br>Rash of fires when A/C equipped with foam<br>A/C currently equipped with conductive foam<br>With conversion to JP-8, need to continue is being evaluated |

Source: Personal communication from C.L. Delaney and W.E. Harrison III, USAF Wright Laboratories, November 1996.



- In 200 survivable accidents with spilled fuel that were reviewed, there were 7 to 19 percent fewer fires with JP-8 than with JP-4 at the 95 percent confidence level.
- In 13 in-flight accidents involving fuel releases or fuel tank explosions that were studied, there were more fires with JP-4 (100 percent) than with JP-8 (44 percent).
- Ground accidents with JP-4 resulted in more aircraft destroyed (78 percent) than ground accidents with JP-8 (0 percent). 13 events were analyzed.

Even after these CRC fire-safety results had been released, and combat benefits of using JP-8 had been identified (Beery et al, 1975), the Air Force conversion was not completed until 1995. Considering that fire-safe fuel has greater pay offs in terms of flight safety and combat survivability for the military than for commercial aviation, and considering that the military uses only one-tenth of the fuel used by U.S. airlines (see Figure 5-2), the fuel change of this type should have been easier to justify and less difficult to implement for the military than for commercial aviation. The total time for the military's conversion to JP-8 was 28 years. The number of aircraft involved in commercial aviation, combined with the number of airports and airlines and their associated infrastructures, suggest that a commercial fuel change would involve a significant phase-in time. Operational compatibility between the old and new fuels will therefore be essential.

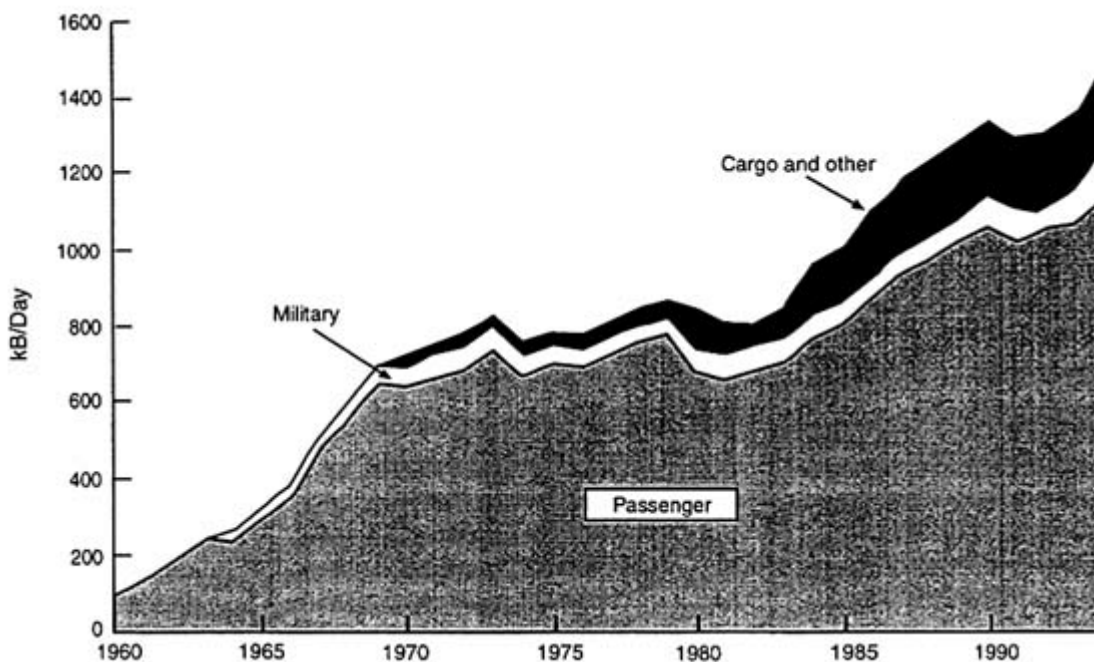


FIGURE 5-2 Demand for kerosene jet fuel in the United States.

Source: Personal communication from C.L. Delaney and W.E. Harrison III, USAF Wright Laboratories, November 1996.

Despite these concerns, it is appropriate to address periodically opportunities for the development of a fire-safe fuel. Technical people tend to be optimistic about achieving the short-term goals but pessimistic about the long-term possibilities. It is possible that an AMK-type fire-safe fuel could be developed in the distant future. Against this backdrop, a brief discussion of jet fuels, fuel flammability, the fire problem (including fire prevention and protection techniques), cost/benefit analysis, and future aircraft trends follows.

### JET FUELS

Jet fuels in the United States have been evolving since the 1940s (Martel, 1987). JP-1, the first jet fuel specified in the United States (1944), was a kerosene with a freeze point temperature of  $-77^{\circ}\text{F}$  and a minimum flash point temperature of  $109^{\circ}\text{F}$ . The availability of JP-1 was limited to about 3 percent of the average crude oil. JP-2 (1945) was an experimental fuel that was found to be unsuitable because of its viscosity and flammability.

JP-3 (1947 to 1951), the second operational fuel, had a high vapor pressure similar to aviation gasoline. Because of its high vapor pressure and because jet aircraft tend to fly at higher altitudes than reciprocating engine-powered aircraft, losses from fuel boil-off and vapor lock were problems.

JP-4 fuel (1951 to 1995), also designated as NATO F-40 and Jet B, a blend of gasoline and kerosene with a Reid vapor pressure restriction of 2 to 3 psi has fewer problems with boil-off and vapor lock. JP-4 has a freeze point of  $-77^{\circ}\text{F}$  and a flash point temperature of about  $0^{\circ}\text{F}$  (not a specification requirement). JP-4 was the primary jet fuel used by the U.S.



Air Force from 1951 to 1995. In the mid 1980s an antistatic additive was added to JP-4 for fire-safety reasons.

JP-5 fuel (1952 to the present), also called NATO F-44, has a 140°F minimum flash point temperature. This kerosene fuel is currently the primary fuel used by the U.S. Navy and was developed mainly in response to fire-safety concerns on ships. JP-5 fuel has a freeze point temperature of -51°F and does not contain an antistatic additive.

JPTS (1956), developed for the U-2, is a highly refined kerosene with a low freeze point of -64°F and a thermal stability additive package (CJFA-5). Its minimum flash point temperature is 109°F.

JP-6 (1956), developed for the XB-70, is similar to JP-5 but has a lower freeze point (-66°F) and more thermal stability. The flash point temperature is not a specification requirement. JP-7 (1960s), developed for the SR-71, has a low vapor pressure and excellent thermal stability for high altitude and mach 3+ operations. It has a freeze point of -47°F and a minimum flash point temperature of 140°F.

Jet A and Jet A-1 (1950s to the present) are the two fuels used by commercial airlines. Both fuels have a 100°F minimum flash point temperature for fire-safety reasons. Jet A has a freeze point of -40°F and Jet A-1 has a freeze point of -53°F. Because of its lower freezepoint, Jet A is more widely available and is, therefore, more widely used. Commercial fuels in the United States are not required to contain antistatic additives and generally do not.

Finally, JP-8, also known as NATO F-34, was first introduced at NATO bases in 1978 and is currently the primary fuel used by the U.S. Air Force. JP-8 is very similar to Jet A-1, but it contains an icing inhibitor, a corrosion/lubricity enhancer, and an antistatic additive (see Table 5-2). The U.S. Air Force conversion to JP-8 was virtually complete in 1995 and was undertaken for fire-safety and combat survivability reasons.

### FUEL FLAMMABILITY

The classic fire pyramid or fire tetrahedron (shown in Figure 5-3) illustrates the four elements necessary for a sustained hydrocarbon fire: heat for ignition, fuel, oxygen, and free radicals. The first three elements must be in the proper range and state for ignition and chain branching reactions must occur to maintain the reaction process. The first three elements must also be available in the proper balance for a sufficient period of time for ignition to occur. The required time increases near the flammability and ignition energy limits. All fire prevention, fire protection, or fire-safe fuel must negate at least one of these elements in some way. By this criterion, the two basic fuel properties used for first order assessments of a fuel's hazardous nature were established.

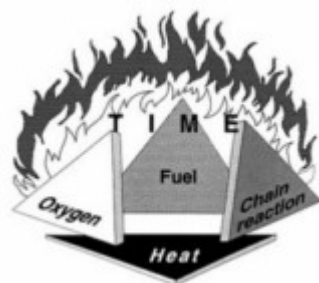


FIGURE 5-3 The fire pyramid.

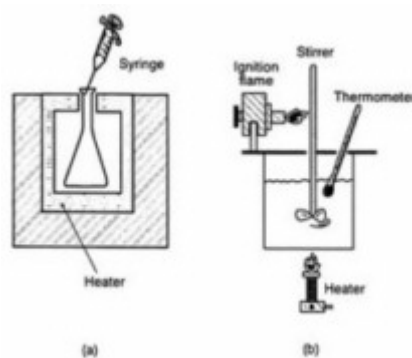


FIGURE 5-4 Autoignition temperature (AIT) and flash point temperature measurement apparatus.

The first and most important fuel property in many fire-safety scenarios is flash point temperature. Figure 5-4 is a simplified sketch of the equipment used to determine the flash point temperature of a fuel. The test fuel is placed in a container, the liquid fuel is slowly and uniformly heated and its temperature monitored. Periodically, as the temperature is increased, a large ignition source is inserted into the fuel container, until the lowest temperature at which a flash occurs is identified. This temperature is called the flash point and is

a measure of the availability of fuel vapors for ignition. In relation to the fire pyramid, the flash point temperature is a good estimate of the minimum fuel-air ratio necessary for ignition. The flash point temperature is close to, but slightly higher (5 to 10°F) than, the lower flammability limit. The flash point test involves downward flame propagation whereas the lower flammability limit test involves upward flame propagation. Because upward flame propagation is easier to achieve than downward flame propagation, it requires fewer fuel vapors at a lower temperature.

The apparatus used to determine the minimum autoignition temperature (AIT), or spontaneous ignition temperature, of a fuel is also illustrated in Figure 5-4. A 500-ml flask is slowly and uniformly heated. At a known temperature, a small amount of fuel is injected. This is followed by a 10-minute period during which any flash or light emitted from the flask is noted. This procedure is repeated a number of times with varying amounts of injected fuel at various temperatures to determine the lowest temperature at which an indication of ignition is observed.

In terms of the fire pyramid, the AIT of a fuel can be viewed as the lower limit at which a hot surface can cause ignition. Unfortunately from a fire-safety point of view, these two properties (flash point temperature and AIT) relate to each other in different directions for most fuels. For example, aviation gasoline (Grade-100) has a flash point temperature of -50°F (bad) and an AIT of 824°F (good). JP-8 has a flash point temperature of 100°F (good) and an AIT of 435°F (bad). In most real world situations, however, JP-8 is considered much less hazardous than aviation gasoline (see Figure 5-5 for the fuel hazard classification used by the National Fire Protection Association [NFPA] and in the Hazardous Substances Act). The relative fire hazard of a fuel can be better estimated from the flash point temperature than the AIT. However, many fuel combustion characteristics must be evaluated under real world conditions and then assessed against operational problems to evaluate potential fire hazard benefits as a function of fuel properties.

Can the number of aviation fatalities and injuries be reduced in a cost-effective manner by using a fuel with a higher flash point temperature, a lower probability of ignition in a crash situation, or some combination of other fuel properties? A commercial aviation switch to a higher flash point fuel (similar to JP-5) seems possible with reasonable effort and would result in some fire-safety benefits. An AMK-type fuel may have more potential fire-safety benefits, but a conversion of operational aircraft may be impractical in the final analysis. Before a conversion is initiated, detailed study of the aircraft fire problem covering these two fire-safe fuel approaches and their potential operational problems must be done.

Some fuel characteristics that should be assessed when evaluating the fire-safety benefits of a fuel are:

- volatility/atomization
- flash point
- autoignition temperature (AIT)
- flame spread rate over a pool
- burning velocity (vapor-air mixture)
- fuel-air mixture, including equilibrium and nonequilibrium (venting, sloshing, vibration, spray, mists, foams) conditions
- electrical characteristics (static accumulation)
- extinguishing characteristics

Some environments that should be considered when assessing the fire-safety benefits of a fuel are:

| NFPA 321 Classification                    | Hazard Level      | Hazardous Substances Act Classification |
|--|-------------------|---|
| Combustible<br>Classes II and III<br>100°F | Less<br>Hazardous | 150°F<br>Combustible                    |
|  |                   | 100°F<br>Flammable                      |
| Flammable<br>Class I                       | More<br>Hazardous | 20°F<br>Extremely<br>Flammable          |

FIGURE 5-5  
 Flammable liquids classification from the National Fire Protection Association (NFPA) and Hazardous Substances Act as related to flash point.

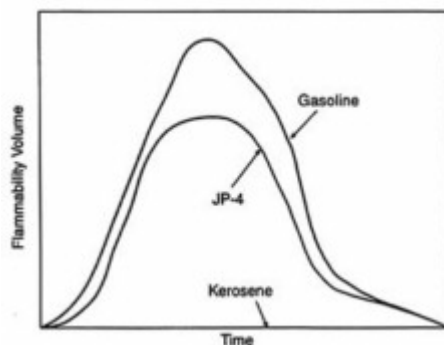


FIGURE 5-6 Rate of flammability volume buildup.

- in-flight operations
- ground operations
- combat threats (projectiles, fragments, high explosive incendiary, etc.)
- terrorist activities

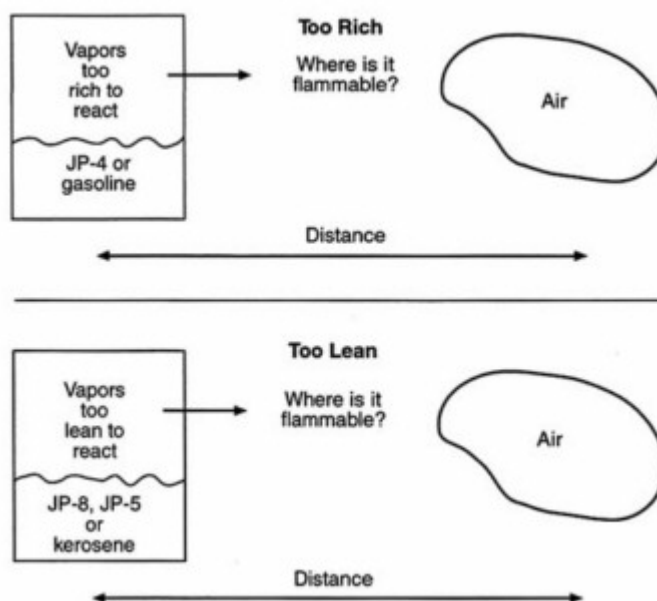


FIGURE 5-7 Flammable zone between leaking fuel-rich vapors and ambient air.

Figure 5-6 illustrates the relative rate of fuel-vapor generation and the flammability volume associated with a fuel spill at ambient conditions for kerosene, JP-4, and gasoline. Fuels with a flash point temperature above the ambient temperature have no flammable zone. Figure 5-7 illustrates the flammable zone between a leaking fuel rich mixture and ambient air. Leaking fuels with a flash point temperature above the ambient temperature have no flammable zone, assuming that no sprays or mists are present. Flammable regions for JP-4 under equilibrium conditions are shown in Figure 5-8, including the important flammable zone below the flash point temperature when sprays and mists may be present. The rates of flame spread across a spill of JP-4, JP-8, and JP-5 are shown in Figure 8. The flame spread rate is strongly dependent on flash point temperature. The flammability properties of several common aircraft fluids are given in Table 5-3, where the safe hot surface temperature is the temperature at which the probability of ignition is about  $10^{-3}$  (Clodfelter, 1990).

### THE FIRE PROBLEM

The general fire problem is the same for military and commercial aircraft, except for the combat threat to military

aircraft (the projectile threat is illustrated in Figure 5-10). Some fire prevention, detection, and control measures are given in Table 5-4. In addition to the measures in Table 5-4, several active and passive fuel system and dry bay fire protection techniques have been studied over the years. Some of these techniques are listed below:

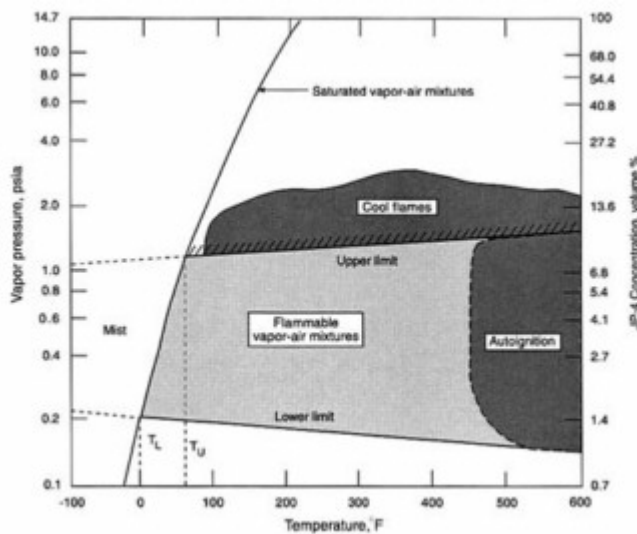


FIGURE 5-8 Flammable regions for JP-4.

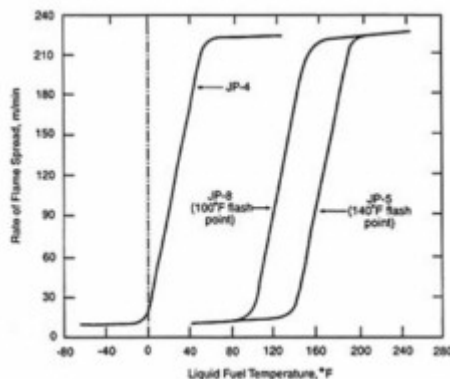


FIGURE 5-9 Flame spread across a jet fuel spill.

- flame arrestor foam
- inerting (nitrogen enriched air [NEA], N<sub>2</sub>, CO<sub>2</sub>, halon 1301 [CF<sub>3</sub>Br]) systems
- explosion suppression systems
- self sealing fuel tanks
- crash resistance fuel tanks
- dry bay protection (void filler materials, extinguishing systems, purge mats, powder packs)
- fire proofing, fire resistance, fire hardening
- gelled/emulsified fuels
- antimisting kerosene (AMK)
- fuel fogging

All but the last three protection techniques have been successfully used on operational aircraft. Flame arrestor foams have been used very successfully on many military fighter aircraft to prevent fuel tank explosions. Inerting systems are currently used to protect the fuel tanks of SR-71, C-5, OV-22, C-17, AH-64, and F-22 aircraft. As a result of the recent TWA 800 accident, fuel tank inerting systems will be conscientiously reconsidered for commercial aircraft.

### COST/BENEFIT ANALYSIS

Changing fuels or adding fire protection hardware to an aircraft will require cost/benefit analysis prior to approval and

funding. A cost/benefit analysis for specific protection techniques may also include similar cost/benefit analyses for other prevention/protection techniques that may achieve the same safety goal. Some of the effects of fuel properties on aircraft operations/performance and fire safety are shown in Table 5-5. Unfortunately, in many cases, the fuel characteristics desired for optimal operation are different from those desired for optimal fire safety.

TABLE 5-3 Flammability Properties of Aircraft Fluids

|  | Fuels           |                            |      | Hydraulic     |                | Lubricants    |
|--|-----------------|----------------------------|------|---------------|----------------|---------------|
|  | JP-4<br>(Jet B) | JP-8<br>(Jet A,<br>Jet A1) | JP-5 | Mil-H<br>5606 | MIL-H<br>83282 | MIL-L<br>7808 |
| Flash Point (°F)                                   | -10 to 10       | 100                        | 140  | 210           | 435            | 425           |
| Auto Ignition Temperature (°F)                     | 445             | 435                        | 435  | 435           | 650            | 750           |
| Lower Flammability Limit (vol pct)                 | 1.3             | 0.6                        | 0.6  | 1.2           | 1.4            |               |
| Upper Flammability Limit (vol pct)                 | 8.2             | 4.7                        | 4.5  | 7.1           | 7.7            |               |
| Hot Surface Ignition <sup>a</sup> Temperature (°F) | 840             | 820                        | 820  | 625           | 675            | 915           |
| Safe Hot Surface <sup>b</sup> Temperature (°F)     | 690             | 670                        | 670  | 475           | 525            | 765           |

<sup>a</sup> Minimum based on six different references.

<sup>b</sup> For bleed air ducts and fluids at ambient temperature.

The factors in Table 5-5 should be included in any decision regarding a fuel change. In addition, a minimum number of operational factors regarding aircraft performance should be addressed. These include:

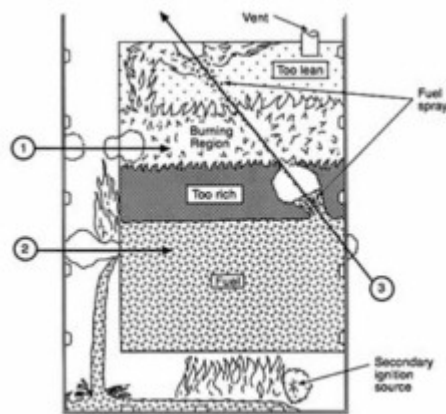


FIGURE 5-10 Fire problem associated with projectiles piercing the fuel tank.

- cold engine starting (viscosity at low temperature, fouling/coking)
- engine relight envelope (viscosity, vapor pressure, fouling/coking)
- engine control anomalies (fouling/coking)
- augmentor performance
- engine maintenance (fouling/coking)
- fuel transfer (viscosity, freeze temperature, vapor pressure)
- fuel system maintenance
- range (BTU density)

The following economic factors (at a minimum) should be considered:

- price per gallon
- ground handling (storage, transfer, special procedures and equipment)

The following strategic factors regarding fuel availability should be considered:

- local
- worldwide
- interchangeability

The following safety factors should be considered:

- ground handling (storage, transfer)
- combat (fuel tanks, dry bays, weapons bays, engine compartments)
- flight safety (fuel tanks, dry bays, engine compartments)
- safety hazards

TABLE 5-4 Fire Prevention, Fire Detection, and Fire Control Techniques (MIL-F-87168)

| Aircraft Fire Safety Goals           | Techniques  |
|--------------------------------------|---|
| Fire and Explosion Hazard Prevention | Combustible material hazard reduction<br>Subsystem hazard reduction<br>Isolation<br>Separation<br>Ventilation<br>Cooling<br>Drainage<br>Electrical Bonding and Lightning Protection<br>Post crash fire prevention   |
| Fire and Explosion Hazard Detection  | Detection system location<br>Performance<br>Alarm output<br>alarm set point and clearance   |
| Fire and Explosion Hazard Control    | Control adjacent area hazards<br>Fluid control<br>Ventilation termination<br>Electrical ignition source control<br>Fire barriers<br>Fire hardening<br>Smoke and hazardous vapor control<br>Overheat control<br>Fire extinguishing<br>Ground fire fighting |

Source: Department of Defense, 1992.

A cost/benefit analysis includes the cost of an item/system over its useful life compared to the benefits of the item/system during the same time period. The total cost or life cycle cost (LCC) of a system is the total cost at the end of its lifetime, including all expenses for research and development, production, modification, transportation, introduction of the item/system into the inventory, new facilities, training, performance, operations, support, maintenance, disposal, and any other costs of ownership penalties, less any salvage revenue at the end of its lifetime. LCC by itself is useful only when two or more competing items/systems provide the same total benefits or the same performance. On the other hand, the benefits of an item/system include performance enhancement, increased probability of mission completion, risk reduction benefits to personnel, equipment, facilities, products, lost revenue, and any other benefits during the ownership period.

TABLE 5-5 Effects of Fuel Properties on Aircraft Performance and Fire Safety

| Fuel Property      | Best for Operations | Best for Fire Safety |
|--------------------|---------------------|----------------------|
| Heat of Combustion | high                | low                  |
| Flash Point        | depends             | high                 |
| Viscosity          | low                 | high                 |
| Density            | high                |                      |
| Atomization        | high                | low                  |
| Vapor Pressure     | depends             | low                  |
| Freeze Point       | low                 |                      |
| Thermal Stability  | high                |                      |
| Resistivity        | unknown             | low                  |

The cost/benefit analysis involves determining the difference between prevention/protection system costs (LCC) and the benefits over a specific period of time, usually 20 years for aircraft systems. These costs and benefits will not occur in the same year. Therefore, all values must be converted to present value. For aircraft fire protection systems and fire-safe fuels, the parameters associated with a cost/benefit analysis are affected by the number and type of aircraft, the different types of air bases and airports affected, domestic vs. overseas operations, number of military and commercial aircraft affected, peace/war, sortie rate, flight hours, weight, volume, fuel costs, and performance factors.

### FUTURE TRENDS

Research and development of aircraft fire-safety should be compatible with current and future trends in aircraft design.



Higher performance aircraft and higher thermally efficient engines are a given for the future. Also, composite fuel tanks have the potential for more effective fuel containment on ground impact. Heat sink requirements will increase because of increased electronic equipment cooling, hotter engines, and associated thermal loads. Because engines will be more efficient, there will be less fuel flow to the engines for cooling; therefore, more hot fuel will be recirculated to the fuel tanks.

The overall effects of these trends will be higher fuel system temperatures and higher engine surface temperatures. The upper limit for the fuel temperature at the engine combustor nozzles is about 325°F for current fuels. The Air Force is currently conducting operational tests on JP-8 fuel with antioxidant additives (personal communication with C.L. Delaney and W.E. Harrison III, USAF Wright Laboratories, November 1996). This test fuel is designated as JP-8+100. The "+100" denotes an increase in the upper limit for the fuel at the combustor nozzles from 325°F to 425°F. In terms of fire safety, these trends mean a higher probability of flammable mixtures in fuel tanks with the current fuels, a higher probability of hot surface ignition, a faster buildup of flammable zones, and larger flammable zones associated with fuel release into aircraft compartments or on the ground.

### SUMMARY

The search for a fire-safe fuel involves many complex operational issues and technical challenges. To be successful, a long-term commitment will be required. Given the always limited resources available to address safety concerns, the potential for the highest payoff, the greatest reduction in aircraft related deaths/injuries, must be determined in relation to the technical risks. It appears to this author that a switch to a higher flash point fuel similar to JP-5 is possible with reasonable effort and that this would result in some fire-safety benefits. An AMK-type fuel may have the potential for more fire-safety benefits, but a conversion to operational aircraft may be impractical in the final analysis. Fuel tank inerting and antistatic fuel additives may be the next big steps for improving the fire safety of commercial aircraft. In any case, a detailed study should be done of the aircraft fire problem and the two fire-safe fuel approaches and the potential operational problems of each before a fire-safe fuel program is initiated.

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## 6

# Rheology: Tools and Methods

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### INTRODUCTION

In this paper, we attempt to give the reader a basic understanding of rheology, a scientific discipline of great utility in characterizing complex, microstructured media. Rheology is formally defined as the study of deformation and flow behavior in various materials (Macosko, 1994). Since its humble origins in the 1920s in the laboratories of Eugene Bingham at Lehigh University, rheology has developed into a mature field of wide-ranging applicability.

Systems investigated using rheology can typically be classified as soft condensed matter or as complex fluids. Examples include macromolecular systems, such as polymer melts and solutions, gels, and biological fluids, as well as colloidal and multiphase systems, such as dispersions, emulsions, foams, and surfactant solutions. Typically, these materials are *viscoelastic*, i.e. they exhibit a combination of viscous and elastic properties. Such complex behavior cannot be characterized purely in terms of simple parameters, such as the material viscosity or elastic modulus.

One of the objectives of this paper is to indicate the possible applications of rheology towards designing improved aviation fuels. Although an aviation fuel typically behaves like a viscous liquid, the introduction of certain additives can cause the system to show a viscoelastic response (Hoyt et al., 1980). In that case, the rheology of the system becomes important, and rheological studies will be necessary for accurately modeling the flow in the aircraft engine. Moreover, it is possible that a controlled amount of viscoelasticity may prove to be beneficial to the overall performance of the aviation fuel. For instance, the addition of an "antimisting" component to the fuel can reduce the fire hazard in case of a fuel leak (Chao et al., 1984).

Our agenda for this paper is ambitious: we would like to cover the most important rheological principles, techniques, and methods, as well as indicate specific applications—all within about 20 pages. Clearly, we have to be very selective in the topics we choose to describe. Our focus will be on reviewing the material parameters obtained using rheology and the correlation of these parameters to material microstructure. In this context, the *microstructure* implies the spatial disposition of molecules, particles, or other entities in the system over length scales on the order of microns (Barnes, 1993). We will consider the three most common kinds of rheological techniques, viz. steady-shear rheology, dynamic rheology, and extensional rheology. We will then provide some specific examples for the applications of rheology to materials characterization and design. For the interested reader, we have supplied an extensive list of references for obtaining more detailed information on various aspects of rheology as well as on specialized rheological methods.

### VISCOELASTIC BEHAVIOR

The science of rheology attempts to bridge the gap between solid mechanics (which deals with perfectly elastic solids) and fluid mechanics (which deals with perfectly viscous liquids). Thus, the rheologist is typically interested in viscoelastic systems that exhibit a combination of elastic and viscous behavior. To understand viscoelasticity, it will be helpful to consider first the cases of perfect elasticity or viscosity, which can be interpreted in terms of simple relationships such as Hooke's law for solids and Newton's law for liquids, respectively. We will now consider these two laws and indicate their applicability, or lack thereof, for various materials.

Fundamental relationships linking force and material deformation are called constitutive equations (Bird et al., 1987). For an elastic solid, the *constitutive equation* is Hooke's law, which states that the applied shear-stress ( $\tau$ ) is proportional to the produced shear-strain ( $\gamma$ ) or alternately:

$$\tau = G\gamma \quad (1)$$

Here, the shear-stress ( $\tau$ ) is the shear force per unit area, and the strain ( $\gamma$ ) is defined as the relative change in length. The proportionality constant ( $G$ ) is called the shear modulus

and is an intrinsic property of an elastic solid. For Hookean solids when the stress is removed, the strain becomes zero and the material regains its original shape and structure. Thus, the elasticity of a material represents its ability to regain its shape and structure after deformation, i.e., to store deformation energy. Most metals and ceramics obey Hooke's law at small strains.

A similar constitutive equation exists for a viscous or Newtonian liquid. Newton's law of viscosity states that the shear stress ( $\tau$ ) is proportional to the rate of strain, or shear rate ( $\dot{\gamma}$ ).

$$\tau = \eta \dot{\gamma} \quad (2)$$

The proportionality constant ( $\eta$ ) is defined as the viscosity of the material. Thus, a Newtonian liquid will undergo a constant rate of deformation under an applied stress, and when the stress is removed it will remain in the shape and structure it has adopted. The viscosity of a material is a measure of its internal resistance to flow and reflects the rate at which energy is dissipated in the material. Many small-molecule liquids, such as water, honey, and various oils, obey Newton's law.

As we have indicated, there are several materials that obey these constitutive equations. These materials can be completely characterized by measuring the respective parameters,  $G$  or  $\eta$ . But in reality, many systems, such as colloids, polymers, and gels, do not obey these simple constitutive relations. Instead, these materials have properties between those of a Hookean solid and a Newtonian liquid and can be classified as non-Newtonian or viscoelastic. For these materials, the viscosity is a function of shear-rate and, hence, not constant, and the shear modulus has two components signifying elastic and viscous character respectively.

Many simple experiments can demonstrate viscoelastic or non-Newtonian behavior (Boger and Walters, 1993; Bird et al., 1987; Schramm, 1994). First, consider "silly putty," which is a poly(dimethyl siloxane) (PDMS) elastomer of moderate molecular weight. When a ball of silly putty is dropped onto a solid surface, it bounces back like a rubber ball, thereby behaving almost like an elastic solid. However, if the putty is placed on that same solid surface for some time, it will slowly flow under the stress of gravity, thus showing behavior characteristic of a highly viscous fluid. Therefore, silly putty can behave both like an elastic solid or a viscous liquid, depending on the time scale of the deformation.

A second example of non-Newtonian behavior is "rod climbing" (or the Weissenberg effect). When a vertical rod is rotated in a container of Newtonian fluid, such as water, the inertial forces acting on the fluid cause it to move away from the rod. This creates a situation where the fluid level at the rod is lower than the fluid level at the container walls (Figure 6-1a). If the same experiment is run in a container of polymeric fluid, the flow changes directions and moves toward the rod. This phenomenon is called rod climbing and is caused by the influence of normal stresses on flow properties (Figure 6-1b). These normal stresses create tension along the circular lines of flow and generate pressure toward the center, which drives the polymeric fluid up the rod.

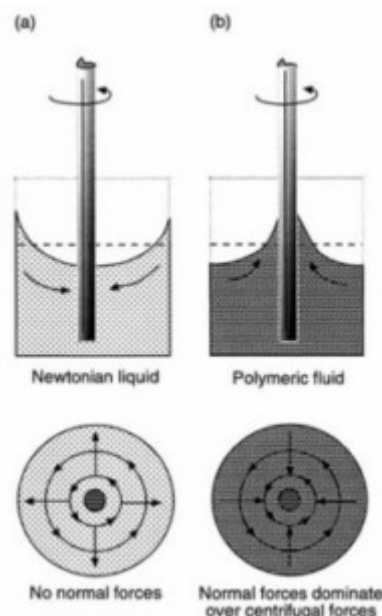


FIGURE 6-1 Rod climbing (Weissenberg effect). (a) In Newtonian fluids, centrifugal forces generated by the rotation push the fluid away from the rod. (b) In non-Newtonian fluids, normal forces are stronger than centrifugal forces and drive the fluid inward toward the rod.

Another dramatic illustration of viscoelastic effects is the "tubeless siphon" experiment. When a Newtonian liquid, such as water, is drained out of a container through a siphon, the tube must remain under the level of liquid in order for the liquid to continue to flow. However, a polymeric (non-Newtonian liquid) can continue to flow up and through the siphon even after the tube is raised above the liquid level (Figure 6-2). The fluid undergoes extensional flow (stretching) in this case, and the elastic nature of the polymeric fluid enables it to be extended upwards and sucked into the tube.

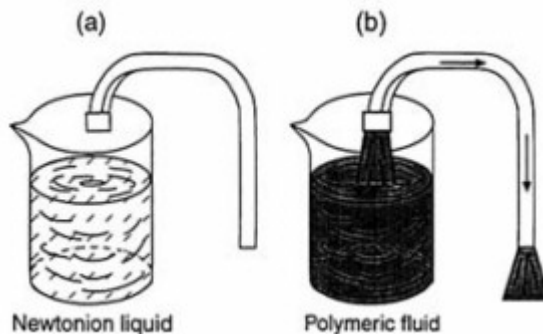


FIGURE 6-2 Tubeless siphon. (a) Newtonian fluid cannot be siphoned unless tube is below fluid level. (b) Normal stresses allow non-Newtonian fluid to be siphoned even when tube is above fluid level.

### STEADY-SHEAR RHEOLOGY

Simple steady-shear flow is the easiest flow to generate and is, therefore, of central importance in rheology. Most of the rheological data reported in the literature is for steady-shear material functions. Moreover, flows occurring in a number of industrial processes, such as extrusion or flow-through circular dies, approximate steady-shear flow.

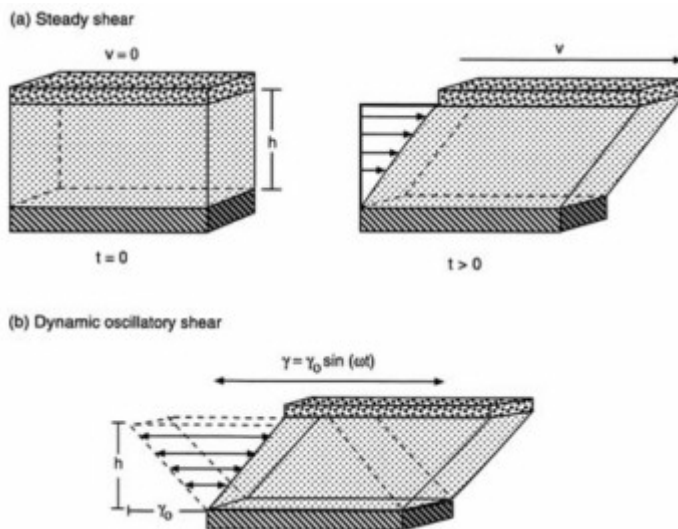


FIGURE 6-3 Two types of shear deformation. The arrows represent the velocity field in the fluid in each case. (a) Steady shear of a fluid between two parallel plates. At time  $t = 0$ , the system is at rest. At  $t > 0$ , the top plate is made to attain a constant velocity ( $v$ ). (b) Dynamic (oscillatory) shear of a fluid between parallel plates. The top plate moves in a sinusoidal fashion with a maximum strain amplitude ( $\gamma_0$ ).

We will try to provide a basic understanding of steady-shear flow (Bird et al., 1987). In Figure 6-3a, two parallel plates are shown, between which lies a generic fluid. Suppose that both plates are initially at rest with no flow occurring. At a time  $t = 0$ , the upper plate is made to instantaneously attain a constant velocity ( $v$ ). This results in the generation of a shear stress ( $\tau$ ) in the fluid from the cohesive forces between the fluid molecules. As the fluid flows, specific fluid elements (i.e., tiny packets of fluid that remain together at all times during the experiment) can be tracked as a function of time. It is easy to see that every fluid element will undergo the same strain, and that the local strain everywhere in the fluid will be equal to the overall shear strain. In the same way, the shear rate ( $\dot{\gamma}$ ) which is the rate of change of shear strain, can be shown to be constant throughout the fluid and equal to  $(v/h)$ . Thus, the shear rate applied on the system can be estimated from the velocity ( $v$ ) applied to the top plate and the distance ( $h$ ) between the plates.

From a steady-shear flow experiment, three material functions can be measured, viz. the viscosity ( $\eta$ ), and the first and second normal-stress coefficients ( $\psi_1$  and  $\psi_2$ ). Among these, the viscosity ( $\eta$ ) is the simplest and most important material

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function and can be calculated from the measured shear stress ( $\tau$ ), and the applied shear rate ( $\dot{\gamma}$ ) by:

$$\eta(\dot{\gamma}) = \frac{\tau(\dot{\gamma})}{\dot{\gamma}} \quad (3)$$

Note that this expression is analogous to Newton's law for simple liquids, with the caveat that the viscosity here (more properly termed the apparent viscosity) is a function of shear rate and not a constant parameter. The normal-stress coefficients ( $\psi_1$  and  $\psi_2$ ) are estimated in a similar manner by measuring the force per unit area exerted in directions normal to the direction of flow. However, they are much harder to measure accurately. The interested reader is referred to books by Ferry (1980) and Bird et al. (1987) for discussions of normal stresses.

Rheological experiments under steady shear are performed using "viscometric flows" that are indistinguishable from simple steady flow for all practical purposes (Dealy and Wissbrun, 1990). Thus, the three material functions that govern the behavior of the fluid ( $\eta$ ,  $\psi_1$ , and  $\psi_2$ ) can be obtained experimentally. Let us now examine some typical examples of material behavior under steady shear. We will focus on the most important material parameter, the steady-shear viscosity as a function of shear-rate,  $\eta(\dot{\gamma})$ . Four types of behavior can be distinguished: Newtonian, shearthinning, yield stress (followed usually by shear thinning), and shear thickening. The last three are all examples of non-Newtonian or viscoelastic behavior.

A plot of viscosity versus shear-rate or shear-stress is called a flow curve. It is common practice to plot the flow curve on a log-log plot as shown throughout Figure 6-4. The simplest type of steady-shear response is Newtonian behavior (Figure 6-4a), which implies a constant viscosity for the system, independent of shear rate. This is also manifested as a linear relationship between shear stress and shear rate (Newton's law), with the slope of the line defining the viscosity. Most low molecular-weight liquids and gases show Newtonian behavior.

Among non-Newtonian phenomena, the most widely observed is shear thinning, which implies a decrease in viscosity over a range of shear rates. This behavior is exhibited by most polymeric solutions and melts (Ferry, 1980), as well as by a large number of colloidal systems (Russel et al., 1989). In the simplest case, the sample shows Newtonian behavior at low shear rates and shear thinning at higher shear rates (Figure 6-4b). Thus, at low shear rates, the viscosity attains a constant value called the zero-shear viscosity ( $\eta_0$ ). However, as the shear rate is increased, there occurs a critical shear rate ( $\dot{\gamma}_c$ ), above which the viscosity of the sample decreases. Examples of shear thinning fluids include blood, saliva, various sauces, and creams.

Shear thinning sometimes occurs in conjunction with yield-stress behavior (Macosko, 1994). In this case, the system will not show any motion until a certain critical or yield stress ( $\tau_y$ ) is reached. Below the yield-stress, the viscosity of the material approaches infinity (Figure 6-4c), and the system responds in a plastic-like fashion. Above the yield stress, the material typically shows shear thinning. When viscosity is plotted versus shear rate, the existence of a yield stress is reflected as a characteristic slope of -1 in the low shear rate portion of the plot (Figure 6-4c). Some materials approximate Newtonian behavior beyond the yield stress, and these materials are called viscoplastics or Bingham plastics, after Eugene Bingham who first described paint this way in the 1920s. Materials that show a yield-stress appear to have a solid-like consistency when at rest, but when stirred or agitated, they can be made to flow quite easily. Food substances, such as mayonnaise, ketchup, and salad dressing, are good examples.

Modeling the steady-shear response has been a constant endeavor for rheologists. Several models have been formulated, particularly for shear thinning and yield-stress behavior. We will only mention two of the simplest and most convenient models. For shear thinning, the power-law model is most frequently used:

$$\eta(\dot{\gamma}) = K \dot{\gamma}^{n-1} \quad (4)$$

The model contains two parameters, the consistency ( $K$ ) and the power-law index ( $n$ ). A value of  $n = 1$  corresponds to Newtonian behavior; for shear thinning fluids  $n < 1$ . The simplest model that captures yield-stress behavior is the Bingham model used to describe viscoplastics:  $\dot{\gamma} = 0$  for  $\tau < \tau_y$ ,

$$\tau = \eta \dot{\gamma} + \tau_y \text{ for } \tau \geq \tau_y \quad (5)$$

This model allows no motion below the yield stress ( $\tau_y$ ) and Newtonian flow behavior above  $\tau_y$ . Numerous other models have been proposed for various shapes of flow curves, discussions of which can be found in Macosko (1994), Barnes (1993), and Larson (1988).

Shear thickening is a form of non-Newtonian behavior that is observed much less frequently (Barnes, 1989). As its name implies, shear thickening involves an increase in viscosity over a range of shear rates. This can be seen from Figure 6-4d, where the viscosity begins to increase at a critical shear rate,  $\dot{\gamma}_c$ , until it reaches a maximum value at a shear-rate,  $\dot{\gamma}_m$ , following which it begins to drop. The viscosity increase typically occurs over a narrow range of shear-rates. This is in contrast to shear thinning, where the viscosity can decrease continuously over several decades of shear rate. Shear thickening phenomena are observed in a few concentrated colloidal dispersions and some polymer solutions.

In the examples given above, the flow curves represent equilibrium or steady-state behavior. Some materials, however, take a long time to reach steady state at constant shear,

i.e., their viscosity shows a continuous change with time of shear. The time-dependent phenomenon where the viscosity continuously decreases with time of shear is called *thixotropy* (Mewis, 1979). Thixotropic materials may also take considerable time to return to an at-rest state after being subjected to intense shear. These phenomena are widely observed in paints, adhesives, sealants, etc.

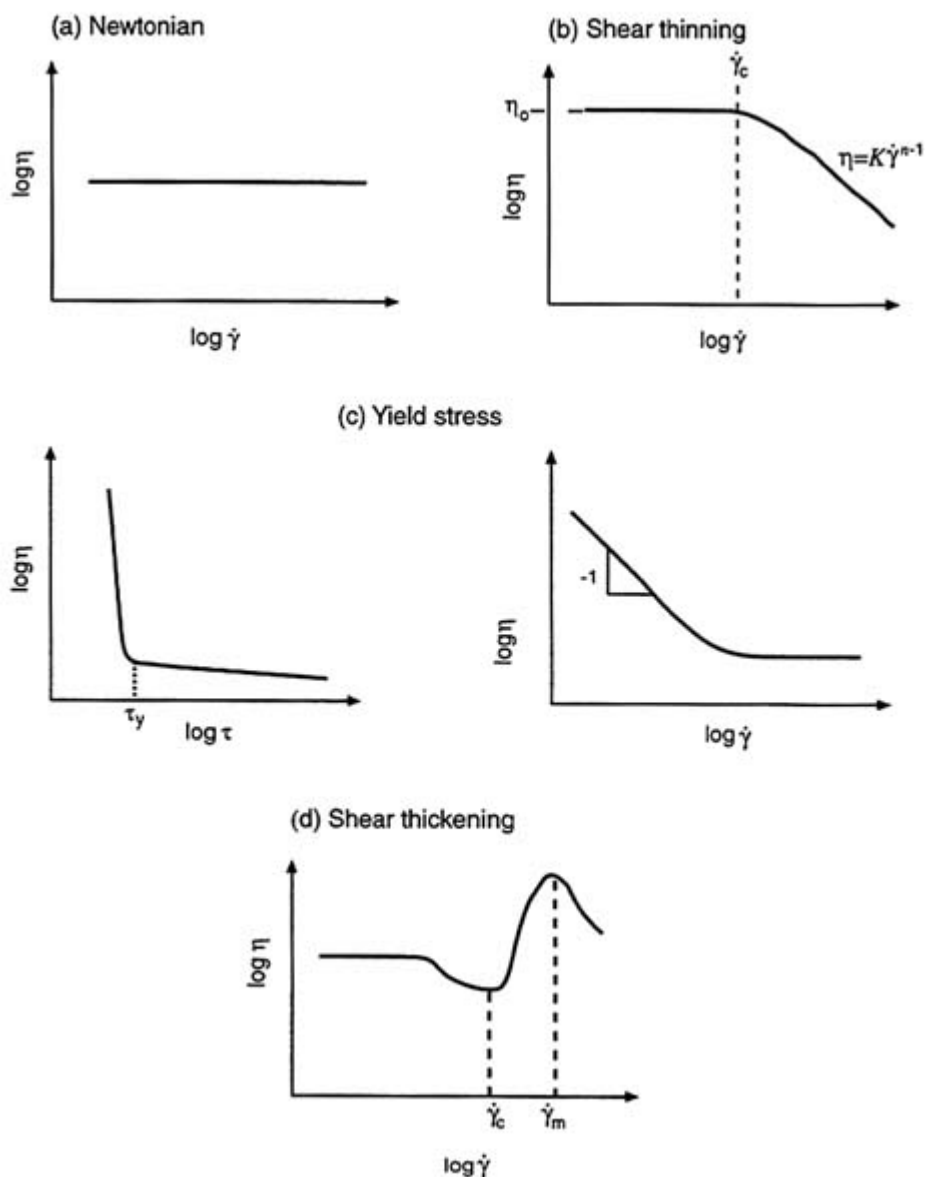


FIGURE 6-4 Examples of material behavior under steady shear (flow curves): (a) Newtonian; (b) shear thinning; (c) yield stress, shown in plots of viscosity vs. shear stress and shear rate; and (d) shear thickening.

All rheological behavior, whether time-dependent or related to changes in shear, arises from changes in the microstructure of the system. This aspect will be a recurring theme in this paper. For example, consider a colloidal dispersion that shows yield stress and shear thinning. Such behavior typically signifies the presence of a particulate network structure in the system at rest and the shear-induced breakdown of the network into individual particles. The correlation between rheology and microstructure can be better understood after we discuss dynamic rheology and the linear viscoelastic response of different materials.



## DYNAMIC RHEOLOGY

In dynamic shear flow (also called oscillatory shear), a sinusoidally varying deformation (strain) is applied to the sample (Ferry, 1980):

$$\gamma = \gamma_0 \sin(\omega t) \quad (6)$$

where  $\gamma_0$  is the strain-amplitude (i.e. the maximum applied deformation) and  $\omega$  is the frequency of the oscillations. Figure 6-3b is a schematic representation of dynamic shear flow, and this can be compared to Figure 6-3a, which shows steady shear flow. The shear stress generated by the oscillatory shear will again be sinusoidal but will be shifted by a phase angle ( $\delta$ ) with respect to the strain waveform:

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (7)$$

Using trigonometric identities, the stress wave can be decomposed into two components, one in-phase with the strain and the other out-of-phase by 90 degrees:

$$\tau = \tau_0 \cos(\delta) \sin(\omega t) + \tau_0 \sin(\delta) \cos(\omega t) \quad (8)$$

We can rewrite the above expression in terms of two material functions ( $G'$  and  $G''$ ):

$$\tau = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)] \quad (9)$$

$$\text{Elastic or storage modulus, } G' = \left(\frac{\tau_0}{\gamma_0}\right) \cos\delta \quad (10)$$

$$\text{Viscous or loss modulus, } G'' = \left(\frac{\tau_0}{\gamma_0}\right) \sin\delta \quad (11)$$

The elastic modulus ( $G'$ ), which is related to the stress in phase with the imposed strain, provides information about the elastic nature of the material. Because elastic behavior implies the storage of deformational energy in the system, this parameter is also called the storage modulus. The viscous modulus ( $G''$ ), on the other hand, is related to the stress component, which is completely out-of-phase with the displacement. This parameter characterizes the viscous nature of the material. Note that the out-of-phase component of the stress would be in phase with the sinusoidal deformation rate ( $\dot{\gamma}$ ). Because viscous deformation results in the dissipation of energy, the  $G''$  parameter is also called the loss modulus.

A purely elastic material would exhibit a non-zero elastic modulus and a viscous modulus  $G'' = 0$ . In contrast, a purely viscous material would show a zero elastic modulus, and its stress response would be 90 degrees out-of-phase with the strain ( $\gamma$ ) and in-phase with the shear rate ( $\dot{\gamma}$ ). A viscoelastic material will exhibit non-zero values for both  $G'$  and  $G''$ . The above analysis assumes that the measurements are made in the "linear viscoelastic" (LVE) regime of the sample under consideration (Ferry, 1980). The conditions for linear viscoelasticity are that the stress be linearly proportional to the imposed strain and that the torque response involve only the first harmonic. The first condition requires that the moduli  $G'$  and  $G''$ , in the LVE regime, should be independent of the strain-amplitude. The absence of higher harmonics in the stress response, as stipulated in the second condition, ensures that the response remains sinusoidal.

If these two conditions are met, the elastic and viscous moduli would truly be material functions. They would, however, be functions of the frequency of oscillation ( $\omega$ ). A plot representing the moduli as a function of frequency, i.e.,  $G'(\omega)$  and  $G''(\omega)$ , is called the dynamic mechanical spectrum of the material. Such a plot is extremely useful because it represents a signature of the microstructure in the material. We can also define several auxiliary parameters based on the quantities derived above (Ferry, 1980). One such parameter is the complex viscosity ( $\eta^*$ ), which is defined as:

$$\eta^* = \left[ \left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2 \right]^{1/2} \quad (12)$$

The variation of complex viscosity with frequency is analogous to the variation of steady viscosity versus shear-rate. (Note that both frequency and shear-rate have units of  $s^{-1}$ ). Empirical correlation rules between the steady and complex viscosities, indicate a link between steady and dynamic rheology (Cox and Merz, 1958; Doraiswamy et al., 1991; Raghavan and Khan, 1997).

The two dynamic moduli  $G'$  and  $G''$  represent a clear distinction between elastic and viscous behavior in the same material. This helps to clarify the viscoelastic nature of a given sample. A simple model that captures the essential features of linear viscoelastic behavior is the Maxwell model, originally proposed by James Clerk Maxwell in 1867. In this model (shown in Figure 6-5), a viscoelastic sample is assumed to have two distinct elements: an elastic spring and a viscous dashpot connected in series (Macosko, 1994). The elastic spring has a shear-modulus ( $G_0$ ), and the viscous component has a viscosity ( $\eta_0$ ).

A characteristic parameter of a viscoelastic system is its *relaxation time* ( $\lambda$ ), which in the case of the Maxwell model is equal to  $\eta_0/G_0$ . The relaxation time is a measure of the time required for stresses to relax in a viscoelastic material. Recall that under deformation, the stresses relax instantaneously for a viscous liquid; they never relax for an elastic solid. The Maxwell model is useful for simple viscoelastic systems, such as polymer solutions or melts, which exhibit a single relaxation time. We should mention that there are specific experiments to probe relaxation behavior, e.g., stress relaxation after a step strain, creep at constant stress, etc. A discussion of these experiments falls beyond the scope of this paper; details can be found in Bird et al. (1987), Ferry (1980) and Macosko (1994).

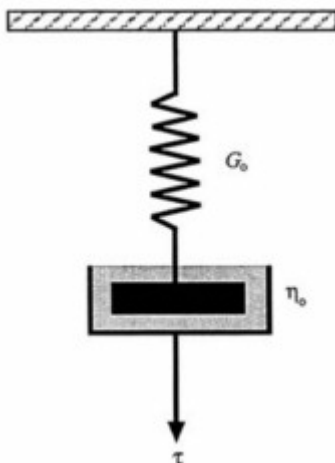


FIGURE 6-5 Maxwell model for a viscoelastic material. The system is considered to be a series combination of two distinct segments: an elastic spring (modulus  $G_0$ ) and a viscous dashpot (viscosity  $\eta_0$ ).

Perhaps the most important advantage of dynamic shear is that *it allows us to characterize microstructures without disrupting them in the process*. The net deformation imposed on the sample is minimal because the experiments are restricted to small deformations (strain amplitudes) within the LVE regime of the sample. As a result, the linear viscoelastic moduli reflect the microstructures present in the sample at rest. This is to be contrasted with steady shear, where the material functions are always obtained under flow conditions that correspond to relatively drastic deformations. Consequently, the microstructure under steady flow will be very different from the microstructure under static conditions. We can, therefore, correlate dynamic rheology to static microstructures and steady rheology to changes in microstructure caused by flow.

We will now illustrate the types of responses seen in dynamic frequency spectra, and furthermore, the correlation of these responses with material microstructure. We will also point out the steady-shear rheological behavior corresponding to these microstructures. Two classes of materials will be considered, colloidal dispersions and polymer melts. Colloidal dispersions are obtained by dispersing solid, colloidal-sized particles in a liquid (which, for simplicity, is assumed to be a purely viscous medium). The extent to which the particles flocculate depends on the strength of colloidal interaction forces between them (Russel et al., 1989). Various microstructures are thus possible, as illustrated in Figure 6-6.

In the simplest dispersions, inter-particle forces are negligible, i.e., each particle is discrete and does not "feel" the presence of its neighbors. These are classified as "non-flocculated" or stabilized dispersions. The typical dynamic rheological response of these systems (Figure 6-6a) consists of a dominant viscous modulus ( $G''$ ) which exceeds the elastic modulus ( $G'$ ) over the complete range of experimental frequencies (Macosko, 1994). The slopes of the  $G' \rightarrow \infty$  and  $G'' \rightarrow \infty$  lines are often close to 2 and 1 respectively (note that frequency spectra are typically plotted in a log-log fashion as were the steady-shear flow curves). Under steady flow, the zero-shear viscosity of these dispersions will be relatively low, and the systems will show Newtonian or shear thickening behavior. (The concentration of solid particles has to be very high for shear thickening to occur). Note that the addition of colloidal particles always leads to an increase in viscosity over the pure liquid, but only a moderate increase is observed if the particles are non-interacting.

If the inter-particle forces are fairly strong, there will be a tendency for the particles to adhere to one another and form larger structures called aggregates or flocs (Mewis and Spaul, 1976). A flocculated microstructure is shown in Figure 6-6b along with its characteristic frequency spectrum. Note that  $G'$  becomes larger than  $G''$  at high frequencies but remains smaller at low frequencies. Both quantities show a weaker dependence on frequency, with lower slopes in the terminal zone (as compared to Figure 6-6a). Thus, dynamic rheology shows the viscoelastic nature of these systems as they exhibit comparable elastic and viscous character. The viscosity of a flocculated dispersion greatly exceeds the viscosity of a non-flocculated system. The steady-shear response is non-Newtonian and shear thinning, corresponding to the breakup of flocs into smaller and smaller units until they are reduced to individual particles.

Under conditions of strongly attractive inter-particle forces and high particle concentrations, flocculation of the system will be significant. Ultimately, the flocs will overlap with one another until a single floc fills the whole volume (Macosko, 1994). This corresponds to a situation where a three-dimensional network of particles extends throughout the system. A system containing a network-type microstructure is called a *gel*. The dynamic mechanical spectrum of a gel shows a frequency-independent elastic modulus ( $G'$ ) that greatly exceeds the viscous modulus ( $G''$ ) (Figure 6-6c). Thus, a gel behaves principally as an elastic material because of the presence of a continuous network. The level of elastic modulus ( $G'$ ) can be correlated to the rigidity (i.e., the density of cross-links) in the network. In steady shear, a gel will show a yield stress at low shear, followed by shear thinning at higher shear rates. The yield stress signifies that a minimum stress is required to disrupt the cross-links in the network. Shear thinning reflects the progressive reduction in floc size as a result of shear.



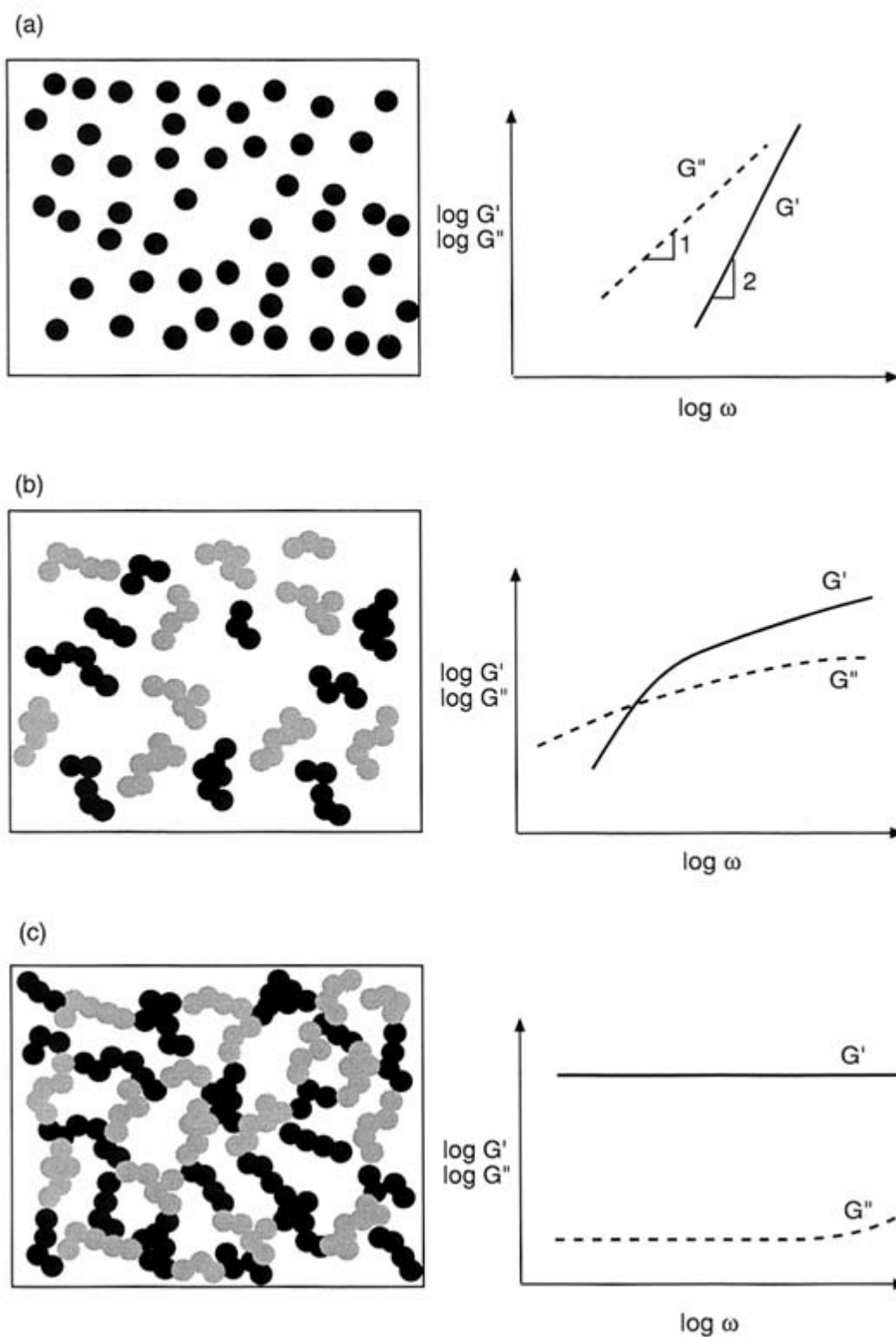


FIGURE 6-6 Dynamic rheology and microstructure of colloidal dispersions. In each case the frequency spectra ( $G'$  and  $G''$  as functions of frequency  $\omega$ ) are shown with their corresponding microstructure. (a) Stabilized dispersion. (b) Weakly flocculated dispersion. (c) Strongly flocculated dispersion (gel).

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We now consider the dynamic rheology of polymer melts over a range of molecular weights. This leads us to a consideration of "time-scales," a factor we largely ignored in the case of colloidal dispersions. Polymer melts can show very different behavior depending on the time-scales (or equivalently, the frequencies) probed in a rheological experiment (Dealy and Wissbrun, 1990). Note that low frequencies correspond to large time-scales and vice-versa. A typical rheological experiment may be conducted in the frequency range of  $10^{-2}$  to  $10^2$  rad/s, but data over a larger span of frequencies can be obtained by a procedure called time-temperature-superposition (TTS) (Ferry, 1980). This procedure utilizes the equivalence of time and temperature in the rheological context, i.e., dynamic rheological data obtained at higher temperatures is equivalent to data at longer time-scales (lower frequencies). Using TTS, we can generate data for a high molecular weight, monodisperse polymer melt over an extremely wide range of frequencies ( $10^{-5}$  to  $10^4$  rad/s), as illustrated schematically in Figure 6-7.

The plot shown in Figure 6-7 (note that both axes are on logarithmic scales) can be divided into three regions (Ferry, 1980). Region I corresponds to low frequencies (i.e., long time-scales) and is called the terminal region. It represents the frequency range that is experimentally accessible at any given temperature. We find that in the terminal zone both  $G'$  and  $G''$  increase steadily with frequency and the viscous modulus  $G''$  is larger than the elastic modulus  $G'$ . The relations  $G' \sim \omega^2$  and  $G'' \sim \omega$  are typically found to be valid in this region, leading to slopes of 2 and 1 respectively for the lines. In Region II, the moduli cross over at a critical frequency,  $\omega_c$ , and  $G'$  becomes greater than  $G''$ . The inverse of  $\omega_c$  corresponds to the longest relaxation time for the polymer melt. The curves also begin to flatten and  $G'$  plateaus off at a value given by  $G^N_0$  (plateau modulus). Finally, in Region III, the moduli again increase with frequency, although to a smaller extent than in the terminal zone.

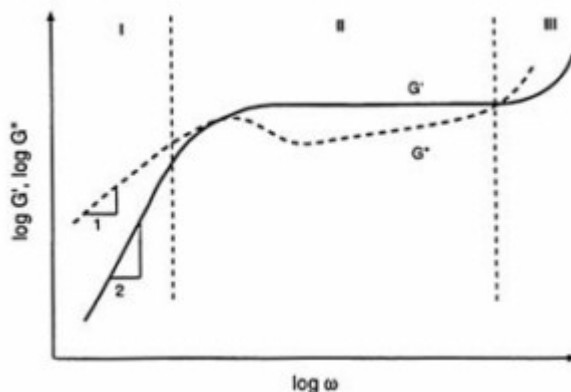


FIGURE 6-7 Dynamic mechanical spectrum ( $G'$  and  $G''$  as functions of frequency  $\omega$ ) for a typical polymer melt over a wide range of frequencies (typically  $10^{-3}$  to  $10^4$  rad/s). The expanded frequency range is made possible by time-temperature-superposition (TTS). Region I is the terminal zone. Region II is the crossover/plateau region. Region III is the high-frequency regime.

The existence of a plateau in the frequency spectrum is caused by the presence of *entanglements* in the polymer melt. Entanglements can be envisioned as kinks in the polymer chain caused by segment to segment contacts with neighboring chains (Ferry, 1980; Macosko, 1994). The effect of entanglements is significant only for polymers with a molecular weight that exceeds the entanglement molecular weight ( $M_e$ ). The length of the plateau region gives an indication of the extent of polymer chain entanglement. Thus, for a lower molecular-weight melt, the plateau region would be much smaller in width, and the crossover of  $G'$  and  $G''$  would occur at a higher frequency (smaller relaxation time).

The steady-shear rheology of a polymer melt is very sensitive to its molecular weight (Ferry, 1980; Bird et al., 1987). Low molecular weight melts are Newtonian liquids. As the molecular-weight increases, shear thinning begins to occur beyond a critical shear rate ( $\dot{\gamma}_c$ ). The curves resemble the schematic shown in Figure 6-4b (and again in Figure 6-10) with a viscosity plateau ( $\eta_0$ ) followed by shear thinning. As the molecular weight increases, shear thinning begins to set in at lower shear rates. From a microstructural point of view, shear thinning reflects a decrease in the density of entanglement with increasing shear because of progressive stretching and uncoiling of polymer chains (Ferguson and Kemblowski, 1991). An important trend in polymer rheology is the increase in zero-shear viscosity ( $\eta_0$ ) with molecular weight ( $M$ ) of the polymer melt (Ferry, 1980):

$$\begin{aligned} \eta_0 &= KM & M < M_e \\ \eta_0 &= KM^{3.4} & M > M_e \end{aligned} \quad (13)$$

Thus,  $\eta_0$  is initially proportional to the molecular weight but increases more sharply once the entanglement molecular weight ( $M_e$ ) is exceeded. This indicates the critical role played by entanglements in polymer science.

### RHEOLOGICAL MEASUREMENTS (STEADY/DYNAMIC SHEAR)

So far, we have indicated the two most important types of rheological techniques, i.e., steady shear and dynamic (oscillatory) shear. We have concentrated on a few important material functions, viz., the steady viscosity ( $\eta$ ), and the dynamic moduli ( $G'$  and  $G''$ ). In this section, we briefly describe how these parameters are measured in practice. Rheological measurements are typically performed on a rheometer. There are several categories of rheometers, with the most prominent being capillary rheometers (which utilize

pressure-driven or Poiseuille flows) and rotational rheometers (which use drag flows). Capillary rheometers are capable of measuring only the steady-shear properties of a fluid, not the dynamic rheological properties. For this reason, we will focus solely on rotational instruments.

Two types of rotational rheometers exist: stress-controlled rheometers and strain-controlled rheometers (Ferguson and Kembrowski, 1991; Schramm, 1994). In a strain-controlled rheometer, a known deformation (strain or shear rate) is applied to the fluid, and the stress is detected. Typically, the strain is applied by rotating one segment of the geometry, and a transducer connected to the other segment measures the stress. A stress rheometer operates in the opposite fashion, by applying a controlled stress and measuring the resulting deformation. In the past few years, stress rheometers have become immensely popular because of their great sensitivity and wide torque range. Rotational rheometers also can use a multitude of different geometries. Concentric cylinder (Couette), parallel plates, and cone-and-plate are the most common geometries. For the purpose of illustration, we will consider the use of a cone-and-plate geometry on a strain-controlled rheometer and show how rheological quantities are calculated.

A schematic diagram of a cone-and-plate geometry is shown in Figure 6-8. The device consists of a small-angle cone and a flat plate. The cone angle is denoted to be  $\alpha$ , and the radius of the cone/plate is  $R$ . This geometry has several advantages: it requires only a small sample and is easier to load and clean than more complex geometries (Macosko, 1994). More importantly, a homogenous deformation is maintained throughout the sample, provided the cone angle is small ( $<0.2$  radians). Flow is generated in a rotational geometry by moving one of the walls of the system in such a way that the fluid is dragged along with the wall. This explains why these flows are called "drag flows" (Ferguson and Kembrowski, 1991).

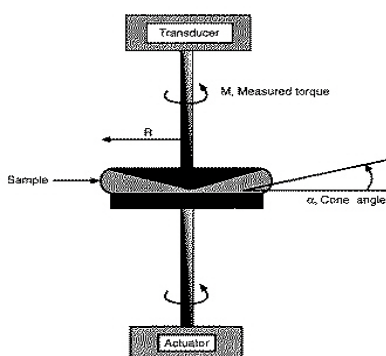


FIGURE 6-8 A rheological experiment on a cone-and-plate geometry on a strain-controlled rotational rheometer. The cone has a radius ( $R$ ) and cone angle ( $\alpha$ ), and its edge is truncated up to a height of 50 microns. The actuator applies a controlled deformation to the bottom plate, and the transducer connected to the cone measures the response of the sample.

In Figure 6-8 we show schematically how a test would be run on a cone-and-plate geometry using a strain-controlled rheometer. The general principle is to input a deformation and measure the torque output. The raw data can be converted into rheologically relevant quantities using the physical dimensions of the cone ( $R, \alpha$ ) and the input parameters. Let us first consider a steady-shear experiment. In this case, the actuator rotates the bottom plate at an angular velocity  $\Omega$  (rad/s). The shear-rate exerted on the sample is given by (Macosko, 1994):

$$\dot{\gamma} = \Omega/\alpha \quad (14)$$

The response of the sample is measured by the transducer in terms of a torque ( $M$ ). The torque can be converted into a shear-stress ( $\tau$ ) as follows:

$$\tau = 3M/2 \pi R^3 \quad (15)$$

The apparent viscosity can then be calculated from the shear-stress and shear- rate by using the expression  $\eta = \tau/\dot{\gamma}$ . Thus,

$$\text{Apparent viscosity, } \eta = 3M \alpha/2\pi R^3 \Omega \quad (16)$$

In dynamic measurements, the bottom plate is oscillated from its mean position, with the peak displacement being up to an angle  $\Phi$  (in radians). The strain-amplitude is then given by (Macosko, 1994):

$$\gamma_0 = \Phi/\alpha \quad (17)$$

The response of the sample is in terms of a sinusoidal torque showing a phase lag with respect to the input strain. The peak torque ( $M$ ), and the phase angle ( $\delta$ ), are measured by the instrument. The peak stress-amplitude ( $\tau_0$ ) is calculated from the peak torque ( $M$ ) using Eq. 15. The elastic and viscous moduli can then be calculated using Eqs. 9 and 10 respectively. The final expressions are:

$$\text{Elastic modulus, } G' = \left(\frac{\tau_0}{\gamma_0}\right) \cos\delta = \frac{3M\alpha}{2\pi R^3 \Phi} \cos\delta \quad (18)$$

$$\text{Viscous modulus, } G'' = \left(\frac{\tau_0}{\gamma_0}\right) \sin\delta = \frac{3M\alpha}{2\pi R^3 \Phi} \sin\delta \quad (19)$$

Similar governing equations can be derived for other geometries (Macosko, 1994; Whorlow, 1992). It is important to note that these equations are obtained directly from the physical laws of motion. The rheological quantities calculated using these equations are, therefore, independent of any constitutive model.

### EXTENSIONAL RHEOLOGY

In the previous sections we considered steady-shear and dynamic shear, which are by far the most common types of rheological techniques. Most texts on rheology are devoted primarily to shear flow, and most laboratories are equipped only with shear rheometers. However, many viscoelastic phenomena are better perceived in extensional (elongational) flow, which is fundamentally different from shear flow. For simplicity, we will confine our discussion to steady uniaxial extension. (In the case of dynamic rheology, the type of deformation, i.e., shear versus elongation, is not important, because we consider only small deformations).

Uniaxial extension can be visualized to occur when a rod of fluid is gripped on each end and pulled (Figure 6-9) (Macosko, 1994; Dealy and Wissbrun, 1990). In the process, the sample is extended along the direction of imposed deformation and gets constricted along the two perpendicular directions. Thus, a cylindrical fluid element becomes longer and thinner as it is stretched. One of the main problems in extensional rheometry is the difficulty of achieving steady extensional flow, especially for low viscosity liquids. In discussing steady shear, we showed how a constant shear-rate could be imposed simply by moving the top plate at a constant velocity ( $v$ ) (Figure 6-3a). However, to apply a constant elongation rate ( $\dot{\epsilon}$ ) the ends of the cylindrical sample shown in Figure 6-9 have to be moved at an exponentially-increasing velocity, given by (Macosko, 1994):

$$v_{\text{end}} = \frac{1}{2} \dot{\epsilon} L_0 e^{\dot{\epsilon} t} \quad (20)$$

$L_0$  is the initial length of sample. The sample length ( $L$ ) increases exponentially with time, while the area of the end-surface ( $A$ ) decreases exponentially (assuming that the material is incompressible, so that the sample volume would not change). The stress causing the sample to elongate is the normal stress difference ( $T_{xx} - T_{rr}$ ) which is the force ( $f$ ) per unit area acting on the end of the sample. The extensional viscosity is obtained by dividing the normal stress by the elongation rate ( $\dot{\epsilon}$ ).

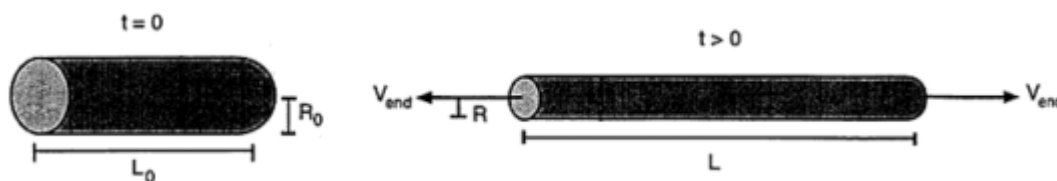


FIGURE 6-9 Uniaxial extensional flow on a cylindrical fluid element. Initially, the fluid is at rest, while at time  $t > 0$ , it is stretched by pulling the ends at a velocity ( $v_{\text{end}}$ ). Note that the cylindrical sample becomes longer and thinner as it is stretched.

$$\eta_e(\dot{\epsilon}) = \frac{T_{xx} - T_{rr}}{\dot{\epsilon}} = \frac{f/A}{\dot{\epsilon}} \quad (21)$$

From this discussion, we can appreciate the difficulties involved in designing an extensional rheometer, e.g., in designing clamps that move at an exponential pace to maintain a constant deformation. Other problems are the generation of a purely extensional flow free of shear effects and gravity effects. New rheometer designs (e.g. "opposing jets") are being developed to solve these problems (Macosko, 1994). Despite the difficulties, extensional rheology is worth studying for several reasons. Flows occurring in industrial processes, such as injection molding, extrusion, and calendering, often have a strong elongational component. Also, several viscoelastic phenomena including the tubeless siphon pointed out earlier are mainly elongational effects.

The behavior of a material under extension cannot be directly extrapolated from its behavior under shear. Consider the rheology of a polymeric melt under steady-shear as well as extension, as represented schematically in Figure 6-10. The steady-shear viscosity  $\eta$  is constant at low shear rates and decreases at higher shear rates (shear thinning behavior). The extensional viscosity ( $\eta_e$ ) is also a constant at low elongation rates, but  $\eta_e$  increases at higher  $\dot{\epsilon}$ . Within the regime of constant  $\eta_e$ , its value is three times the zero-shear viscosity ( $\eta_0$ ).

$$\eta_e \text{ (at low } \dot{\epsilon}) = \text{constant} = 3 \eta_0 \quad (22)$$

This result, sometimes called Trouton's rule, was originally found by F.T. Trouton in 1906 and can be predicted from the continuum mechanics of the various flows. The increase in  $\eta_e$  at higher deformations is called extensional-thickening and occurs for melts of polymers, such as polystyrene and low-density polyethylene. Thus, the same material can show shear

thinning under shear flow and extensional-thickening under elongational flow.

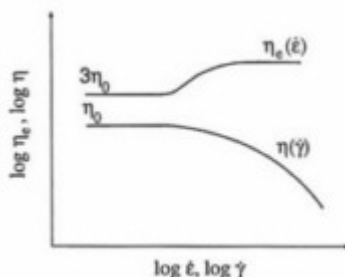


FIGURE 6-10 Typical behavior of a polymer melt under steady shear and steady uniaxial extension. Under steady shear the sample shows shear thinning; under extension it shows extensional thickening.

Extensional measurements can be more sensitive to small changes in the system composition than shear rheology. This is particularly true for polymer solutions containing very small amounts of polymer (in the 100 to 1000 ppm range), which show purely viscous behavior under shear and viscoelastic effects under extension (Chao et al., 1984). Similarly, solutions of associative polymers show anomalous effects that are much more pronounced under extension than under shear (Ballard et al., 1988).

### RHEOLOGY OF SILICA DISPERSIONS

In the next two sections, we provide a few examples of the use of rheology for characterizing and designing complex materials. We first consider the rheology of fumed-silica dispersions in oligomeric liquids, such as low molecular-weight glycols. These disperse systems have potential applications in state-of-the-art technologies, including "cable gels" for fiber-optic cables and composite polymer electrolytes for rechargeable lithium batteries (Khan et al., 1991; Khan and Zoeller, 1993). Colloidal dispersions can exhibit complex microstructures, as we pointed out in the previous section. The microstructure is a direct result of colloidal interactions between the particles, and therefore, varying the surface chemistry of the particles can have a significant effect on the microstructure. Because rheology is highly sensitive to microstructure, it is an invaluable tool for studying the origins of microstructural changes.

As an illustration, consider Figure 6-11 where we show the steady-shear rheology of two silica dispersions in the same liquid (a polypropylene glycol). Each dispersion has the same concentration of silica; the only difference is in the surface chemistry of each silica. One of the silicas (A200) is hydrophilic because of the presence of surface hydroxyl groups. This silica gives rise to a relatively low viscosity at low shear rates, and to shear thickening at higher shear rates. The other silica (R805) is hydrophobic, having an appreciable fraction of non-polar (octyl) surface groups. Its corresponding dispersion shows shear thinning over the entire range of shear-rates, and the viscosity at low shear rates is significantly higher than for the A200 silica dispersion.

In order to study the at-rest microstructures, we resort to dynamic rheological measurements. We show the elastic ( $G'$ ) and the viscous ( $G''$ ) moduli as a function of frequency in Figure 12 for the same systems shown in Figure 6-11. For the A200 (hydrophilic) silica dispersion, the viscous modulus ( $G''$ ) is greater than  $G'$  over the entire frequency range. Moreover, both moduli depend strongly on frequency. This signifies a non-flocculated microstructure composed of distinct particles (Figure 6-6a). In contrast, for the R805 (hydrophobic) silica dispersion, the moduli are independent of frequency, and the elastic modulus ( $G'$ ) exceeds  $G''$  over the entire frequency range. This frequency spectrum signifies that the latter system is a flocculated gel with a three-dimensional network structure.

We can form a picture of the colloidal interactions present in each dispersion by considering the steady and dynamic responses together. The A200 (hydrophilic) silica exists as

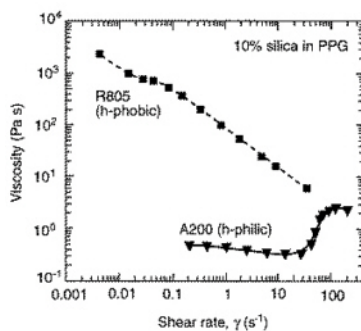


FIGURE 6-11 Steady shear viscosity ( $\eta$ ) as a function of shear rate for two colloidal dispersions. Each dispersion contains 10 percent fumed silica in a poly(propylene glycol) of molecular weight 425 g/mol. The two silicas differ only in their surface chemistry, with one of them being hydrophilic and the other hydrophobic.



isolated particles that exhibit little or no tendency for flocculation. Consequently, the system behaves like a viscous fluid, as evidenced by the dominant  $G''$  in its frequency spectrum (Figure 6-12) as well as its low zero-shear viscosity (Figure 6-11). It appears that the hydrophilic A200 surface preferentially interacts through hydrogen bonding with the polar groups present on the glycol, leading to steric stabilization of the particles (Raghavan and Khan, 1997). This contributes to an effective repulsive interaction between the particles, which acts as a barrier to flocculation. In contrast, the non-polar groups present on the R805 (hydrophobic) silica can interact with each other through van der Waals dispersion forces (Raghavan and Khan, 1995). This leads to the flocculation of silica particles, as shown by a pronounced elastic response in the dynamic data (Figure 6-12) and high viscosities under steady shear (Figure 6-11). The shear thinning of the R805 dispersion is caused by progressive reduction in floc size due to shear.

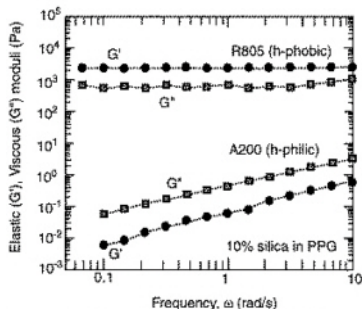


FIGURE 6-12 Elastic ( $G'$ ) and viscous ( $G''$ ) moduli as a function of frequency for the fumed-silica dispersions shown in Figure 6-11.

We would also like to comment briefly on the microstructural origins of shear thickening. This is a reversible flow-induced phenomenon where the viscosity increases under flow but where the system reverts back to its low-viscosity state at rest (Barnes, 1989). Current experimental and theoretical investigations have confirmed that shear thickening is caused by the formation of temporary clusters under flow (Raghavan and Khan, 1997). These "hydrodynamic clusters" are formed by the action of hydrodynamic forces that squeeze particles together into larger groups (Bossis and Brady, 1989). In order for these clusters to be formed, the hydrodynamic forces (which increase steadily with shear-rate) first have to overcome the steric repulsion forces. Therefore, shear thickening occurs only beyond a critical shear rate, as seen in Figure 6-11.

### RHEOLOGY OF ASSOCIATIVE-POLYMER SOLUTIONS

We now proceed to consider the rheology of polymeric systems formed by dissolving an "associative polymer" in water. An associative polymer is typically a water-soluble polymer that also possesses hydrophobic groups (Hansen et al., 1996). Small amounts of these polymers can greatly increase the viscosity of aqueous media, due to strong interactions between the hydrophobic groups. Thus the concentration, type, and length of the hydrophobic moiety are important in determining the properties of the system. In our laboratories, we have done extensive work on aqueous solutions of hydrophobically modified alkali-soluble emulsion (HASE) polymers. These polymers possess a comb-like structure, with pendant hydrophobic groups sticking out of the polymer backbone (English et al., 1997a).

We will briefly look at two effects, polymer concentration and the presence of surfactants. In Figure 6-13, we show steady-shear data (viscosity as a function of shear-stress) for aqueous solutions containing different polymer concentrations. As the concentration is increased from 0.4 to 1.0 g/dl, the zero-shear viscosity ( $\eta_0$ ) increases by a factor of 1000. In fact, if we plot  $\eta_0$  versus polymer concentration ( $c$ ) we find that ( $\eta_0 \sim c^8$ , a much more dramatic increase than for regular polymers, for which  $\eta_0 \sim c^{3.4}$  (scaling similar to the variation of  $\eta_0$  with melt molecular weight). Note also that there are basic differences between the shapes of the viscosity curves at low concentrations and high concentrations. At low concentrations, the initial Newtonian plateau is followed by an intermediate range of mild shear thickening and then a region of drastic shear thinning. At high concentrations, the shear thickening is no longer observed but a viscosity plateau exists at intermediate stresses. Also, the viscosity drops abruptly by

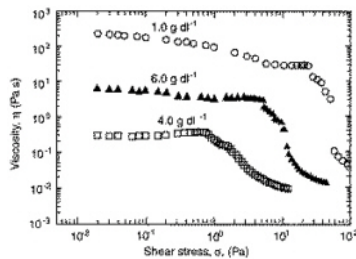


FIGURE 6-13 Steady shear viscosity ( $\eta$ ) as a function of shear stress for aqueous solutions of an associative polymer. Data is shown for three different polymer concentrations.

orders of magnitude at a higher stress (behavior reminiscent of a pseudo yield-stress).

Clearly, the rheology of associative polymer solutions is much more complex than the simple cases we have considered thus far. This is because hydrophobic interactions can be either intrapolymeric (between hydrophobes on the same chain) or interpolymeric (between hydrophobes on adjacent chains), with a combination of both mechanisms at any given stress level. We believe that the dominant mode of interaction is intrapolymeric at low stresses and interpolymeric at intermediate stresses (English et al., 1997). The interpolymeric interactions contribute to shear thickening and to the viscosity plateau (Ballard et al., 1988). At very high stresses, all hydrophobic interactions are precluded, as the hydrodynamic forces in the system begin to dominate. The transition from a state of appreciable interactions to negligible interaction occurs at the pseudo yield-stress.

Another significant effect in these systems is caused by the presence of surfactant. Consider an aqueous solution of HASE polymer at a polymer concentration of 0.6 g/dl (Figure 6-14). The elastic modulus ( $G'$ ) for this system varies with frequency as  $\omega^{0.8}$  (at low  $\omega$ ) and exceeds the viscous modulus ( $G''$ ) only at high frequencies. When we add 1.5 g/dl of a non-ionic surfactant to the system, we find that the levels of both  $G'$  and  $G''$  are increased. Moreover, the elastic modulus ( $G'$ ) shows plateau-like behavior over most of the frequency range and is higher than the viscous modulus ( $G''$ ) over the entire spectrum. This indicates that the addition of surfactant renders the system more elastic. We conjecture that this behavior is caused by enhanced hydrophobic interaction in the system, with the surfactant molecules acting as links between polymer hydrophobes. Note that the molecular structure of the surfactant is crucial to its behavior; other types of surfactants can produce the reverse effect, i.e., they can reduce the elastic character of the system.

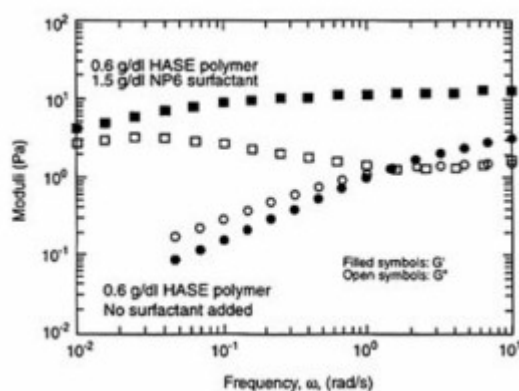


FIGURE 6-14 Elastic ( $G'$ ) and viscous ( $G''$ ) moduli as a function of frequency for two associative polymer solutions. In one system only polymer is present; the other contains 1.5 g/dl of a non-ionic surfactant (NP6) in addition to polymer. The steady-shear data for the polymer solution in the absence of surfactant was shown in Figure 6-13.

### RHEOLOGY OF AVIATION FUELS

Currently, the fuels used in the gas-turbine engines of commercial aircraft are kerosene-based jet fuels (Hutchinson, 1995). The two main types are Jet A fuel, used in North America, and Jet A-1, used in most other regions of the world. Jet fuels are among the most tightly specified products of oil refineries, the specifications involving boiling point, water content, aromatic content, etc. The important qualities jet fuels must generally exhibit under all operating conditions are as follows (Kroes and Wild, 1995):

- pumpability and ease of flow, with negligible volatility
- efficient combustion and high calorific value
- adequate lubrication for the moving parts of the engine
- minimal corrosive effects, fire hazards, etc.

The viscosity of an aviation fuel is a factor in calculating pressure drops in fuel lines, through its relationship to the Reynolds number (Bird et al., 1987). A lower viscosity corresponds to smaller pressure drops and lower pumping requirements. The viscosity increases with decreasing temperature, and when the freezing point of the fuel is approached, waxy particles begin to form. Many fuel specifications, therefore, include a maximum viscosity limit at low temperatures to ensure pumping and flow capabilities (CRC report, 1984). Research on aviation fuels has also led to the development of additives for specific purposes, e.g. to prevent ice and bacterial contamination in the fuel or to reduce the buildup of static charge (Kroes and Wild, 1995).

One class of additives is intended to reduce the flammability of aviation fuels in the event of an accident or crash. These additives, called "antimisting" (AM) agents, are essentially linear polymers of high molecular weight ( $> 10^6$ ) (Chao et al., 1984). A small amount of polymeric additive (100 ppm) is sufficient to reduce the formation of atomized droplets or "mist." Droplets in sprays of antimisting fuels tend to be larger and, in some cases, deformed to strings or filaments (Hoyt et al., 1980). The reduction of surface area available for vaporization, combined with the greater distance between droplets, inhibits flame propagation.

The antimisting behavior of fuels containing polymeric additives is a consequence of the viscoelastic nature of the fuel system (Hoyt et al., 1980; Chao et al., 1984). Accordingly, it is important to study the rheology of AM fuels. Under shear flow, however, non-Newtonian effects cannot



be detected for these systems because of the low level of polymer concentrations. On the other hand, the appearance of filaments in antimisting fuel sprays is an indication that there is a strong elongational component in spray hydrodynamics. This points to the significance of extensional rheology in AM fuels. Chao et al. (1984) attempted to correlate the extensional viscosity ( $\eta_e$ ) of the fluid to its antimisting behavior. They resorted to an indirect, yet simple and inexpensive indicator of  $\eta_e$ , viz., the ductless siphon height. The height ( $h^*$ ) to which a viscoelastic fluid can raise itself in the absence of an immersed duct (see Figure 6-2) can be taken as a measure of the fluid's extensional viscosity ( $\eta_e$ ). The researchers found that AM fuels showing large values of the ductless siphon height ( $h^*$ ), and thereby  $\eta_e$ , also exhibited strong antimisting behavior. Moreover, as the polymer molecular weight or concentration in solution was increased, the fuel became more viscoelastic (greater  $h^*$ ), and the antimisting action was enhanced.

One of the penalties of using polymeric additives in fuels is the increased viscosity of the system (Chao et al., 1984). It should be noted that large increases in fuel viscosity caused by additives is undesirable because it increases pumping requirements, and affects the temperature at which the viscosity exceeds specifications. Thus, care must be taken in selecting polymeric materials to be added to jet fuels. The study by Chao et al. (1984) found that using a high molecular-weight polymer, for which kerosene was an extremely good solvent, is desirable. If such a polymer was used at a low concentration, the viscosity increase could be kept within manageable limits, and antimisting properties would be conferred to the fuel.

This example illustrates the utility of rheology for aviation fuel research, especially for systems that are rendered non-Newtonian or viscoelastic by additives. Future research on aviation fuels might involve designing new additives and considering alternate fuels to prevent fire in "survivable" crashes. Possible additives are combinations of associative polymers and surfactants to produce materials with "tunable" properties. Very small amounts of these materials may be sufficient to produce changes in fuel rheology. Furthermore, one can obtain different rheological behavior depending on the operating regimes (cf. Figure 6-13, where the viscosity varies in a complex manner with shear-rate). Thus, we expect rheology to play a greater role in the design of the next generation of aviation fuels.

### SUMMARY

In this paper, we have presented a primer on rheology, the science of flow and deformation in various kinds of matter. We showed that rheologically interesting materials do not obey either Newton's law of viscosity or Hooke's law of elasticity; instead they can be classified as "viscoelastic," i.e., they exhibit a combination of viscous and elastic properties. Most colloidal and macromolecular systems fall into this category.

We considered three rheological methods: steady shear, dynamic oscillatory shear, and extensional flow. The most important material parameters obtained using these methods were outlined, viz., the steady-shear viscosity ( $\eta_e$ ), the elastic ( $G'$ ) and viscous ( $G''$ ) moduli in the linear viscoelastic regime of dynamic shear, and the extensional viscosity ( $\eta_e$ ). We showed how these parameters can be correlated to the underlying microstructure of various materials. Finally, we also discussed an example of how rheology could be used to evaluate polymeric additives for aviation fuels. On the whole, we hope to have shown the utility and efficacy of rheology for characterizing condensed matter.

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7

## Jet Fuel Chemistry and Formulation

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### ABSTRACT

Jet fuel requirements are determined by translating engine and airframe technical needs into specifications. Most civil and military jet fuels are kerosene-based and are predominantly straight-run distillates. Processing and finishing steps can vary considerably and include both chemical treatment and catalytic treatment with hydrogen. Jet fuel contains predominately C<sub>8</sub>/C<sub>9</sub> to C<sub>15</sub>/C<sub>16</sub> hydrocarbons with trace levels of sulfur, oxygen, and nitrogen-containing heteroatoms. Additives, which are tightly controlled in jet fuel, can potentially add low levels of a number of different compounds to the fuel. Jet fuel is transported by a complex system designed to control or eliminate water, particulates, and contamination from other fuels.

### INTRODUCTION

This paper is an overview of jet fuel formulation. The discussion includes definitions of jet fuel requirements, representative production methods, additives, and chemical compounds and their resulting reactivity. The important topic of distribution and handling is also discussed.

### DEFINING JET FUEL REQUIREMENTS

In the early stages of the development of the jet engine, designers believed that this new power plant—freed from the demanding octane requirements of reciprocating spark-ignition engines—would be able to use almost any liquid fuel (Smith, 1970). However, just the opposite turned out to be true. Many fuel properties reflecting both bulk and trace components were found to be important to both engines and airframes (Dyroff, 1993; ASTM, 1967). Over the years, jet aircraft evolved into highly integrated, interdependent fuel-engine-airframe systems (Taylor, 1988). The energy crises in the 1970s also demonstrated the importance of the availability and cost of jet fuel, and fuel requirements are now defined by the technical needs of engines and airframes, as well as producibility and cost. Technical requirements are translated into fuel specifications that define physical properties, chemical composition, and performance tests designed to predict specific needs. As a result, today's jet fuel is a high technology, tightly specified commodity.

During the development of jet engines, early in World War II, illuminating kerosene was chosen as the fuel because it did not conflict with the strong demand for very high octane aviation gasoline. Kerosene-based fuels for aircraft turbine engines are still used. In fact, the majority of fuels in use today in the West are kerosene-based. For civil aircraft, Jet A is the fuel used in the U.S. (Jet A-1 is used extensively elsewhere). The major difference between Jet A and Jet A-1 is the freezing (wax crystallization) point. The international Jet A-1 fuel specifies a -47°C freezing point because it may be used for longer, polar flights. Jet A has a freezing point of -40°C. The primary fuel used by the U.S. Air Force and NATO is kerosene-based JP-8, which is very similar to Jet A-1. The U.S. Navy uses JP-5, a fuel with a higher flash point (60°C versus 38°C), on aircraft carriers because of fire safety concerns. The Air Force used to use a wide-cut fuel, JP-4 (a mixture of kerosene and naphtha), but converted to JP-8 to reduce combat losses, post crash fires, and handling incidents (Martel, 1987). The use of a wide-cut civil aviation fuel called Jet B is currently limited to Arctic areas (Dukek, 1992). Wide-cut fuels have a very low flash point, which increases the hazards of flammability regardless of whether the fuel is intended for military or civil use (Dukek and Strauss, 1979). For this reason, kerosene-based fuels are emphasized in this paper.

A number of jet fuel specifications are used by Western countries. Major civil specifications include the American Society for Testing and Materials (ASTM) D 1655, an industry consensus specification; Defense Standard 91/91, which is issued by the United Kingdom Ministry of Defense for the United Kingdom Civil Aviation Authority; and the International Air Transport Association (IATA) Guidance Material (Dyroff, 1993). Other governments and the U.S. military also issue jet fuel specifications. At many major airports that use jointly operated fueling systems, a combination of the most

stringent requirements of ASTM D 1655, Defense Standard 91/91, and IATA Guidance Material called the "check list" is used. In recent years efforts have been made to harmonize Western specifications and to encourage non-Western countries to move in this direction.

TABLE 7-1 Examples of Some Jet Fuel Specifications

| Characteristic              | Value                           |
|-----------------------------|---------------------------------|
| Volatility                  | Min 38°C                        |
| Flash Point                 | Max 205°C                       |
| Distillation (10% Rec)      | Max 300°C                       |
| Final Boiling Point         | 775 to 840 kg/m <sup>3</sup>    |
| Density                     |                                 |
| Direct Compositional        | Max 25.0 vol pct                |
| Total aromatics             | Max 3.0 vol pct                 |
| Naphthalenes                | Max 3,000 ppm S                 |
| Total sulfur                | Max 30 ppm S                    |
| Mercaptan sulfur            | Max .015 mg KOH/g               |
| Acidity                     |                                 |
| Indirect Compositional      | Max -47°C                       |
| Freeze Point                | Min 18 mm                       |
| Smoke Point                 | Max 8 mm <sup>2</sup> /s        |
| Viscosity @ -20°C           | Pass @ 260°C                    |
| Thermal Stability Test      | Pass                            |
| Copper Strip Corrosion Test | Min 42.8 MJ/kg                  |
| Net Heat of Combustion      |                                 |
| Additives                   | Only listed additives permitted |

Some typical specification requirements for a Jet A-1 type fuel are shown in Table 7-1. The specification puts many limits on what is acceptable as jet fuel. These include direct limits on volatility, which controls the size of the compounds in the fuel, and on the type of chemical compounds that can be used. There are also indirect restrictions on composition imposed via requirements that fuels meet various performance tests (e.g., thermal stability) and physical properties tests (e.g., freezing point). Additives in aviation fuels are also strictly controlled.

Unlike other transportation fuels, aviation fuel specification requirements are deemed absolute in ASTM D 1655. Every batch of jet fuel is tested to prove its conformance to all specification requirements, and test results are not subject to correction for tolerance of test methods. In many cases, refineries impose even more stringent internal requirements to ensure conformance statistically.

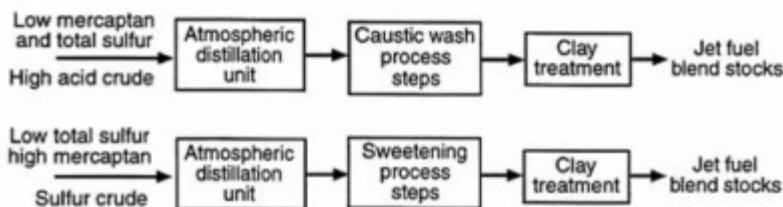


FIGURE 7-1

Two examples of chemical processing sequences used to produce jet fuel blend stocks.

### PRODUCTION METHODS AND THEIR EFFECT ON CHEMICAL COMPOSITION

Aviation turbine fuels are generally blended from straight-run kerosene fractions that have been subjected to some form of additional processing (Dukek, 1992). In some cases, jet fuel blending stocks are produced by hydrocracking heavier fractions. Fractions obtained from Tar Sand bitumen that have been coked and hydrotreated may also be used. All processing sequences employ distillation at some point. The initial boiling points are generally controlled to produce a product that meets flash-point requirements. The final boiling points are generally set to meet other requirements, such as freezing point, smoking point, or naphthalene content. Fuels with a lower freezing point, such as Jet A-1, require reducing the boiling point of the back end (the heavier boiling part of the fuel). Kerosene jet fuels generally contain hydrocarbon compounds from the C<sub>8</sub>/C<sub>9</sub> carbon number range up to the C<sub>15</sub>/C<sub>16</sub> range.

The sequence of processing and finishing steps used in the production of jet fuel blending stocks can vary widely depending on factors such as crude oil type, the complexity of the refinery, and concerns about specification limits. Detailed processing sequences are generally regarded as proprietary. However, processing sequences used to produce JP-5 have been surveyed for the U.S. Navy (Lieberman and Taylor, 1980; Varga, 1985). Examples of jet fuel processing sequences reported in this survey are discussed below.

Crude oils that produce kerosene fractions with low total sulfur can be chemically processed to reduce mercaptan sulfur (thiol) or organic acid content to meet specification requirements (Dukek, 1992; Taylor, 1992). Two examples of chemical processing sequences are shown in Figure 7-1. In the first example, a kerosene with a high acid content but low mercaptan sulfur and total sulfur is first treated with a caustic followed by water washing. Treating the fuel blending stock with sodium hydroxide converts the carboxylic acids, which are soluble in the hydrocarbon phase but not soluble in the

aqueous phase, to sodium carboxylic salts, which are insoluble in the hydrocarbon phase but soluble in the aqueous phase, where they are removed. Phenols and hydrogen sulfide can also be removed, but jet fuel range mercaptans and other sulfur compounds are left unconverted in the fuel. Clay treatment using attapulgus clay is employed to remove trace levels of sodium carboxylate salts left in the fuel and/or other trace polar compounds.

If the fuel blending stock contains excess odorous mercaptan sulfur compounds but acceptable total sulfur levels, it can be treated by a sweetening process (example 2). The sweetening process converts mercaptans into odor-free disulfides, which are left in the fuel. Older processes (e.g., Doctor or Bender sweetening) involve the oxidation of mercaptans using elemental sulfur, which can produce unwanted polysulfides. Newer processes (e.g., Merox) involve the catalytic oxidation of mercaptans with air over a fixed bed (Duval, 1968; Scheumann, 1956; Brown, 1973; Verachtert et al, 1985). The Merox oxidation step is preceded by a caustic wash to reduce the carboxylic acid level and followed by a water wash to remove carryover caustic and/or sodium carboxylate salts. A salt drier may be used to lower free-water levels prior to clay treatment.

Catalytic treatment in the presence of hydrogen can also be used to manufacture jet fuel blending stocks, for example, when higher sulfur levels mandate sulfur removal (Figure 7-2). Sulfur removal can involve either hydrotreating kerosene fractions or hydrocracking heavier fractions down to the boiling range of kerosene. The nature and magnitude of specific changes in compounds is a function of the type of hydrotreating process and its operational severity (e.g., catalyst type, pressure, temperature, hydrogen consumption, and space velocity). Hydrotreating usually removes sulfur from compounds such as mercaptans, sulfides, disulfides, and condensed thiophenes, removes oxygen from compounds such as carboxylic acids, peroxides, and phenols and removes nitrogen from nitrogen compounds such as indoles, carbazoles, and quinolines. In the hydrotreating process, organically bound sulfur is converted to H<sub>2</sub>S, oxygen is converted to H<sub>2</sub>O, and nitrogen is converted to NH<sub>3</sub>. Non-heteroatom compounds are left in the fuel. Hydrotreating also removes olefins by adding hydrogen to olefin molecules, thus converting olefin to a saturated compound. Hydrocracking generally is done under high severity conditions. In addition to affecting boiling range conversion, hydrocracking also removes most heteroatoms and olefins (Mohantry et al, 1990).

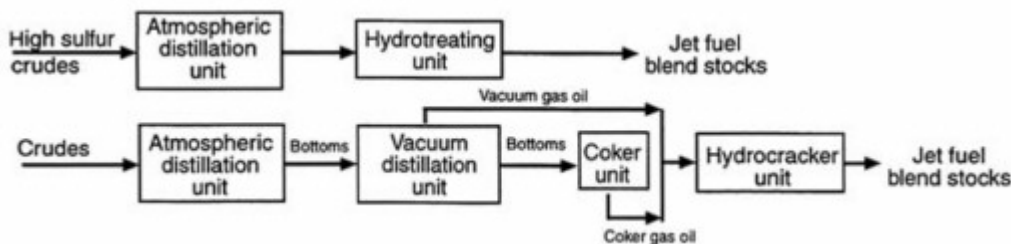


FIGURE 7-2  
 Two examples of catalytic treatments in the presence of hydrogen used to manufacture jet fuel blend stocks.

### ADDITIVES

Additives can have a significant impact on both the chemical composition and the chemical reactivity of jet fuel. Additives are strictly regulated by the specification to which the fuel is being manufactured. The approval process for a jet fuel additive is lengthy and involves extensive laboratory testing for material compatibility as well as testing for compatibility with other additives already approved for use in jet fuel. Specific approval by major engine and airframe manufacturers is also required.

In general, military fuels require more additives than civil fuels. Most of the Jet A civil fuel used in the U.S. contains no additives. Outside the U.S., civil jet fuel, Jet A-1, contains up to 5 ppm of an additive to increase electrical conductivity, which increases the rate of dissipation of any electrostatic charge that may have built up in the fuel as a result of microfiltration. The additive in use today, Stadis 450, is a mixture of polysulfones, polyamines, and dinonylnaphthyl sulfonic acid (Henry, 1975). Antioxidants may also be added (up to 24 ppm) to prevent the formation of hydroperoxide and gum from free radical reactions involving dissolved molecular oxygen, which is present in all fuel exposed to air. A number of different compounds from the family of sterically-hindered alkyl phenols are permitted or mandated, particularly in hydroprocessed jet fuel. ASTM D 1655 permits the use of N, N-diisopropylparaphenylene diamine, but hindered alkyl phenols are generally the antioxidant of choice in a clear product like jet fuel. A metal deactivator is permitted (up to 5.7 ppm) to chelate dissolved metals, such as copper. Chelation eliminates the deleterious catalytic effects of dissolved metals on fuel stability. ASTM D 1655 and Defense Standard 91/91 only allow one metal deactivator, N, N disalicylidene-1, 2-propane diamine.



A number of additives have been approved by the US Air Force and Navy for use in JP-8 and JP-5 as corrosion inhibitor and lubricity improving additives at concentrations ranging from 9 to 23 ppm. These additives are organic fatty acids, typically a C<sub>36</sub> dicarboxylic acid. They were used initially to prevent rust pickup in the fuel from pipelines and tanks, but they were subsequently found to improve the lubricity properties of fuel that had been severely hydrotreated. Hydroprocessing tends to remove the trace impurity lubricity-enhancing compounds that are naturally present in the fuel. Although individual specifications vary, it is common to require a purchaser agreement for the use of a metal deactivator or corrosion inhibitor/lubricity improver in civil fuels.

Military aircraft fuel systems do not include fuel filter heaters, which are used in civil aircraft (Dukek, 1992). As a result, military fuels require up to 0.15 vol pct of a fuel system icing inhibitor. Diethylene glycol monomethyl ether is approved for this purpose, replacing ethylene glycol monomethyl ether, which is being phased out because of concerns about toxicity.

The U.S. Air Force is currently developing and introducing into service an improved thermal stability JP-8 jet fuel called JP-8+100, which contains proprietary detergent/dispersant additives in conjunction with the sterically-hindered phenolic antioxidant, 2,6 di-tertiary butyl-4- methyl phenol, and a metal deactivator.

### CHEMICAL COMPOSITION AND REACTIVITY

The overwhelming majority of chemical compounds that make up jet fuel are hydrocarbons, including normal and branched paraffins, single and multi-ring cycloparaffins, single and multi-ring aromatics, hydroaromatics, and olefins. The relative proportions of hydrocarbon compound types can vary considerably, depending on the type of crude oil (see Table 7-2). Specifications limit the total of aromatics as measured by ASTM D 1319, "Hydrocarbon Types In Liquid Petroleum Products by Fluorescent Indicator Adsorption," to a maximum of 25.0 vol pct. This adsorption method reports alkyl benzenes, polycyclic aromatics, and aromatic olefins as aromatics. Naphthalenes are generally limited to 3.0 vol pct. Older specifications limited olefins by ASTM D 1319 to a maximum of 5.0 vol pct. Surveys indicate that the actual vol pct of olefins, in general, is much lower (Dickson, 1995).

Trace levels of heteroatom compounds are also present in jet fuel. Sulfur compounds are restricted to a maximum of 30 ppm from mercaptan (thiol) compounds and 3,000 ppm from all sulfur compounds. NIPER surveys indicate that the actual total sulfur levels are generally much lower (Dickson, 1995). In addition to thiols, sulfur compounds include sulfides, disulfides, and condensed thiophene-type compounds. Carboxylic acids (which are typically alkyl cyclo paraffinic acids) and phenols are also present and are limited by the acid number specification. A typical acid number specification limit of 0.015 mg KOH/g by ASTM D 3242 suggests an upper limit of approximately 60 ppm monocarboxylic acids in the jet fuel boiling range. Nitrogen compounds are not controlled by any specification, but analyses indicate that straight-run kerosenes typically have very low total nitrogen levels, e.g., less than 5 ppm. Nitrogen compounds are predominately alkyl indoles, carbazoles, pyridines, and quinolines (Snyder, 1970).

At ambient conditions, the majority of hydrocarbon compounds present in jet fuel are unreactive toward one another. Because jet fuels are normally saturated with air, there is always the potential for a reaction of the hydrocarbon/heteroatom mixture with the dissolved molecular oxygen. However, autooxidation reactions are typically very slow at ambient temperatures because jet fuels normally contain either natural or added inhibitors and in addition do not contain a strong initiation source for free radicals. Thus, under normal circumstances, jet fuel is by and large chemically unreactive at ambient conditions. However, the fuel can undergo autooxidative thermal stability-type reactions leading to the formation of deleterious surface deposits as the fuel is exposed to higher aircraft and engine temperatures as it is being delivered to the combustor (Taylor, 1992). Heteroatom compounds also tend to be more susceptible to thermal stability autooxidation reactions than hydrocarbons.

Trace impurities and additive compounds can potentially be reactive, although such occurrences are rare. For example, naturally occurring acids or acids present in some additives, such as corrosion inhibitors, have been known to become involved in acid-base reactions to form an adduct or reactions with metal cations to form soaps (carboxylic acid salts), which can have surfactant properties (Hazlett et al, 1991, 1993).

TABLE 7-2 Variations in Kerosene Hydrocarbon Compounds

| Hydrocarbon Type <sup>a</sup> | Variations in 150/280°C Kerosenes |
|-------------------------------|-----------------------------------|
| Paraffins                     | 10–65 %                           |
| Normal and branched paraffins |                                   |
| Cycloparaffins                | 10–35 %                           |
| Single-ring cycloparaffins    | 5–35 %                            |
| Multi-ring cycloparaffins     |                                   |
| Aromatics                     | 12–20 %                           |
| Single- ring aromatics        | 1–3 %                             |
| Multi-ring aromatics          |                                   |
| Olefins                       | 0.5–5.0 %                         |

<sup>a</sup> By mass spectroscopy except for olefins which are by fluorescence indicator adsorption

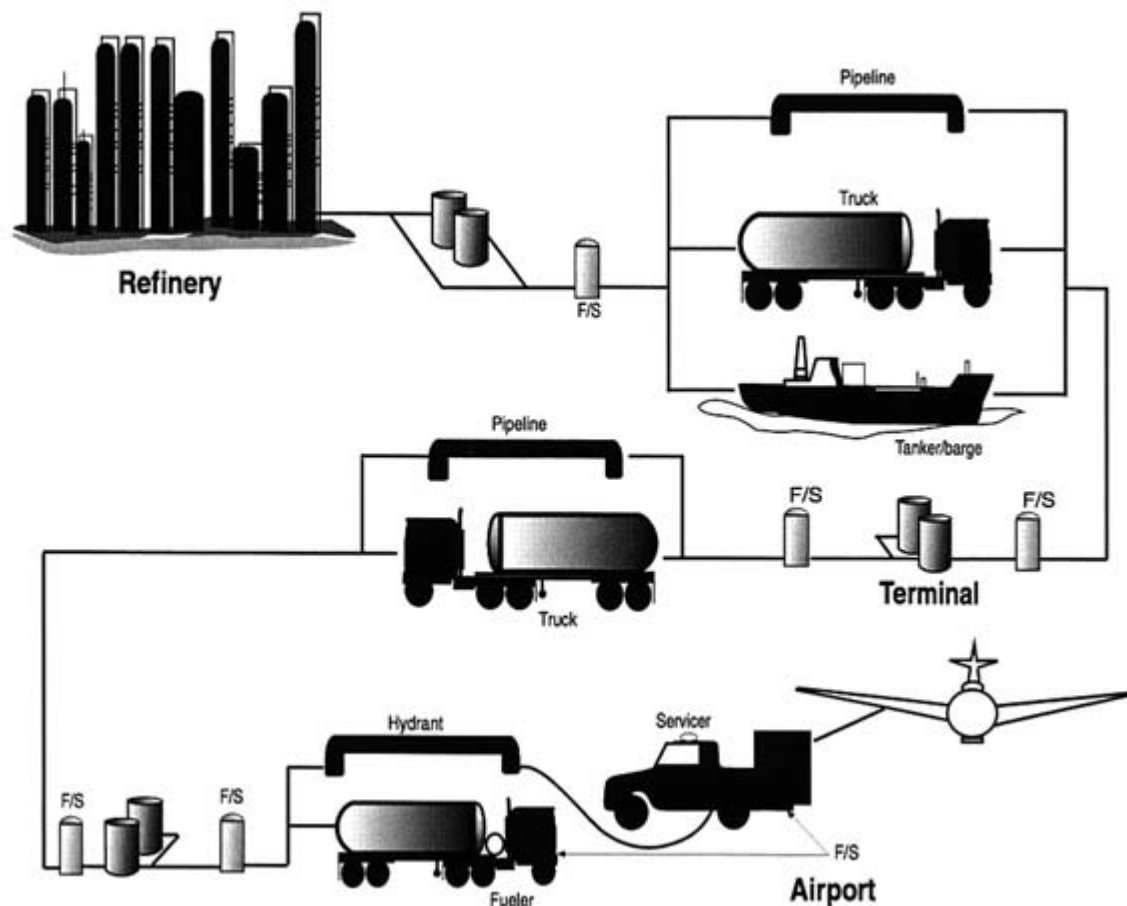


FIGURE 7-3  
 Typical aviation fuel distribution system.

### TRANSPORTATION AND STORAGE

The shipment of jet fuel from the refinery to an intermediate terminal to airport storage facility can involve pipelines, tankers, barges, railcars, and/or trucks. In the U.S., pipeline shipments often involve common carriers, fungible pipelines where fuel from multiple shippers is commingled. Fueling planes at larger airports generally involves using an airport hydrant system or a servicer (Waite, 1989; ATA, 1986).

This complex storage and delivery system (illustrated in Figure 7-3) is designed to eliminate or control excess free water (i.e., water suspended in the fuel above the fuel saturation point), particulates such as rust and dirt, microbial contamination, and contamination from other products and their additives. A highly redundant system is employed with a number of different approaches that reduce fuel contaminants.

Controlled tank settling to remove water and particulates involves quarantining the tank, removing settled water and dirt from the bottom of the tank, and withdrawing clean fuel from the top of the tank via a floating suction take-off. Filters can also be used to remove particulates. Units called filter/separators, which combine the functions of filtration to remove dirt, coalescence to remove excess water, and a hydrophobic barrier or separator that rejects any free water in the effluent fuel are also used.

In addition to controlled tank settling and filter/separators, water-adsorbing media elements (called monitors) are often employed for filtration into and out of airport storage and as the final step before the fuel is loaded into an aircraft. Monitors stop fuel flow in the presence of excess water and filter out dirt. Clay treaters are also employed in the distribution system to remove surfactants, particularly in the U.S. where a large amount of jet fuel is shipped through multi-product pipelines. Surfactants can stabilize water droplets against natural settling and can also disarm coalescers. Removing water from the distribution system is the most effective way of preventing microbial contamination in jet fuel (Swift, 1988). Because of the importance of the distribution system for ensuring that clean, dry, uncontaminated fuel is loaded into aircraft, the effects of any new fuel additive on the integrity of the distribution system must be considered.



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## 8

# Concepts for Safe-Fuel Technology

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### ABSTRACT

Researchers in the field of fuel safety have been on a quest to find replacements for halon and to develop new safety systems for protection against the ignition and burning of fuel in aircraft accidents. Recommended halon replacements have been announced for commercialization. New and undeveloped technologies include surface enhancement, low volatility, and self-activating powder extinguishment. These technologies may be used individually or may be synergistically combined via micro-encapsulation or specific system applications.

### INTRODUCTION

The Montreal Protocol and the U.S. Clean Air Act stopped the production of halon at the end of 1993 because of stratospheric ozone depletion. Regulations governing the production and use of halon came about as a result of scientific assessments conducted under the auspices of the World Meteorological Organization (WMO) and the United Nations Environment Programme. The Scientific Assessment of Ozone Depletion is a collection of scientific reports and a history of those reports in relation to the international policy process (WMO, 1994).

The new regulations created a need for substitute agents that could be used for fire suppression and explosives protection. To meet the new standards, researchers in the field of fuel safety have been on a quest to find new safety systems that will protect against the ignition and burning of propulsion fuel. Previous studies were based on decreasing the flammability and ignition potential of fuel on board the aircraft. The idea was to modify the fuel so it would not sustain a fire. However, fuel treatments to increase fire safety are costly and add weight to the aircraft. In addition, decreasing the flammability or ignition potential of fuel may interfere with the fuel's ability to perform regular operations.

In this paper, new and unproven technologies for fuel protection will be described. These include substances that (1) are consumed with the fuel, (2) are mixed with fuel after an incident, and (3) suppress external fire. Various types of protective agents and fire suppressant agents are also described as replacements or alternatives. These include (1) surface enhancement agents, (2) low volatility agents, and (3) combined technologies, such as micro-encapsulation. The concepts presented in this paper are applicable to fuel itself and to fuel fires, such as fuel fires immediately following survivable air crashes.

### BACKGROUND

#### Previous Safe-Fuel Technologies

Safe-fuel technologies have been developed and implemented with varying degrees of success. Some are already in use, including fuels and hydraulic fluids with improved safety properties. Volatile JP-4 fuel has been replaced by JP-8 fuel (Jet-A/A1), which has a flash point temperature above 100°F so that flame speed is reduced from 12 feet to 1 foot per second. A "fire-resistant-fuel," comprised of fuel, water, and a solubilizing surfactant, has also been developed and patented.

A number of inerting agents and systems have been tested. The U.S. Army mixed halon with fuel for tank propulsion but could not use it because of the caustic/toxic products of combustion. Inerting of the ullage (empty space) in fuel tanks has been implemented. Halon is now used in F-16 aircraft, and nitrogen is used in the Apache helicopter and C-5A aircraft. The on-board inert gas generator (OBIGGS), which has a membrane to separate nitrogen from air, has also been developed and is used in some aircraft. The use of OBIGGS allowed the fuel tank oxygen concentration to be maintained at approximately 9 vol pct, which is too low to ignite. Foams in aircraft fuel tanks are used by the U.S. Air Force. A coannular fuel tank, with an inner space containing fuel and an outer space containing halon, has been demonstrated using halon 2402 but has not been implemented.

A less vulnerable fuel has been developed using a high molecular weight polymer as an antimisting agent. This approach paralleled a Federal Aviation Administration (FAA) project that incorporated an antimisting agent with a shear thickening mechanism. Antimisting kerosene (AMK) was

developed to mitigate fuel misting thereby decreasing fuel flammability and ignition, but the fuel was not ready for propulsion combustion and had to be processed before injection. When AMK was tested at full scale, it did not prove to be cost/performance effective.

Low expansion foam has been used to protect against fires in spilled liquid fuel (Class B) around the outside of the aircraft. The foam is a liquid at standard temperature and pressure and can therefore be projected to an aircraft's critical distance. Foam, which is primarily water, contains surfactants that isolate the fuel from air so that a flammable mixture of fuel and air is prevented. In other words, the lower flammable limit is not reached because of the layer of foam on the fuel surface. Another approach is using dry chemicals around an aircraft to provide for rapid knockdown of fire.

A good deal of progress has been made toward reducing flammability in aircraft interiors. New materials have significantly reduced flame speeds and smoke generation, as well as retardants and intumescent coatings. New exterior materials have been tested and appropriate standards for fire protection have been defined.

### Halon and Halon Replacements

When selecting a substance for protecting against fuel fires, the first requirement is that the agent have the desirable physical-chemical characteristics. Halon 1301 has been the primary agent for fire protection on board an aircraft because (1) it is an effective fire suppressant (through the chemical action of the bromine atom, which acts as a catalytic fire chain breaker); (2) it can be stored as compressed liquid (small volume); and (3) it can flood (in gaseous form) the engine nacelles and cargo compartments.

The initiating study to find a halon replacement for the U.S. Air Force (USAF) was performed by Zallen International Associates (ZIA) (Zallen, 1992). A list of several hundred chemical agents was narrowed down to 12 potential candidates that met the criteria for a clean and effective replacement for halon 1301 fire extinguishing systems in aircraft (Bennett, 1992). Comparative analyses were performed on their physical properties and environmental parameters including boiling point, ozone depletion potential, toxicity, and fire suppression effectiveness.

Iodotrifluoromethane ( $\text{CF}_3\text{I}$ ) was identified in the initial study as the only halocarbon containing iodine that had a sufficiently low boiling point,  $-23^\circ\text{C}$  ( $\text{CHF}_2\text{I}$  has a boiling point of  $+22^\circ\text{C}$ , and  $\text{C}_2\text{F}_5\text{I}$  has a boiling point of  $+12^\circ\text{C}$ ). Because  $\text{CF}_3\text{I}$  was the only agent (Purdue University, 1950) with fire suppression effectiveness close to halon 1301 (6.8 percent suppression agent concentration for  $\text{CF}_3\text{I}$ ; 6.1 percent for halon 1301 [ $\text{CF}_3\text{Br}$ ]) there was a great deal of interest in investigating the environmental and toxicological characteristics of  $\text{CF}_3\text{I}$  data. The Purdue University study of 1950 also demonstrated that several agents were even more effective fire suppressants than halon 1301, namely  $\text{C}_2\text{F}_4\text{I}_2$  (5.0 percent),  $\text{C}_2\text{F}_5\text{I}$  (5.3 percent), and  $\text{C}_2\text{H}_5\text{I}$  (5.6 percent). One agent, which was proprietary at the time, can now be identified as HFC-236fa ( $\text{C}_3\text{H}_2\text{F}_6$ ). The other agents investigated had boiling points that were too high for conventional total flooding, were not efficient fire suppressants, or were too toxic. Effective agents with higher boiling points were considered for streaming, or misting, applications.

The potential halon 1301 replacements were tested at laboratory scale at the National Institute of Standards and Technology (NIST, 1994), at intermediate scale by ZIA at Southwest Research Institute (Zallen, 1994), and at large scale by Wright Laboratory of Wright-Patterson Air Force Base. These investigations led to compatible conclusions, and the recommended agents (with trade names) have been announced for commercialization in the Significant New Alternatives Policy (SNAP) of the Environmental Protection Agency (EPA).

### DEFINING THE PROBLEM

Post-crash fires cause about 40 percent of the fatalities in survivable incidents and are caused by uncontrolled fuel leaks ignited by sparks, hot surfaces, or fire elsewhere. In the critical period following a survivable crash, before ground crews arrive and gain control, immediate protection is needed against external fuel fires. The critical area around the aircraft is defined as the area beyond which heat from a fire does not affect the aircraft.

Fire-safe fuel technologies must be discussed in specific contexts. The specific scenario for this discussion is a survivable aircraft crash. In this scenario, fuel near the aircraft at rest is the major threat to survivors. Fuel spilled during such a crash is not of specific concern because the aircraft is not technically involved with fuel left behind, i.e., fuel beyond the critical distance.

The spilled pool of fuel near the aircraft can ignite and burn. The fuel mist near the aircraft is even more easily ignited than the fuel pool. Although the fuel mist is not a sustained hazard, it is a strong ignition hazard. However, it is not necessary to protect all of the fuel carried aboard the aircraft. Only the fuel that ends up within the critical distance from the crashed aircraft is a sustained hazard. It would therefore be efficient to treat the spilled pool of fuel and, specifically, the surface of the pool.

Although the spilled pool of fuel is the greatest danger, other fire hazards must be taken into account. These include the danger of pressurized fuel being sprayed/atomized, the danger of ignition of flammable fluids in storage tanks and delivery lines, and the danger of ignition of other flammable substances, such as cargo, oxygen, metals, and hydraulic components.

Once the general potential hazards have been analyzed, fuel systems should be characterized to define specific hazard scenarios. Accident investigation reports and fuel systems configurations are typical ways of defining specific hazard scenarios, which can be used to hypothesize various safety concepts.

Many pragmatic concerns must be addressed when evaluating potential safety concepts. After the basic performance of an agent or concept has been hypothesized and tested, the next step is analysis of a practical system's performance. Initial analyses may be done of size, weight, and costs. Cost analyses must include the number of applications and whether the system is new or retrofitted, because these factors determine how the benefits are attributed. Logistical analyses include geographic locations and transportation requirements (e.g., approval requirements in the United States, as opposed to requirements in Europe, for pressure vessels). Reliability studies include analyses of specific parts and repair time and maintenance.

Once initial evaluations have been established, program plans for the safety concept must be developed. For new or undeveloped concepts, full testing plans must be developed, including tests for toxicity and potential exposure. Options and combinations of concepts should also be evaluated. For example, a fire prevention agent might be mixed with fuel by coannular fuel/agent tanks or by honeycomb compartmented agents and fuels. A fire prevention agent that may perform well in one application might not perform well in another. Perfluorohexane, for example, is a good fire suppressant in general and has no ozone depletion potential (it does have a long atmospheric lifetime). However, mixing liquid perfluorohexane with liquid fuel has a low coefficient of mass transport from liquid to gas phase and results in poor protection against open-pool ignition and spreading flames (Naegeli et al., 1993).

### NEW AND UNDEVELOPED SAFE-FUEL TECHNOLOGIES

The following is a discussion of three technologies for making fuels safer: surface enhancement, low volatility technology, and self-activating powder extinguishment. Specific agent compositions are not presented, but recent literature abounds with descriptions of halon replacements and alternatives.

#### Surface Enhancement Technology

Halon replacements with reasonably good weight are commercially available. The effectiveness of replacements has been defined in classic tests, such as total flooding and streaming capabilities in classic halon test fire scenarios, e.g., computer room fires, Army tank engine compartment fires, USAF engine nacelle and dry bay fires, and Navy machine room fires. No halon replacement has all of the good characteristics of halon 1301. In order to get the same protection for similar weight and cost, the physical and chemical characteristics of less desirable agents must be enhanced.

Because the fuel surface provides the vapor for a fire, enhancing the effectiveness of the agent at the fuel surface will enhance agent efficiency and improve its fire prevention potential. So, one idea is to provide surface-enhancement for halon replacements or alternatives. Surfactant mixtures can be used to improve the distribution of the agent at the fuel surface. The mixture must, of course, be environmentally compliant and stable. Surfactant mixtures have been used with water, which is the basis for contiguous foam. Although in principle a water/surfactant mixture works, it is neither weight nor temperature effective in many applications. But it should be possible to use surface enhancement to improve the performance of halon replacements.

#### Low Volatility Technology

The environmental problems associated with effective halons is well known. Bromine and chlorine function well against fire, but their high volatility leads to release into the atmosphere. One approach to mitigate this danger was to use hydrochlorofluorocarbons (HCFCs) whereby a substituted hydrogen atom decreases the stability of the halon molecule in the atmosphere/troposphere on its way to the stratosphere. This hydrogen substitution is also the basis of hydrofluorocarbons (HFCs). However, in general the hydrogen atom substitution implies more reactivity, which also implies more toxicity.

Halon replacement studies have so far concentrated on paraffinic chemicals because the reactivity of olefinic chemicals is known and their toxicity suspect. The boiling points of higher molecular weight chemicals are too high and the vapor pressures too low for halon replacement, but larger molecules do have more bonds (i.e., degrees of freedom) to absorb ignition or fire energy. Some general (not absolute) rules follow: the boiling point of an agent rises with molecular weight; using heavier halogen atoms raises the boiling point; hydrogen substitution raises the boiling point; hydrogen substitution increases reactivity and potential toxicity; fluorine atoms provide stability; and vapor pressure is inversely proportional to the boiling point. These generalities indicate why so few chemicals can readily be identified for replacement of volatile halon 1301.

Using lower volatility agents in fire prevention applications may improve effectiveness. Highly volatile agents have inherent deficiencies in that: the agent can vaporize en route to the fire; the agent may not be concentrated near the fuel surface; and the concomitant large vapor cloud is an environ

mental hazard, may be toxic, and may not increase fire prevention. Low volatility technology (LVT) works by deriving a volatile, efficient fire suppressant from pyrolysis of the initially nonvolatile agent. LVT agents would be effective because no agent would be lost by evaporation along the delivery trajectory, the agent is deliverable because of its low volatility, harmful emissions would be minimized, and agent/surfactant control of the fuel surface would be increased. The agent would be concentrated where the fire was initiated with heat from the fire and hot surfaces releasing the fire prevention chemical.

### Self-Activating Powder Extinguishment Technology

Dry chemical powders have been used as fire fighting agents for many years. It is known that fine particles, on the order of ten micrometers, are more effective fire extinguishers on a mass basis than larger particles, on the order of one-hundred micrometers. Large particle powders are still used, however, for two primary reasons. First, grinding powder to fine particulates, which can cake in storage, is not cost effective. Second, the short throwing (delivery) distance of fine particulate powder makes it difficult to get the agent where it is needed.

Three mechanisms principally account for the fire prevention performance of dry chemicals. The first is the thermal cooling from the intrinsic thermal mass of the cold material; this is augmented by endothermic decomposition reactions. The second mechanism is chemical action, whereby flame propagating species, such as hydrogen and hydroxyl radicals, may recombine either heterogeneously on the surface of the particles or homogeneously as a result of gas phase reactions catalyzed by alkali metal atoms. Third, the water and carbon dioxide produced in the reactions act as local oxygen diluents or inertants. Two of these essential mechanisms are surface effects, so a greater surface area per unit mass of fine particulate powder speeds the mechanisms for better fire prevention.

Comparative tests have shown that fine dry powder is more effective at extinguishing fires than any of the new halon replacements. But, there are some problems: limitations on the fineness of the powder that can be manufactured at reasonable cost; difficulties preventing the agglomeration and coagulation of fine powders in storage; and problems of effectively discharging particles with low momentum.

The use of fine particle powders for fire prevention is currently based on propellant-generated solid aerosols. Pyrotechnic compositions, comprising a potassium-based oxidant and an organic binder, can generate a fire extinguishing aerosol. High reaction temperatures mean that the salts produced are initially gaseous and that the particulates produced by condensation from the vapor phase are extremely fine. Experiments on devices for total flood extinguishment show that suppression by fine particle powder requires significantly lower mass concentrations than halon.

Pyrotechnically-generated aerosols (PGAs) use potassium-based oxidizers to maximize the known fire suppression capability of potassium salt. The fuel may consist of a binder and a metal powder as co-fuels that generate enough heat to vaporize potassium-based fire prevention additives. The oxidizer/fuel ratio is designed to generate the product quickly, absorb energy, and result in optimal composition. PGA aerosol properties give them excellent three dimensional distribution and long term suspension. They have zero ozone depleting potential, low toxicity, and show significant weight reductions compared to halon.

## TECHNOLOGY COMBINATIONS

Known effective fire suppressing agents are limited in number and type. There might therefore be some benefit in combining individual technologies, not by the simultaneous use of two types of prevention, but rather by some synergistic combination of the scientific bases that make certain materials work.

### Micro-encapsulation

In the development of fire resistant fuel wherein 2 to 3 percent water was used in diesel fuel, two things have been shown. First, although evaporative cooling effects are significant, they are not responsible for the self-extinguishing properties of aqueous diesel fuel. Second, when the heat transfer in the liquid surface, which causes preheating of the surface ahead of the flame, is reduced, it generates a water vapor blanket for self-extinguishment (Weatherford and Naegeli, 1984).

One way to both increase the amount of fire suppressant at the fuel surface and lower the volatility of a high volatility agent is micro-encapsulation. Micro-encapsulation would reduce vapor loss from a high volatility agent until the agent is needed. The contents of the microcapsule could include any number of fire suppressants. By making them lightweight for flotation, the microcapsules could be concentrated at the fuel surface for synergistically increasing efficiency. Heavier capsules could be developed for situations where mixing is required.

A urea-based capsule could potentially both release the contained substance and provide fire protection. The outer shell of the capsule might be a dry chemical powder, for example, Monnex™ powder, which provides rapid fire knock-down by cracking apart to form smaller, more efficient particles.

### System Applications

There are many different ways to use new agents for fuel fire prevention or suppression. Insoluble compounds with fire



protection capacity may be added to fuel for protection in the fuel tank, but be physically separated from the fuel before combustion takes place. The stability of the suspension and the chemical composition of the compounds need to be considered in these applications.

Inerting agents which are kept separate from the fuel may be released in a number of ways. The fuel and inertant could be separated by a honeycomb in an intrinsic system. The inertant would thereby be released if the fuel tank ruptured. In a separate system, the inertant could be kept in frangible tubes in the fuel, and released by fire or rupture.

Fire suppressing agents could also be used as fuel additives. Mixtures of salts (acetate, citrate, carbonate) with water have long been used to protect cooking facilities. New investigations (Finnerty et al., 1996) have shown that aqueous solutions of potassium lactate or potassium acetate extinguish fuel fires much better than water alone. The improvement can be attributed to the release of solid salts upon evaporation of the water in the fire zone. This new understanding could be used for fuel fire-safety.

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### III

## Presented Papers Aircraft Fuel System Requirements

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## 9

# Engine Fuel System Design Issues

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### ABSTRACT

In order to optimize the development of improved fire safe aviation fuels, it is necessary to understand how fuel is used in the engine prior to the combustion process. This paper discusses the utilization of fuel as a hydraulic fluid, a coolant, and a component lubricant in the aircraft engine prior to combustion. General fuel system design guidelines are provided to facilitate an understanding of fuel system architecture, system design requirements, and the flammability-related testing of fuel system components. Further discussions provide an insight into the type of components and materials used and the fuel properties considered in fuel system designs to ensure safe and reliable engine performance.

### INTRODUCTION

In the development of more fire-safe aviation fuels, consideration must be given to the entire engine fuel system to ensure that changes are not detrimental. Safe and reliable engine fuel system operation has been obtained through rigorous design and verification test processes that depend to a large extent on current fuel properties, which are both specified and inherent. The noncombustion utilization of fuel depends on these fuel properties for reliable and safe engine operation. Fuel may be used as a hydraulic ("fueldraulic") fluid, a coolant, and a lubricant.

Fuel has traditionally been used for fuel valve actuation, inlet variable geometry actuation, and start bleed and cooling valve actuation. Recent military engine designs that employ thrust vectoring exhaust nozzles have expanded the use of fueldraulics to high power (100 H.P., 3500 psi) exhaust nozzle actuation. In addition, fuel from the airframe tanks has been used as a coolant for engine-mounted electronic controls and diagnostics to enhance the reliability of these controls. Fuel has also been used as a coolant on airframe subsystems and oil systems and actuation components in high temperature environments. Although fuel is generally regarded as a less than optimum lubricant, fuel lubrication plays an important role in the design and performance of fuel pumps, fuel controls, and fuel powered actuators. Wear and sliding friction can adversely affect the life and performance of these components.

### ENGINE FUEL SYSTEM

A typical military engine fuel system is illustrated in [Figure 9-1](#). This engine is a typical high-performance after-burning engine with a modulating exhaust nozzle with a digital electronic engine control. It is an operational engine used on modern military aircraft.

Low pressure aircraft boost pumps provide dedicated fuel coolant to the electronic engine control with a return path to the aircraft tank. The fuel in the aircraft tank is the lowest temperature fuel available on the aircraft and is, therefore, used for cooling electronics. The fuel for combustion is first used to cool aircraft subsystems, such as the environmental, hydraulic, and electrical subsystems. At the engine inlet, fuel is at approximately 40 psi pressure and 200°F temperature. In newer engines, the temperature at the engine inlet can be as high as 250°F.

At the engine inlet the fuel pressure is raised by a centrifugal pump to provide sufficient charging pressure for the main fuel pump, a gear pump, and the augmentor pump, which is a high speed centrifugal pump. The lubricating qualities of the fuel are an important factor in pump durability. The main fuel pump provides fuel for combustion as well as for fueldraulic actuation. The fuel for gas generator combustion is used to cool the engine lubricating oil prior to entering the gas generator combustor. The augmentor pump provides fuel for the augmentor combustor only.

Fueldraulic actuation is used to control start bleeds, fan variable guide vanes, compressor variable guide vanes, and control of the exhaust nozzle. The power to drive the exhaust nozzle is provided by a pneumatic motor and ball screw actuators. More recent engines with thrust vectoring exhaust nozzles use fuel at up to 3500 psi pressure to power actuators that control the exhaust nozzle area and the direction of thrust. Fuel is also used to power and control the fuel metering function in the main fuel control and in the augmentor fuel control.

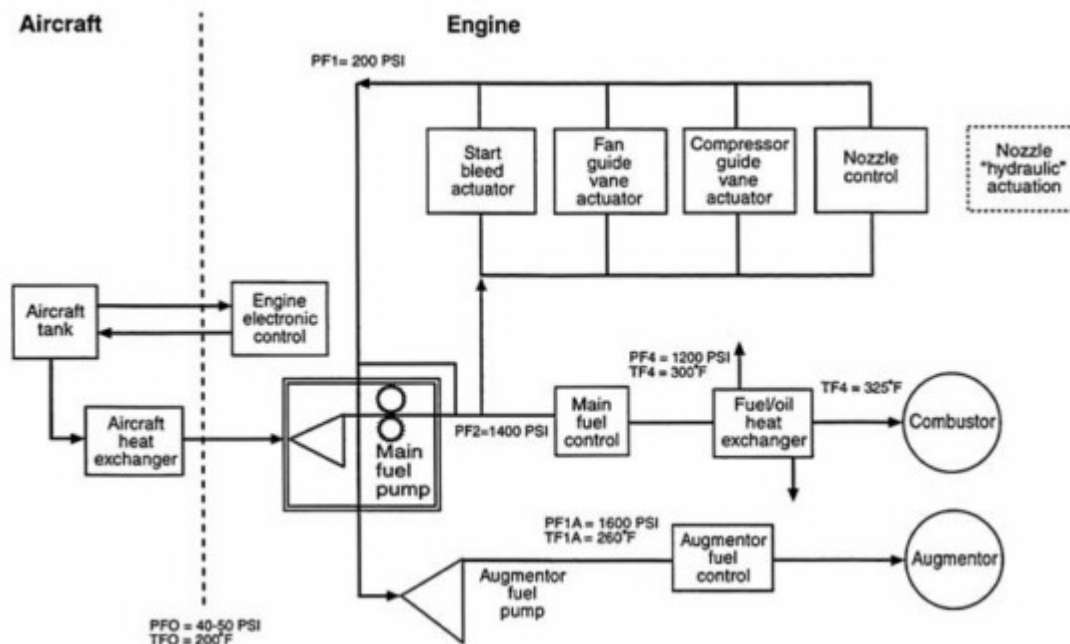


FIGURE 9-1

Fuel system design for military aircraft: schematic drawing of the engine hydromechanical control system.

A typical modern commercial engine fuel system, the PW 4084, is depicted in Figure 9-2. The major difference between military and commercial fuel systems is that there is no afterburner on a commercial engine and, therefore, no fuel system features for controlling this function. The use of fuel as a coolant is limited to cooling engine oil. Electronics are not cooled because the environment is more benign. Fueldraulics is utilized for compressor variable geometry actuation, bleed air valve actuation, and turbine cooling valve actuation.

### DESIGN CONSIDERATIONS RELATED TO FLAMMABILITY

Most fuel systems contain numerous fuel-to-air seals, most of which are elastomeric. Static seals are required to exhibit no external leaks over all operation conditions. Dynamic seals, such as seals on sliding actuator shafts or rotating shafts, incorporate a drain line to an overboard drain for any external leaks. In most cases, dynamic seals on sliding shafts incorporate dual shaft seals for increased reliability. Whenever possible, a minimum level of fuel flow in fuel lines and components is preferred in order to provide cooling and prevent fuel deposit formation due to high ambient temperatures.

In areas where fuel flow is adjacent to extreme high temperature structures, the hot surface ignition characteristics (HSIC), rather than the minimum ignition or autoignition temperature of the fuel, is used to evaluate the potential fire hazard. The HSIC is a more realistic predictor of fire due to fuel leakage. Externally mounted fuel system lines and components are positioned so that the lowest HSIC temperature is not exceeded. Components and component assemblies are electrically bonded to the engine case to provide lightning protection and to prevent a build up of static electricity. The engine case, in turn, is bonded to the airframe. Because most fuel system components are structural pressure vessels that contain fuel at elevated temperatures and pressures, the structural strength margins of all components are designed for overpressure, low cycle fatigue life, and high cycle fatigue life.

### QUALIFICATION TESTING RELATED TO FLAMMABILITY

In accordance with AS1055B, fuel-carrying components and lines are required to be fire resistant for five minutes when exposed to a 2000°F flame at the most adverse operating conditions. This ensures that no component will contribute to

an external fire. All electrical-current-carrying components are required to be explosion proof (per MIL-STD-810 method 511.3) to ensure that the electrical operation of the component will not ignite a combustible atmosphere surrounding the component. Checks are performed to verify electrical bonding between component assemblies and the engine case and between the engine case and the airframe. The integrity margin of structural pressure vessels is verified by proof pressure testing to 1.5 times maximum operating pressure without yielding and burst pressure testing to 2.0 times maximum operating pressure without rupture. Additional structural verification testing includes low and high cycle fatigue life tests and pressure impulse testing.

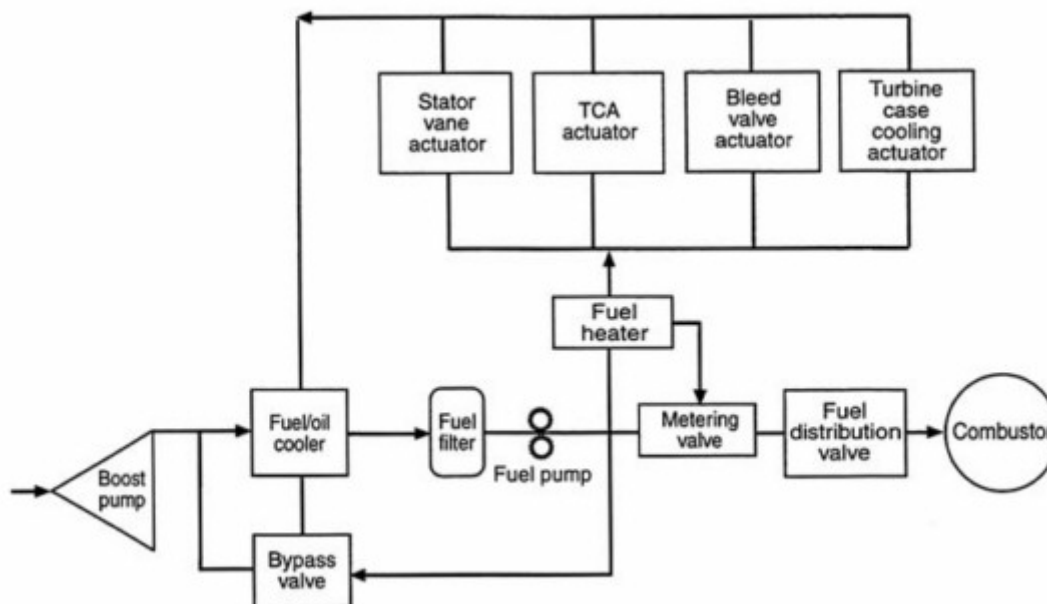


FIGURE 9-2  
Fuel system design for commercial aircraft: schematic drawing of PW 4084 fuel distribution system.

### FUEL SYSTEM MATERIALS

Potential fuel additives or modifications to improve fuel fire safety must be compatible with the materials used in fuel systems. The following is an overview of the materials used in the listed components.

Most fuel pumps are of the centrifugal, gear, and vane design (in some cases, piston pumps are used). Housings are generally made of high grade aluminum castings, such as C355, forgings, or wrought stock, such as 2219. The pumping elements are made of high strength tool steel or stainless hardenable steel; some vane pumps and piston pumps utilize tungsten carbide on wear surfaces to minimize wear.

Fuel controls perform a variety of functions, from simple fuel flow metering to complex fuel flow staging and sequencing and a host of other engine controlling functions. Fuel control housings are generally made of high grade aluminum castings, such as AMS 4225 or A201, with a recent trend toward forgings or wrought stock housings made of 2219 or similar aluminum alloys. A common coating for these aluminum alloys is anodize of different thicknesses to prevent corrosion or to provide a suitable wear surface. Internal valves are mostly made of high grade stainless steel, grade 440C, or similar alloys. Many of these fuel controls contain electromechanical interface devices, such as solenoids, stepper motors, switches, electrohydraulic servovalves, and position feedback devices, such as resolvers or linear variable differential transformers. These electrical devices contain magnet wire and magnet wire insulation and various potting compounds. In many cases, these devices are immersed and operate in fuel.

Fuel hydraulic actuator housings range from aluminum to steel to titanium with exotic coatings. Actuators also contain the same type of electromechanical interface devices as fuel controls. Small actuators are used to position and control hot air valves used to de-ice the engine inlet and to cool the turbine.

Other materials used extensively are elastomeric seals and plastic seal backups. The most widely used elastomeric seal

materials are nitrile, fluorosilicone, and fluorocarbon in the form of O ring seals or gaskets.

### FUEL CHARACTERISTICS

One of the most important characteristics of aviation fuel is the ability to act as a coolant for other systems and to burn the absorbed heat in the combustion process. The ability of the fuel to perform this function is governed by the specific heat of the fuel and the maximum temperature to which the fuel can be raised without incurring detrimental side effects. For JP-8 fuel, thermal stability limits the maximum temperature over long periods to 300°F and short time exposure to 325°F. Exceeding these limits greatly accelerates the thermal breakdown of the fuel and causes deposit formation in fuel system components, which can cause fuel nozzle/injector fouling and other anomalies in fuel system components. Fuel nozzles and electrohydraulic servovalves are valve assemblies that contain matched sets of valves and sleeves with diametrical clearances on the order of 0.0002 inch. A significant deposit in these tight clearances increases friction and degrades performance of the valve. There is a considerable effort under way to qualify and introduce a higher temperature fuel, JP-8+100, that would raise the maximum long time bulk temperature limit to 400°F and the short time excursion limit to 425°F. The objective of this fuel additive package is increase the fuel heat sink without increasing the propensity to form fuel deposits. Modifications to improve the fire safety of aviation fuels must be compatible with this effort.

Fuel lubricating qualities are generally recognized as being less than optimum. But lubricity is an important property that affects wear characteristics of sliding contact surfaces in pumping elements, such as bearings, gears, vanes, and pistons. In the past, the use of low lubricity fuel has required the redevelopment of some pump materials. Lubricity affects the sliding friction and wear between sliding parts in fuel control mechanisms. A desirable lubricity value of fuel is equal to a ball-on-cylinder wear scar of 0.5 mm or less. This will ensure the satisfactory performance of older fuel systems that are more dependent on lubricity for fuel system performance.

Other fuel characteristics that must be considered in the development of a safer fuel are specific gravity; viscosity, specific heat, vapor pressure, bulk modulus, and interaction with contaminants. Specific gravity is used as a parameter to calculate fuel flow. Older hydromechanical fuel controls are calibrated using calibrating fluid with a tightly controlled specific gravity of 0.775 to 0.765. A wide variation from this value makes fuel flow scheduling less accurate. Viscosity affects low temperature pumpability, servosystem damping, and hydrodynamic fluid film lubrication. The low temperature limit of 12 centistokes is the current limit, and a significant increase in viscosity will adversely affect fuel pumpability at the engine inlet. Excessive damping in some servosystems may also result from a significant increase in viscosity at any temperature. At the other extreme, a significant decrease in high temperature viscosity will decrease the hydrodynamic film thickness in certain pump journal bearings and will adversely affect pump durability. Specific heat affects the heat sink capacity of the fuel. Any increase in specific heat will have a positive impact. However, the important aspect of heat sink capacity is specific heat per mass, indicating the amount of heat that can be absorbed per unit mass of fuel. It is highly desirable to maximize specific heat per mass.

Another characteristic of fuels that must be considered is vapor pressure. Although it is highly desirable to keep fuel vapor pressure as low as possible for fire safety reasons and for the sake of fuel system pumpability, low vapor pressure also adversely affects engine starting and altitude relight capability.

The bulk modulus characteristic is generally not a fuel system design driver. Only with the emergence of high response, high power exhaust nozzle actuation systems has the importance of a high value of fuel bulk modulus become apparent. A lower bulk modulus can lower the natural frequency of a fuelraulic servosystem. The maximum bandwidth at which the servosystem can operate is then determined by the bulk modulus. Conversely, operating a servosystem designed to operate with a minimum bulk modulus with a fluid of lower bulk modulus will result in system instability. The solubility of gases, to the extent that this impacts the bulk modulus value, must also be considered in any fuel modification.

How a fuel interacts with suspended contaminants is not a readily definable characteristic but should be considered. It is highly desirable to keep solid contaminants suspended in solution and to prevent coagulation and the formation of larger particles. This is especially true in fuel system branches downstream of the system filters where large contaminant particles can plug orifices and jam mechanisms.

### SUMMARY

Reliable operation of jet engine fuel systems has been developed based on current fuel characteristics, both specified and inherent. Fuels with improved fire safety should consider keeping within the currently known range of characteristic values. Changes resulting in characteristics outside the current ranges will require a significant amount of development and verification testing to establish that there is no detrimental impact from the new fuel. Evaluations of a new fuel must not only consider compatibility with new systems, but also compatibility with current, proven fuel systems.



## 10

# Applications of Vulnerability Analysis and Test Methods to Aircraft Design

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### ABSTRACT

Over a period of many years, the U.S. Department of Defense has developed several ways to lower the number of aircraft lost in combat. This paper outlines a systems engineering based approach and a description of hardening concepts that can greatly reduce the vulnerability of aircraft to fires and explosions. The systems engineering design process includes modeling and testing, which can predict and demonstrate the capability of hardening design features. Known limitations in modeling and testing are highlighted.

### BACKGROUND

This paper describes analysis concepts and vulnerability reduction features that could benefit commercial aircraft. The paper highlights some broad concepts used by the Department of Defense to reduce the vulnerability of aircraft. The systems engineering process is used to categorize threats, effects of threats, and design approaches to hardening aircraft. The categories of threat are presented in tables to clarify the interrelationships of threat effects, design concepts, and hardening options.

Different threats (ballistic, nuclear, laser, chemical, biological, high power microwave, etc.) affect different portions of the aircraft hardware. This paper highlights ballistic threats, which are assumed to be the most likely threats to commercial aircraft. Effects of ballistic threats and relevant hardening features are described below.

### SYSTEMS ENGINEERING PROCESS

Combat data shows that most combat aircraft losses can be attributed to fire and explosions. State-of-the-art vulnerability analyses of current combat aircraft confirm that fires and explosions are a significant vulnerability. Therefore, reducing overall vulnerability requires reducing vulnerability to fires and explosions.

In the systems engineering process, complex technical problems are divided into basic areas, including interrelationships. In order to reduce the vulnerability of complex aircraft systems, these areas must be well defined. The critical areas involved in reducing vulnerability to fires and explosions are listed below:

- fire and explosion elements
- damage modes and effects
- hardening approaches
- modeling and testing

### FIRE AND EXPLOSION ELEMENTS

Fires and explosions require three critical elements, an ignition source, a flammable material, and oxygen. Remove any one of the three elements, and the potential for fire and explosion is eliminated. Figure 10-1 shows the three basic elements and their interrelationship. The following sections define the critical features of each.

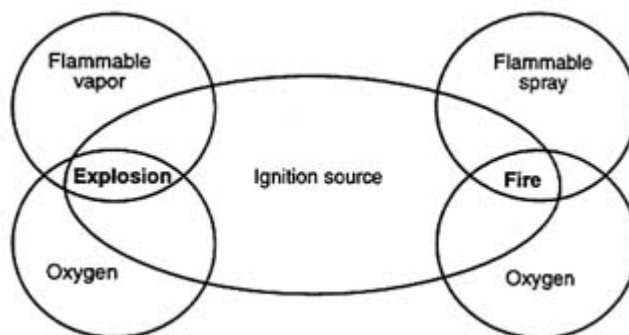


FIGURE 10-1  
Fire and explosion elements.

### Ignition Sources

Fires and explosions can start from a wide range of ignition sources. In order to harden the aircraft effectively, one must understand the causes of fires and explosions. When and how a fire or explosion starts depends on the threat-induced ignition source. Tables 10-1 and 10-2 list some common ignition sources from ballistic threats and mechanical failures.

#### Flammable Materials: Vapors, Sprays, and Liquids

Flammable materials constitute a large portion of the aircraft. Fuel tanks hold thousands of gallons of flammable material, and hydraulic and coolant systems hold tens of gallons of flammable material. A fire involving tens of gallons of flammable material can cause serious damage or even the loss of an aircraft.

Normally, flammable materials and ignition sources do not occupy the same space. As a result of damage from a ballistic threat and/or mechanical failure, flammable materials, ignition sources, and oxygen may occupy the same space, such as a dry bay (a volume adjacent to a fuel tank) or ullage (the air space above the fuel in the fuel tank). A sustained dry bay fire or ullage explosion can result in loss of the aircraft. Table 10-3 shows a more complete list of equipment and the location of flammable materials.

#### Oxygen

The third critical element of fires and explosions is oxygen. Oxygen concentrations are altered by environmental factors, such as temperatures of the fuel and ullage, atmospheric pressure, and internal air flow. These environmental factors alter the fuel/air concentration ratio. As the oxygen concentration and environmental factors change, the probability of fire and explosion changes. Dependent upon numerous factors, the fuel/air concentration ratio may be too rich or too lean to support a fire or explosion.

TABLE 10-1 Ignition Sources from Ballistic Threats

| Class of Threat  | Specific Threat           | Ignition Sources                               |
|------------------|---------------------------|--|
| Guns/Projectiles | Armor piercing incendiary | Incendiary flash<br>Penetration flash          |
| Guns/Projectiles | High explosive incendiary | Incendiary flash Fireball<br>Penetration flash |
| Missiles         | Contact-fuzed missile     | Incendiary flash Fireball<br>Penetration flash |
| Missiles         | Proximity-fuzed missile   | Penetration flash<br>Incendiary flash Fireball |
| Bombs            | High explosive materials  | Fireball                                       |

TABLE 10-2 Ignition Sources from Mechanical Failures

| Class of Threat | Specific Threat             | Ignition Sources                         |
|-----------------|-----------------------------|--|
| Electrical      | Damaged wiring              | Sparking and arcing                      |
| Electrical      | Static discharge            | Sparking and arcing                      |
| Electrical      | Lighting                    | Sparking and arcing                      |
| Leaks           | Spray of flammable material | Hot surface ignition                     |
| Mechanical      | Engine part penetrates case | Flame and hot air outside of engine case |

Most test data are based on results from ground test facilities, some of which have the capability to simulate internal and external air flow. Air flow is critical in determining whether or not there will be a fire or explosion because it changes the fuel/air concentration ratio. Holes from ballistic damage can change the internal air flow; air flow in or over the ullage can decrease the ullage temperature quickly during flight. Fuel temperature remains relatively constant because of the fuel's large thermal mass, except when heated fuel is transferred to another tank.

In order to determine the probability of fire and explosion with ground tests, in-flight environmental conditions must be considered. Generally, the ullage temperature and oxygen concentration decrease as the altitude increases. According to computer models that simulate typical in-flight conditions, the probability of fire and explosion is nearly constant from sea level to 30,000 feet, but decreases at higher altitudes.

### DAMAGE MODES AND EFFECTS

Damage modes and effects depend on the nature of the threat and on the affected component. Threat-induced damage may result in component failure. How the component fails is called the failure mode. The importance of the failure depends on the type of component (i.e., flight controls) and the type of failure mode (i.e., loss of structural capability).

Equipment can be organized into three classes: nonredundant components (i.e., primary wing structure), redundant components (i.e., hydraulic flight controls), and non-critical components. Modeling of redundant components includes both cascading failures and the number of failures required to lose the function. Table 10-4 shows both nonredundant and redundant components.

TABLE 10-3 Location of Flammable Materials

| Material         | Equipment |       |                |              |          |
|------------------|-----------|-------|----------------|--------------|----------|
|                  | Tanks     | Pumps | Pressure Lines | Return Lines | Dry Bays |
| Fuel             | X         | X     | X              | X            | X        |
| Hydraulic Fluid  | X         | X     | X              | X            | X        |
| Avionics Coolant | X         | X     | X              | X            | X        |

### Factors that Alter the Probabilities of Fires and Explosions

The probability of a fire or explosion depends on numerous factors. Many of these factors are conceptually similar, but differ greatly in the details. Trade-off studies using a broad range of threats and resultant ignition sources are required to obtain robust designs.

Table 10-5 shows several factors that can alter the probability of fires and explosions. These factors are interrelated. The following are examples of how component details can alter the probability of fire: (1) the probability of fire from fuel pouring through a hole in a fuel tank wall is different from that of fuel spraying through a hole in a 400 psi fuel line; (2) a fire in a small dry bay with no air flow may go out, either because a large volume of fuel pours in and quenches the fire or because the fire burns up the available oxygen; (3) the probability of fire from fuel pouring through a small hole in a fuel tank wall is different from that for a dry bay being flooded, which can occur because of hydrodynamic ram (shock load transmitted through a fluid) damage induced by the impact of a fast large fragment or a high explosive projectile.

TABLE 10-4 Damage Modes and Effects

| Effect of Threat   | Critical Components | Failure Modes                            |
|--------------------|---------------------|--|
| Fire               | Flight controls     | Loss of yaw, pitch, roll control         |
| Fire               | Crew                | Personnel incapacitated by toxic fumes   |
| Fire               | Structure           | Loss of structural capability            |
| Fire               | Electrical          | Loss of power to support flight controls |
| Explosion or Blast | Flight controls     | Loss of yaw, pitch, roll control         |
| Explosion or Blast | Structure           | Loss of structural capability            |
| Penetration        | Flight controls     | Loss of yaw, pitch, roll control         |

### HARDENING APPROACHES

An aircraft that is hit by a ballistic threat will be damaged. Aircraft can be hardened to withstand this damage by removing the vulnerability, by using less vulnerable components, by shielding the components, and by adding features that increase damage tolerance. Removing the vulnerability is the desired approach, but often this is not practical. Hardening approaches that enable aircraft to tolerate damage are generally complex. In order to design a damage-tolerant aircraft, an allowable damage criteria must be developed. For example, a damage criteria might specify that the damaged structure withstand 50 percent of the worst case flight loads. Worst case flight loads should not include safety factors or aircraft life expectation. Defining the allowable damage criteria will facilitate trade-off studies (see Figure 10-2) and minimize the cost, weight, and maintenance impacts of hardening approaches.

#### Reducing Fires

General approaches to reducing fires are as follows: filtering personnel air; filling the dry bay with lightweight material (foam); adding a system that extinguishes fires; rapidly shutting off sources of flammable material; adding fire walls; and separating flammable materials from ignition sources. These hardening approaches are applicable to several classes of dry bays and equipment. Table 10-6 present additional information regarding hardening approaches shown to reduce the vulnerability of combat aircraft to fire. Each hardening approach has positive and negative attributes. For example, foam is very effective against small fragments but does not work well for high explosive threats because the blast displaces the foam.

#### Reducing Explosions

Two classes of hardening approaches to reduce the likelihood of explosions are shown in Table 10-7. The first method

is intended to prevent an ullage explosion. This approach uses foam or inerts the ullage by increasing the nitrogen (reducing the oxygen) concentration to eliminate the explosion. The same hardware is required to inert an ullage space or a dry bay. The second approach increases the aircraft's capability of with standing an explosion but has huge weight and cost penalties.

TABLE 10-5 Factors That Alter the Probability of Fires and Explosions

| Item                                       | Fires  |   | Explosions  |      |
|--|--|---|---|------|
|  | Factors  | Item                                      | Factors   | Item |
| Dry Bay Environment                        | Oxygen content<br>Fuel/air ratio<br>Distance of ignition source from liquid spray                            | Ullage Environment                        | Oxygen content<br>Fuel/air ratio<br>Explosion temperature limits  |      |
| Factors That Alter the Dry Bay Environment | Pressure and hole size<br>Bay size and fluid flow<br>Clutter<br>Air flow (internal and external)<br>Altitude | Factors That Alter the Ullage Environment | Fuel and ullage temperature<br>Shock propagation distance<br>Fuel splashing<br>Internal air flow (internal and venting)<br>Altitude |      |
| Ignition Sources                           | Energy intensity, size, and length of flash<br>Type of threat  | Ignition Sources                          | Energy intensity, size, and length of flash<br>Type of threat   |      |

**TEST AND MODELING CONCERNS**

**Fire Modeling**

Modeling of a dry bay fire is very complex. The three methods of dry bay fire modeling are described below.

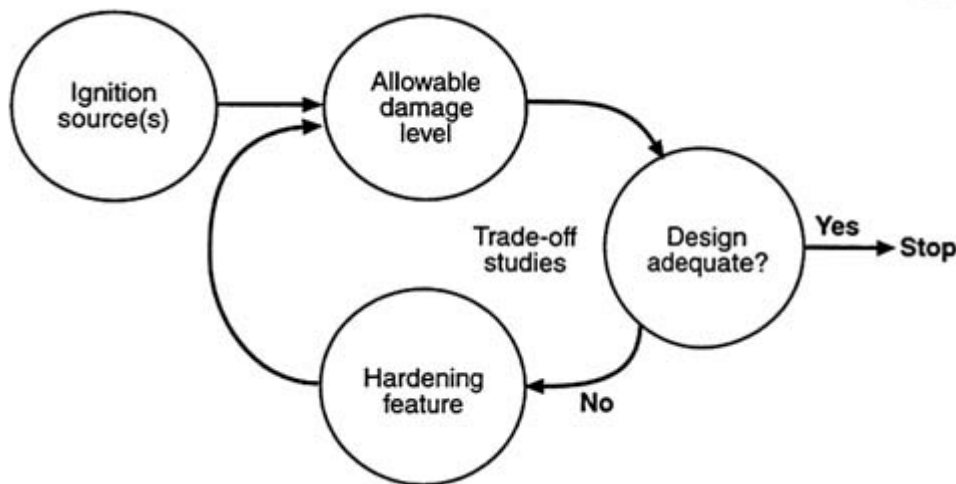


FIGURE 10-2 Trade-off study approach.

The computation of vulnerable area and repair time (COVART) model assesses the probability of aircraft loss for a wide range of threats. The COVART model determines the component and system probability of kill for several kill mechanisms, such as functional failure, fire kills, blast kills, and others. The fire and explosion kill methodology uses the air gap method which involves tables that are a function of fragment mass, fragment velocity, air gap distance from a striker plate, and the component being hit. The data come from predictive models and test data. The air gap tables and numerous rules are used to predict the probability of fire.

The WINFIRE model is a physics/chemistry-based model that assesses the probability of a sustained fire in a dry bay

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TABLE 10-6 Hardening Approaches to Reducing Fires

| Location             | Equipment                           | Reason for Design Concern   | Hardening Approach  |
|----------------------|-------------------------------------|---|---|
| Pilot                | Pilot air                           | Smoke and fumes can overcome the crew.  | Oxygen mask and filtered air supply   |
| Pilot                | Crew station materials              | Smoke and fumes can overcome the crew.  | Nonflammable materials for cockpit and crew ensemble  |
| Flight Controls      | Mechanical and electrical lines     | Fire can damage flight controls causing loss of yaw, pitch, and roll control.   | Separated critical redundant equipment  |
| Flight Controls      | Flight computers and power supplies | Fire can damage flight controls causing loss of yaw, pitch, and roll control.   | Separated critical redundant equipment  |
| Internal Weapons Bay | Surrounding structure               | Sustained fire around weapons will result in high order explosion.  | Fire resistance/ablative material added to contain fire<br>Critical equipment and lines removed from internal weapons bay |
| Internal Weapons Bay | Air through weapons bay             | Sustained fire around weapons will result in high order explosion.  | Weapons bay sealed to eliminate flame propagation to other dry bays   |
| Dry Bays             | Hot equipment                       | Leaking flammable material on hot surfaces can start a fire.  | Fluid path restricted by use of double walls  |
| Dry Bays             | Fuel lines                          | Removing or shutting off source of flammable material from dry bay will limit cascading fire damage. Sustained fire will damage critical equipment. | Valves shut at fire walls<br>Fuel lines routed within fuel tanks  |
| Dry Bays             | Hydraulic lines                     | Removing or shutting off source of flammable material from dry bay will limit cascading fire damage. Sustained fire will damage critical equipment. | In-line shut-off valve and sensor for each redundant branch   |
| Dry Bays             | Avionics coolant lines and modules  | Removing or shutting off source of flammable material from dry bay will limit cascading fire damage. Sustained fire will damage critical equipment. | Reservoir sensor with pump shut-off switch  |
| Dry Bays             | Tank walls                          | Sustained fire will damage critical equipment.  | Power packs to suppress fire<br>Bladders to seal small holes<br>Foams to fill the dry bay                                 |
| Dry Bays             | Dry bay fire suppression system     | Sustained fire will damage critical equipment.  | Active or passive fire suppression system<br>Inerted dry bay air  |
| Dry Bays             | Engine bay fire suppression system  | Sustained fire will damage critical equipment.  | Pilot-activated shut-off of engine fuel supply and pilot-activated fire suppression system                                |
| Dry Bays             | Engine inlet                        | Fuel in engine inlet can cause a rapid explosion or cascading fire.   | Fuel removal from inlet before going into combat<br>Bladders to seal small holes and limit fuel into engine inlet         |

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and provides air gap data for the COVART model. This model assumes the flammable material spray and ignition flash shape and size, and determines responses (temperature and pressure) within a volume. Based on the physical overlap of the spray and ignition flash, the model predicts if a fire will start. With sufficient heat and oxygen, the model predicts the dry bay temperature and pressure. The WINFIRE model accounts for the threat initial ignition conditions.

TABLE 10-7 Hardening Approaches to Reducing Explosions

| Location  | Equipment  | Reason for Design Concern   | Hardening Approach   |
|-----------|--|---|--|
| Ullage    | Foam   | Ullage explosion pressure can induce structural damage that results in global structural failure. | Foam to stop the explosion flame/shock front from growing and propagating across the ullage volume |
| Ullage    | Inerting by advanced air-separating module-permeable membrane, molecular sieve, liquid nitrogen, or gaseous nitrogen | Ullage explosion pressure can induce structural damage that results in global structural failure. | Addition of nitrogen enriched air to ullage to lower (less than 12%) oxygen concentration          |
| Structure | Fuel tank structure  | Ullage explosion pressure can induce structural damage that results in global structural failure. | Structural dynamic load allowable pressure increased   |

Heat transfer finite difference/finite element models are numerical/physics/chemistry-based models that determine responses (temperature and pressure) within solid elements. The user must define the threat initial ignition conditions and environmental conditions. This method of modeling is used to study localized, detailed effects.

### Fire Testing

Fire test results are probabilistic. In general, parametric tests are required to obtain reasonable data. For example, a test series with two shots (one with a fire and one without) has a probability of fire of 0.5 with a range of  $\pm 0.5$ . In cases where test results are mixed, additional shots are needed to obtain quality data. Mixed test results indicate that something is changing. Understanding the reason for the change is critical, but difficult.

Defining a fire is difficult. The classical measures are temperature and pressure. Based on numerous tests, the classical methods of evaluation appear to be inadequate for many tests. Most test measurements are made along the dry bay edge, although the WINFIRE model temperature prediction is the average dry bay temperature. Hence, comparing test results and the WINFIRE model is difficult. Finite element results and test data need to be collected at various locations in a dry bay.

### Explosion Modeling

The objective of an ullage model is to predict the ullage concentrations, peak pressure, and pressure time history over the volume of the fuel tank. Ullage environmental conditions are very complex. The fuel acts as a large heat sink because of its large thermal mass. The ullage has internal air flow which may have liquid splashing. The outer skin can either add or subtract heat from the ullage depending on aircraft velocity and altitude. Pretest predictions of ballistic explosion pressures do not correlate well with test results, although our understanding is improving.

### Explosion Testing

Ballistic tests of JP-8 fuel have shown that bomb samplers do not adequately define the edge of the temperature explosion curves. A bomb sampler ignition source is less intense than some threats; but more intense ignition sources could expand the explosion curves.

Hardware that is capable of measuring fuel tank oxygen and fuel/air ratio is very limited. Hence, it is difficult to determine the concentrations in aircraft or in test articles. This problem makes it difficult to compare model and test data.

### SUMMARY

This paper has used a systems engineering process to break down a complex technical problem into its basic elements: flammable material; ignition source; and oxygen. The goal of this paper is to inform aircraft designers and managers of the basic elements and concepts involved in reducing an aircraft's vulnerability to fires and explosions.



Reducing aircraft vulnerability requires considerable activity early in the design phase. Add-on features to reduce vulnerability are generally less effective and incur higher life cycle costs than features incorporated in the design. An effective vulnerability reduction program requires a robust and comprehensive systems engineering process based on tests and analyses. Early analyses of vulnerability and numerous critical tests using components, simulators, and replicas are needed to support design decisions. Using models for making pretest predictions, then testing, correlating test results to pretest predictions, and correcting models is critical to understanding this complex problem. Unfortunately, lack of funding has hampered the development of effective models.

The cost of modeling and testing may appear to be high; however, it is much lower than the cost of an ineffective design. We know that inerting ullage and dry bays would significantly reduce the vulnerability of aircraft but may be too costly.

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## 11

# Aircraft Fuel System Design Issues

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### ABSTRACT

This presentation is intended to provide an understanding of design considerations for the fuel system of a typical commercial aircraft, with an emphasis on safety. Current design methods to make the fuel systems as safe as possible are a culmination of technological advances combined with information from operational experience and accident investigations. The presentation briefly addresses past efforts to improve post-crash fire safety and concludes with recommendations for future research.

### AIRCRAFT FUEL SYSTEM

The aircraft fuel system is designed to store and deliver fuel to engines and auxiliary power units (APU) safely for a variety of flight missions, including emergency situations. The major design considerations for the system, in addition to the necessary basic performance requirements, are safety, compatibility, reliability, and maintainability. In this paper, a description of the aircraft fuel system performance, safety, and compatibility will be followed by specific considerations for safety fuels.

#### Performance

Major components of a typical commercial jet airplane fuel system are:

- vented tank system primarily using the wing box (mainly a structural design issue)
- engine fuel feed and transfer system (plumbing design using electrically driven pumps)
- fuel quantity measurement and indication system (capacitance or ultrasonic gauging)

#### Fuel Tanks

Fuel tanks are usually located within the wing box of the airplane. A minimum of one tank for each engine is provided. For example, on a twin engine airplane, there is one main tank on each side of the fuselage. If the airplane size and range require additional fuel capacity, then the center wing box is designed to hold fuel. On a four engine aircraft, there are two main tanks on each side of the fuselage with additional capacity provided by the center tank. The fuel system may also include reserve tanks and surge tanks and, occasionally, body tanks. The tanks are integral type sealed structures and vented to the atmosphere; there is at least one open vent port (for each tank) under all conditions. The vent system is designed not to exceed pressure limits for tanks. The tank structure mainly consists of spars, ribs, and stringers. An example of the system is shown in [Figure 11-1](#).

#### Engine Feed System

Independent fuel feed to each engine must be provided with a capability for cross-feeding when necessary. In addition, suction feed capability must be provided to ensure fuel flow to engines when boost pumps are inoperative. Another important consideration is negative 'g' operation. A typical engine feed system consists of electrically driven pumps, fuel lines, valves, and fittings (shown in [Figure 11-2](#)). An independent fuel feed is also provided for the auxiliary power unit. The system is designed to minimize the volume of unusable fuel in the tank and incorporates means to remove accumulated water.

#### Fuel Quantity Measurement and Indication System

The fuel quantity measurement system employs either capacitance or ultrasonic gauging usually combined with density measurement to indicate the quantity to the flight crew and the wing fueling station. Each tank has 10 to 14 probes to determine the height of the fuel at locations throughout the tank using one of the above methods. Capacitance gauging may also include a compensator in each tank. The fuel height and density data are input to processors where, using the airplane wing data, they are converted into fuel mass in each tank. Accuracy and reliability of the system are important for managing the system in flight as well as for determining the weight of the aircraft at takeoff. Other means of calculating

fuel quantity are fuel measuring sticks (to be used on the ground) and fuel flow meters.

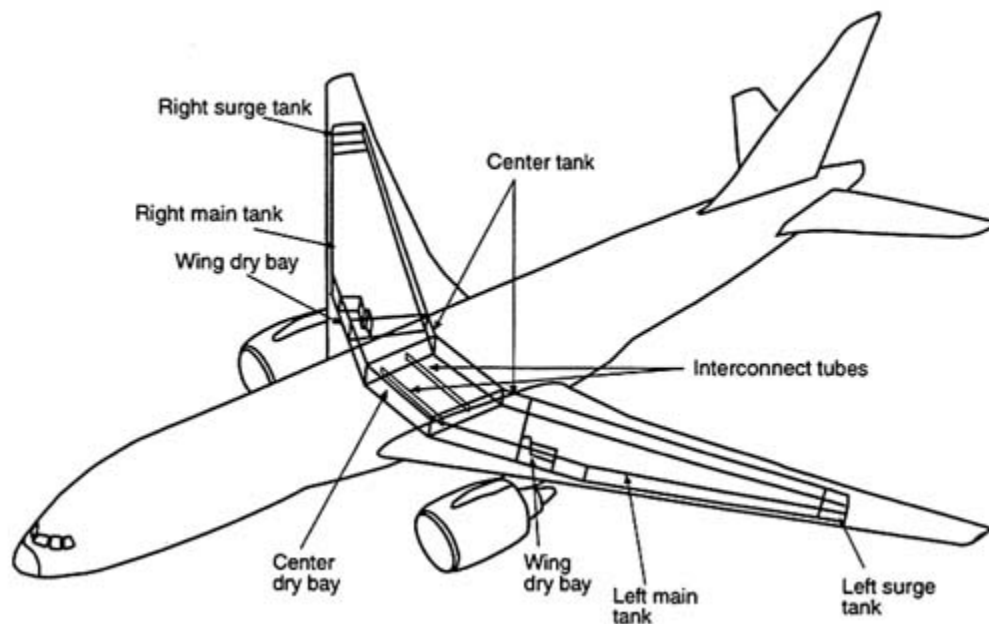


FIGURE 11-1  
Airplane fuel system, general arrangement.

### Fuel Jettison

The fuel system is designed for pressure fueling and defueling. Some aircraft are also equipped for jettisoning fuel overboard to reduce aircraft weight in an emergency landing.

### Fuels

Typical aircraft turbine fuels include Jet A and Jet A-1, which are commonly used throughout the world except in China, the former Soviet Union, and Eastern Europe; Jet B, which has higher vapor pressure than Jet A and is used in some countries with extremely cold weather; JP-8, which is the US and NATO military equivalent of Jet A-1; and JP-4, which is a higher vapor pressure fuel which was used in military aircraft in the past but is in limited use now. Russian fuels, designated TS-1 and RT, and a Chinese fuel, designated Jet 3 (RP-3), are also used in aircraft produced in Western countries.

### Safety

When considering fuel management, designs are aimed at minimizing the hazards of fire and explosion. Three elements are necessary to produce a fire or explosion, flammable material, oxygen, and an ignition source. Eliminating any one of these elements reduces the risk of fire to zero. The system designer has the most control over the ignition source. Therefore, major emphasis has been placed on eliminating potential ignition sources. In areas where ignition sources cannot be completely avoided, attempts have been made to minimize inadvertent leaks of flammable fluids and to provide ventilation to prevent the accumulation of vapors. In addition, structural designs have been made crashworthy to reduce the fire risk following a crash. Thus, three major ways of making a fuel system safer are: ignition source control, flammable fluid control, and crashworthiness. Details of how these methods are employed in fuel system installations follow.

### Tank Installations

Spaces adjacent to fuel tanks, such as the leading and trailing edges of the wing, are provided with ventilation and drainage. This prevents the accumulation of hazardous vapors or liquid fuel. Ventilation and drain outlets are located to avoid discharging flammable fluids into potentially hazardous areas. Flight tests are carried out to verify that vent areas are adequate and that there is no pressure buildup. Fuel tanks are always isolated from occupied compartments by fume-proof and fuel-proof barriers. An uncontained engine failure can damage a fuel tank, causing a fuel leak. Dry bays are provided in tank installations to avoid fuel leakage in the zone above the engine where it could create a fire hazard by dripping onto hot engine surfaces.

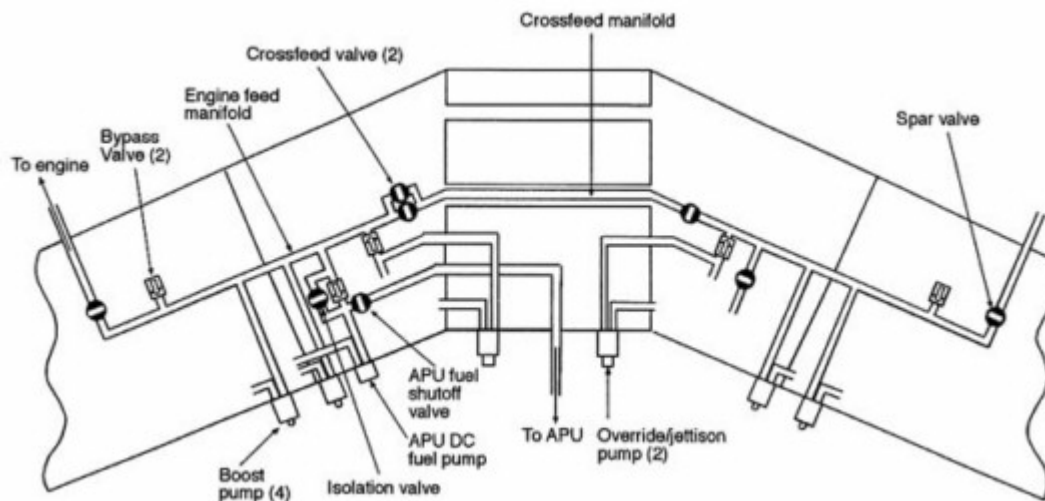


FIGURE 11-2  
Engine and APU fuel feed system.

### Fuel Shutoff

Fuel shutoff capability is provided for each engine and auxiliary power unit installation. Independent fuel shutoff valves are located outside the fire zones at the fuel tank boundary in a protected area, typically on the wing spar. When the valve is closed, it prevents fuel from being delivered to the engine or large quantities of fuel from being liberated through a broken line in case of a complete engine separation. Wiring to the valve is duplicated and separated, and two sources of actuation are provided, one by the fire handle and the other at the engine cutoff lever. The valve is commanded closed when the engine is shut down and remains attached to the tank if the line is broken.

### Ignition Source Control

Maintaining tank-mounted equipment below the maximum allowable external-surface temperature provides a margin of safety against fuel vapor ignition in normal and failure modes. A sample of each component is tested to verify that the safe temperature limit is not exceeded. Equipment located within fuel tanks, such as electrically driven fuel pumps, must be explosion proof. This capability is demonstrated in tests in which a combustible mixture is intentionally ignited inside the component while the component is surrounded by a second explosive mixture. To be considered explosion proof, the component must retain its structural integrity without igniting the surrounding mixture.

The power input to quantity measurement and indication systems is kept extremely low to prevent the risk of any malfunction causing sparks with sufficient energy to cause ignition. For the same reason, electrical equipment is bonded to the aircraft structure. To prevent the accumulation of hazardous charge on components through which there is high fuel flow, bonding is provided for static electricity dissipation. Fuel flow during fueling operations is also controlled and distributed to minimize the accumulation of electrostatic charge.

Fuel lines are adequately separated from electrical wiring; as a further precaution, fuel lines are routed below the wiring runs to ensure that any fuel leakage will not contact potential ignition sources, such as wires and electrical components.

### Fuel Carrying Components

Components and lines carrying fuel are sometimes located in or near fire zones where leaking fuel poses a potential risk. Inside the fire zones, these components and lines are made fireproof. Potential for leakage from fuel line connections and components is controlled by shrouding the possible source with a second sealed barrier. The shroud is drained overboard, and the drain exit is located where it is safe and observable so that leaks can be detected and repaired before they become hazardous. Fuel lines routed through the pressurized areas have a drainable and vented shroud that completely encloses the line. The vent line leads to a safely located drain mast. An

example of a shrouded fuel line and shroud drain with a flame arrester is shown in [Figure 11-3](#).

### Crashworthy Designs

The fuel system is designed with extreme care to maximize system protection during wheels-up landing as well as in crash situations. Fuel system components are located in areas protected by the aircraft structure and away from the "wipe-off" zone to minimize the possibility of fuel leakage and ignition in the event of a wheels-up landing. The heavy structural members and fuselage skin absorb the energy of the landing impact and provide protection against scraping action on the ground.

Break-away landing gear, break-away strut attachments, and break-away flap attachments are designed to prevent the rupture of the fuel tanks. All tanks within the fuselage contour are designed to withstand specified emergency landing loads. In aircraft equipped with auxiliary fuel tanks to extend their range, the tanks are normally contained within the fuselage lower cargo compartment and are suspended from the main fuselage floor to provide additional ground clearance. Fuel and vent lines that connect these tanks to the main fuel system incorporate drainable and vented shrouds. These lines are either designed to break away or to be sufficiently flexible to accommodate tank movement without causing fuel spillage. This flexibility is also required for lines to the auxiliary power unit, which is normally installed in the aircraft tail section.

### Vent System

The vent system maintains inside tank pressure at near ambient pressure by allowing airflow into and out of the tanks during fuel usage and fueling. The vent outlet is located in the lower wing surface, away from the wing tip and edges to avoid areas that are most subject to lightning strikes. The outlet is either flush or recessed to preclude corona and streamers. [Figure 11-4](#) illustrates a typical arrangement. A flame arrester system in the vent outlet line protects the system from an external ground fire source.

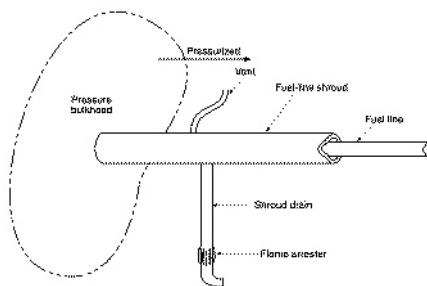


FIGURE 11-3  
A shrouded fuel line in a pressurized compartment.

### Lightning Protection

A significant consideration of aircraft fuel system safety is lightning protection. Skin panels in the fuel tank area are sufficiently thick to preclude a lightning strike penetrating them, and structural joints are conductive to prevent internal sparking in the event of a lightning strike. Removable doors and panels located in critical vapor areas are designed to maintain electrical continuity to preclude sparking during a lightning strike. Tests are conducted to demonstrate a safe design.

### Compatibility

In addition to performance and safety requirements, the aircraft fuel system must be evaluated for compatibility with materials to which it will probably be exposed. In other words, materials used in the system structure, plumbing components, and pumps and valves must be evaluated for compatibility with both domestic and foreign fuels, with and without common additives. Various coatings, seals, and sealants must also be compatible with fuels and additives. Material compatibility is usually established by conducting extensive testing.

The fuel system must be able to handle small quantities of water, which may separate from fuel or may result from the condensation of water vapors ingested through the vent system. When the aircraft hydraulic system is cooled through a fuel heat exchanger, there is a potential for hydraulic fluid leakage into the fuel tank. Therefore, possible fuel contamination from hydraulic fluid must also be considered. Small amounts of particulate contamination must be safely handled by the system. In addition, engine hardware and materials are designed to be compatible with hot fuel and products of combustion at high temperatures. The aircraft fuel system interface must also be compatible with airport fuel systems and ground supply equipment.

### Considerations for Safety Fuels

#### Performance and Uses

In view of the focus of this workshop on fuels with improved fire safety, it will be helpful to review the secondary uses of fuel in an aircraft fuel system. The fuel is used as a



heat sink for excess heat from engine accessories. When fuel is being pumped, it also keeps the pump temperature under control. In many systems, ejector pumps are provided to move accumulated water from low areas of the tank to the main pump inlet. These pumps require fuel from the boost pump to operate. Fuel can be used to feed any engine from any main or center tank and, on some aircraft, can be transferred from tank to tank relatively easily; therefore, fuel can be used effectively for controlling the aircraft center of gravity. Proper fuel management also provides wing bending relief as well as airplane flutter control. In the engine, fuel also serves as a hydraulic fluid and a coolant. The many uses of the fuel mean it is handled many times. The fuel must flow through a complex fuel metering unit with narrow passages as it is delivered to the engine combustor.

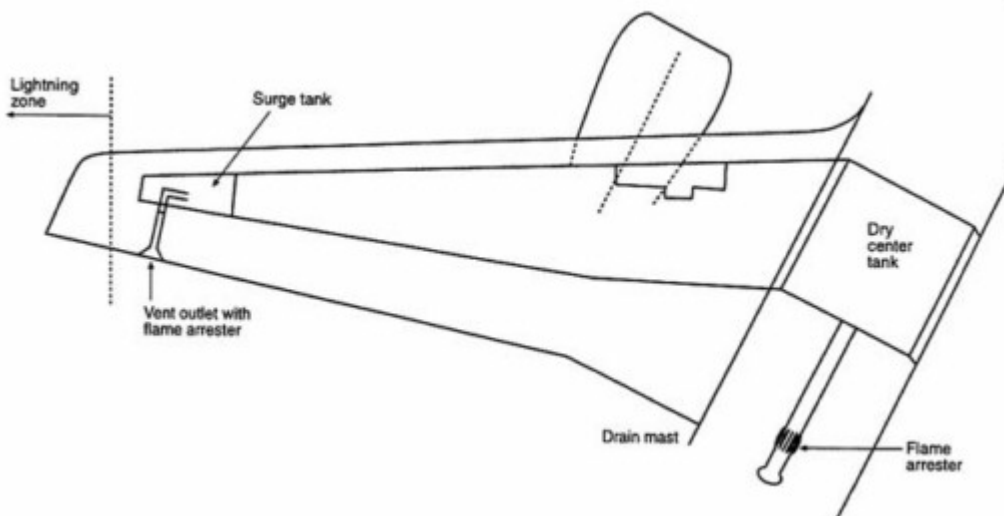


FIGURE 11-4  
Typical installation of a fuel tank vent system.

Recovering fuel from tanks (minimizing unusable fuel quantity) is important to aircraft range and performance. The fuel recovery efficiency is currently about 99.5 percent. The current fuels provide adequate suction feed capability (flow with minimal pressure drop), which must be maintained with fuels modified for safety. The fuel must flow at low temperatures, and there should be no significant increase in freezing point. To maintain the ranges and routes currently offered by airline operators, modified fuels must have volumetric energy content nearly equivalent to current fuels. Fuel electrostatic (charging) characteristics should be no worse than current fuels to ensure that the current safety levels are not adversely affected. The preferred conductivity range is 50 picosiemens per meter (pS/m) to 450 pS/m. In general, the fuel must meet the ASTM D-1655 specification or other acceptable specification and should not adversely affect engine starting, engine operation, or emissions.

### Compatibility

Safety fuels must also demonstrate compatibility with existing engine and airframe fuel systems and materials (small modifications may be acceptable), current fuels and additives, existing airport fuel systems and ground supply equipment, and be capable of accepting different fuels (switch loading). Finally, the safety characteristic must remain intact after fueling the aircraft. That is, the characteristic that makes the fuel safe must not be altered by the process of fueling under pressure and high flow rates.

### History of Safety Fuels

Some of the concepts investigated in the past to improve post-crash fire safety include gelled fuels, emulsions, and long chain polymer additives. Gelled fuels were not successful because of the large amount of unrecoverable fuel or ineffectiveness with volatile fuels (JP-4, Jet B). Antimisting kerosene (AMK) fuels were promising in many laboratory and field tests but required degrading before the fuel could be used in engines. Adding systems to convert a safety fuel back to normal fuel could decrease reliability and efficiency while

increasing the weight and cost of the overall system. A controlled impact demonstration showed that AMK would not be effective in all post-crash situations.

### RECOMMENDATIONS

The excellent safety record in the commercial aviation industry has been achieved by continuous emphasis on design improvements, guidelines for safe operations, and improved facilities. Fuel treatment or conditioning may further improve aircraft fire safety and would be a desirable goal for research and development if economic constraints were satisfied.

- In any concept that involves modifying fuels to improve safety, higher vapor pressure fuels and foreign fuels should be included.
- A user panel should assist in evaluating different concepts and detailed R&D activities.
- An early economic assessment should be done for various concepts and should include not only the fuel costs and performance penalties but also the cost of introduction.
- Maximum use should be made of previous experience to guide the development.
- A rigorous assessment of the impact of fuel modification on other aircraft components and operations should be conducted.

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## IV

# Presented Papers Characterizing Fuel Fires

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## 12

# Combustion Fluid Mechanics: Tools and Methods

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### ABSTRACT

Current understanding and methods of modeling combusting fluid flows are briefly reviewed, emphasizing liquid-fueled buoyant turbulent diffusion flames that are of interest for developing more fire-safe aviation fuels. Liquid fuel/air combustion in both spray flames and pool fires is discussed, considering laminar diffusion flames, buoyant turbulent noncombusting flows, buoyant turbulent diffusion flames, and turbulent sprays and spray flames.

### INTRODUCTION

Post-crash fires caused by the ignition of jet fuel released from damaged fuel systems are an important problem of aircraft fire safety. In particular, fuels with improved fire safety are needed to reduce injuries, loss of life, and the loss of property associated with post-crash aircraft fires. Naturally, a good understanding of the properties of liquid-fueled fires burning in air is a prerequisite for developing fire-safe fuels. Current knowledge about the combustion and fluid-flow phenomena of fires, as well as about available methods of predicting fire properties, are discussed briefly, with emphasis on the burning of liquid fuels both as sprays and pools. The following topics are discussed in turn: laminar diffusion flame structure, buoyant turbulent noncombusting flows, buoyant turbulent diffusion flames, and turbulent sprays and spray flames.

### LAMINAR DIFFUSION FLAMES

#### Modeling Laminar Diffusion Flames

Post-crash aircraft fuel fires are invariably turbulent; nevertheless, an understanding of steady laminar flames is a prerequisite for understanding the complex, unsteady, three-dimensional combusting flow phenomena of turbulent flames. Many contemporary models treat turbulent flames as a collection of distorted laminar flames using laminar flamelet concepts. Thus, consideration of combustion fluid mechanics begins with understanding the properties of laminar flames, examining methods of modeling laminar flames, understanding laminar diffusion flame structure, and conceptualizing laminar diffusion flamelets.

Except for a few cases associated with flame ignition and attachment, laminar flames are either nonpremixed (diffusion) flames, where the supplies of fuel and oxidant are separated prior to combustion (e.g., a kerosene lamp flame), or premixed flames, where the fuel and oxidant have been combined before combustion (e.g., a laboratory Bunsen burner flame). Post-crash aircraft fuel fires either involve fuel sprays produced by ruptured fuel lines and fuel tanks to yield spray flames, or liquid fuel spread along aircraft surfaces and the ground to yield pool fires. In both cases, the most representative corresponding laminar flame is a laminar diffusion flame; therefore, this flame configuration will be emphasized, considering both models and experiments.

Contemporary methods of modeling laminar diffusion flames emphasize detailed fluid mechanics, transport, and chemical reaction mechanisms. The fluid mechanics and transport aspects of these models are usually based on the CHEMKIN family of computer codes developed by Kee et al. (1986, 1989, 1990, and 1991). These codes allow for effects of multicomponent transport, including thermal diffusion, and variable thermochemical and transport properties under ideal gas approximations that are appropriate for approximating flames at atmospheric pressure. One-dimensional steady calculations are typically based on available detailed chemical reaction mechanisms that provide information about the hundreds of reversible reactions needed to model complex hydrocarbon-fuel/air combustion chemistry (see Chelliah et al., 1992, for typical examples). In spite of relatively uncompromising treatments of fluid mechanics, transport, and chemical reactions, however, these models frequently ignore radiation, which affects temperature distributions in flames, even though radiation can be treated using available technology (Faeth et al., 1989). Other limitations of detailed models of laminar diffusion flames are discussed below.

### Laminar Diffusion Flame Structure

An example of the structure of a heterogeneous liquid-fueled laminar diffusion flame burning in air is illustrated in Figure 12-1. Measured concentrations of major gas species and temperature (Kent and Williams, 1975), along with corresponding predictions (Chelliah et al., 1992), are plotted as a function of distance along the axis of an opposed-jet diffusion flame involving liquid n-heptane and air at a modest strain rate. The results illustrate the main features of laminar diffusion flames proposed by Burke and Schuman nearly 70 years ago: fuel vapor ( $C_7H_{16}$ ) and oxygen ( $O_2$ ) diffuse from opposite sides toward a flame sheet where they react so that the concentrations of saturated combustion products ( $CO_2$  and  $H_2O$ ) and the temperature reach maximum values; subsequently, heat flows away from the flame sheet and preheats the fuel and oxygen streams and also provides enough heat to vaporize the fuel at the liquid surface. A more complete chemical reaction mechanism used for the predictions illustrated in Figure 1, however, captures features not considered by Burke and Schuman or other classical models, e.g., the decomposition of the fuel into CO and  $H_2$  and the leakage of small concentrations of  $O_2$  to the fuel-rich side of the flame.

Although the agreement between the predictions and the measurements illustrated in Figure 12-1 is encouraging, there are many problems that must be resolved before the structure of even very simple laminar diffusion flames can be reliably predicted. First of all, fuel-decomposition chemistry is not known very well for the heavy hydrocarbons present in aircraft fuels. More importantly, laminar diffusion flames of hydrocarbon fuels in air generally involve processes of soot chemistry that are not understood well enough to make predictions regarding concentrations of soot precursors and soot of comparable accuracy to those in Figure 12-1.

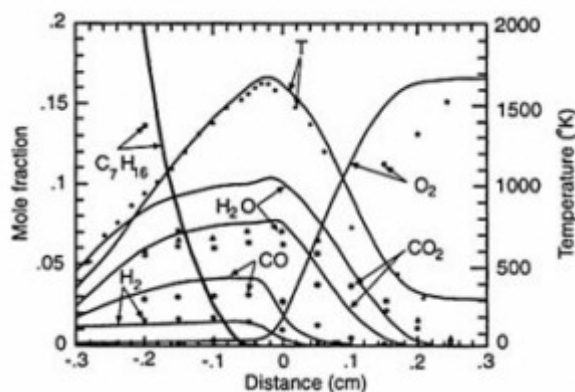


FIGURE 12-1  
 Measured and predicted structure of a laminar liquid-fueled diffusion flame.  
 Measurements and predictions from Kent and Williams (1975) and Chelliah et al. (1992).

This is unfortunate because soot is an obvious feature of hydrocarbon-fueled fires and must be considered for accurate predictions of emissions of toxic materials and flame radiation (Köylü et al., 1991). But, concentrations of soot precursors and soot are relatively small in diffusion flames, which tends to mitigate the penalty of ignoring these properties for some purposes (Sunderland et al., 1995). Finally, full chemical reaction mechanisms are too computationally intensive at the present time for making tractable calculations in more than one independent variable. Various approximate methods have been developed to avoid these difficulties.

### Laminar Diffusion Flamelet Concepts

Numerous reduced chemical reaction mechanisms have been proposed to provide computationally tractable ways of treating the multidimensional time-dependent laminar diffusion flames to be used in developing laminar flamelet concepts for turbulent flames. For present purposes, however, an effective way to model soot-containing hydrocarbon-fueled flames is needed, which is beyond the capabilities of current detailed reaction mechanisms. Fortunately, a reasonably effective alternative has been found.

The conserved-scalar formalism, combined with the laminar flamelet concept, has proven to be a reasonably effective way to treat soot-containing hydrocarbon-fueled turbulent diffusion flames (Bilger, 1976; Faeth, 1983, 1987, and 1996; Gore and Faeth, 1988a, 1988b). This approach is based on an extension of Burke and Schuman's ideas about laminar diffusion flames developed by Bilger (1976). In particular, Bilger noticed that scalar properties in soot-containing laminar diffusion flames could be correlated effectively in terms of the extent of mixing (usually represented either by the local mixture fraction, defined as the fraction of mass in a sample that originated in the fuel, or the local fuel-equivalence ratio). This behavior was observed for wide ranges of flame sheet combustion rates, or flame strain rates, in spite of the effects of finite reaction rates associated with fuel decomposition and soot chemistry. These correlations have been termed state relationships, and they are applied to turbulent flames by assuming that turbulent flames correspond to wrinkled laminar flames (Bilger, 1976).

Numerous measurements of state relationships for both liquid and gaseous hydrocarbon-fueled laminar diffusion flames have been reported (see Bilger, 1976; Faeth and Samuelsen, 1986; Gore and Faeth, 1988a, 1988b; Sivathanu and Faeth, 1990, for typical examples). Recent predictions using detailed chemical reaction mechanisms for laminar opposed-jet diffusion flames justify this behavior over strain rate ranges extending from near zero up to quenching conditions for nonsoot-containing flames (Lin and Faeth, 1991). This behavior is explained by the strong nonlinearity of reaction rates with temperature so that the flame structure changes



very little prior to abrupt extinction as strain rates are increased. Nevertheless, corresponding results for soot-containing flames have not been reported.

Although the laminar flamelet concept clearly is very helpful, the need for measurements in laminar flames to provide state relationships for soot-containing hydrocarbon-fueled flames is a significant limitation. Fortunately, universal state relationships have been found for hydrocarbon/air diffusion flames that circumvent this difficulty. A universal state relationship for the concentration of  $\text{CO}_2$  in diffusion flames is illustrated in Figure 12-2, where the universal state relationship function defined by Sivathanu and Faeth (1990),  $(\bar{Y}_{\text{CO}_2})$ , is plotted as a function of the local fuel-equivalence ratio based on measurements for a variety of fuels and flame strain rates (see original sources for the details of these flames). The universal functions were motivated by the expectations of chemical equilibrium at fuel lean conditions; clearly, the equilibrium predictions illustrated in Figure 12-2 support this hypothesis. Although finite rate effects cause significant departures from equilibrium at fuel rich conditions, these departures are fortuitously universal. Thus, universal state relationships and laminar flamelet concepts provide a reasonable treatment of scalar properties in soot-containing diffusion flames pending improved understanding of finite-rate effects associated with fuel decomposition and soot chemistry, as well as the development of increased computer capabilities that will make consideration of detailed chemistry in practical calculations computationally tractable. The next problem involves predicting mixing levels (mixture fractions) within the buoyant turbulent flows of interest for post-crash fires.

## BUOYANT TURBULENT NONCOMBUSTING FLOWS

### Modeling Buoyant Turbulent Flows

Post-crash fires are reasonably represented by liquid-fueled buoyant turbulent diffusion flames. Given state relationships to find scalar properties in diffusion flames, methods of predicting mixing levels in liquid-fueled buoyant turbulent diffusion flames must be addressed. We must first understand noncombusting single-phase buoyant turbulent flows for the present before we address complications due to combustion and multiphase flow.

Several methods are commonly used to model noncombusting single-phase buoyant turbulent flows. Integral models are the simplest approach and are often used to treat unit flow processes (e.g., fire plumes, flows along ceilings, etc.) in comprehensive models of fires in structures. This approach is less attractive, however, for the open flames in post-crash fuel fires, and integral models will probably not be widely used to assist the development of fuels with improved fire safety. Thus, integral methods will not be considered here.

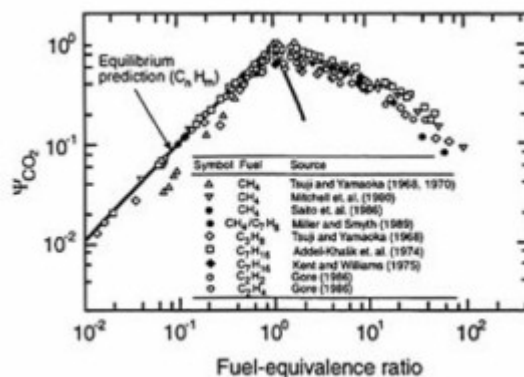


FIGURE 12-2

Measured universal state relationship for carbon dioxide species concentrations in laminar hydrocarbon-fueled diffusion flames. Source: Sivathanu and Faeth, 1990.

Turbulence models and numerical simulations of turbulence, however, should be of interest for fuel development and have already been applied to open liquid-fueled turbulent diffusion flames typical of post-crash fires (Tieszen et al., 1996).

The following discussion will begin with consideration of self-preserving flows that can be helpful for evaluating predictions of models of buoyant turbulent flows. The description and the findings of turbulence models and numerical simulations will then be considered.

### Self-Preserving Buoyant Turbulent Flows

Many classical stationary turbulent flows become self-preserving sufficiently far from the source that effects of source disturbances are lost, and properly scaled flow properties become independent of the distance from the source. Such self-preserving flows are fundamentally important because they simplify the interpretation of scaled flow properties even though few flows reach these conditions in the real world. Self-preserving flows also are valuable for testing models of turbulent flows because source disturbances are avoided while modest streamwise development rates (in scaled variables) enhance numerical accuracy.

As discussed by Dai and Faeth (1995, 1996) and Dai et al. (1994, 1995a, 1995b), self-preserving buoyant turbulent flows have only been reliably established for round buoyant turbulent plumes. The development of these flows toward self-preserving behavior is illustrated in Figure 12-3 where mean mixture fractions,  $\bar{Y}_{\text{CO}_2}$ , are plotted as a function of radius,  $r$ , normalized by streamwise distance from the virtual origin of the flow,  $(x-x_0)$ , for various values of  $(x-x_0)$  normalized by the source diameter,  $d$ . Self-preserving variables are used for this plot (see Dai et al., 1994) for specification of all notation. Near the source, scaled profiles of  $\bar{Y}_{\text{CO}_2}$  clearly vary with

$(x-x_0)/d$ , however, once  $(x-x_0)/d > 80$ , the scaled profiles become universal indicating that self-preserving behavior has been achieved. These results showed that self-preserving plumes were present farther from the source, were narrower in terms of  $r/(x-x_0)$ , and had larger mean scaled property values near the axis than was previously thought (Dai et al., 1994, 1995a, 1995b). This finding has significant implications for modeling flows.

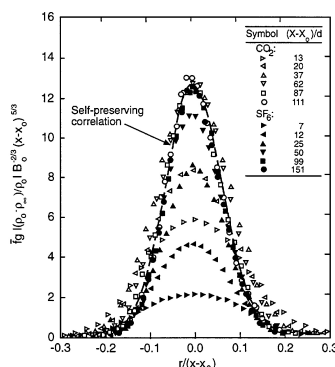


FIGURE 12-3 Measured mean mixture fraction distributions for round buoyant turbulent plumes plotted in terms of self-preserving variables. Source: Dai et al., 1994.

### Turbulence Model Predictions

Various properties of round self-preserving buoyant turbulent plumes have been used to evaluate models of buoyant turbulent flows. An example for the scaled self-preserving mean streamwise velocity,  $U$ , is plotted as a function of  $r/(x-x_0)$  in Figure 12-4. These results involve the turbulence model predictions of Dai and Faeth (1995) and Pivovarov et al. (1993), along with the measurements of Dai et al. (1995a), Shabbir (1987), Ogino et al. (1984), Nakagome et al. (1979), and George et al. (1977). All these measurements were originally thought to represent self-preserving behavior, but this behavior has only been established for the recent findings of Dai et al. (1995a). In order to match the earlier measurements of  $U$  with their predictions, Pivovarov et al. (1993) were forced to increase substantially the well-known modeling constant,  $C_m$ , from its standard value; in contrast, the new measurements of  $U$  by Dai et al. (1995a) were in excellent agreement with predictions using standard turbulence modeling constants—resolving earlier criticism of the use of turbulence models. All other mean properties behaved the same way (Dai and Faeth, 1995).

Although the agreement between recent measurements and turbulence model predictions of mean properties in self-preserving round buoyant turbulent plumes is encouraging, corresponding predictions of turbulence properties are less satisfactory. An example of this behavior is illustrated in Figure 12-5, where measurements of the turbulent Prandtl/Schmidt number,  $\sigma_T$ , for self-preserving conditions are plotted as a function of scaled radial distance. The measurements show that  $\sigma_T$  progressively decreases from the axis to the edge of the flow rather than remaining constant at  $\sigma_T = 0.7$  as prescribed by the most widely used turbulence models. Similar difficulties were encountered with other turbulence model predictions of turbulence quantities, even when using relatively advanced higher-order turbulence models. This raises questions about the capabilities of turbulence models to predict the properties of rapidly developing complex turbulent flows typical of post-crash fires, where good predictions of turbulence properties are necessary for making reasonable predictions of mean properties. Thus, pending

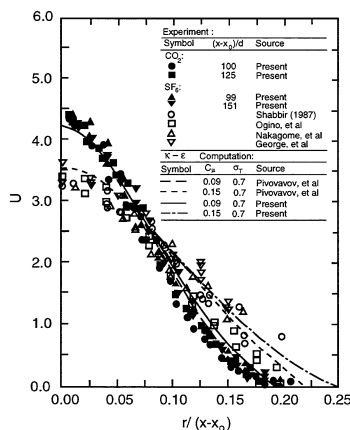


FIGURE 12-4 Measured and predicted profiles of mean streamwise velocities for self-preserving round buoyant turbulent plumes. Source: Dai et al., 1994.

well documented improvements in turbulence models for buoyant turbulent flows, measurements should be used as baselines for turbulence model predictions.

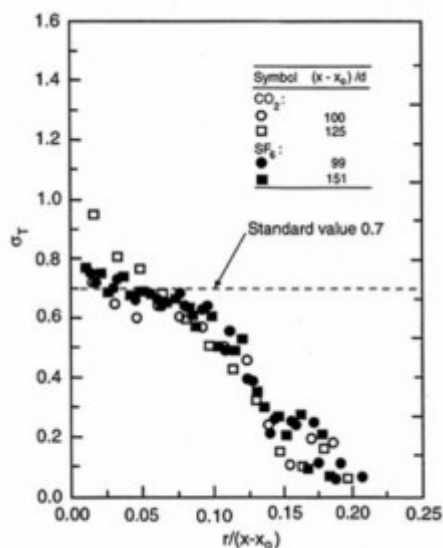


FIGURE 12-5  
 Measured turbulent Prandtl/Schmidt numbers for self-preserving round buoyant turbulent plumes. Source: Dai et al., 1995b.

### Numerical Simulations of Turbulence

Turbulent flows formally satisfy known three-dimensional time-dependent governing equations; therefore, direct numerical simulations potentially offer a model-free way of predicting the properties of buoyant turbulent flows. Unfortunately, the range of length and time scales of practical turbulent flows will far exceed available computational capabilities for the foreseeable future. Thus, simulations must either involve some level of modeling, typically modeling or approximating the small-scale features to yield a large-eddy simulation (LES), or limiting considerations to low Reynolds number quasi-like turbulence in order to gain insight about the properties of turbulence. Using either approach, these methods are of interest for modeling aspects of post-crash fires and have already been used for this purpose (see Tieszen et al., 1996). Thus, some awareness of this methodology is needed and is addressed in the following based on the computations of large fire plumes in a crossflow due to Baum et al. (1994).

The simulations of Baum et al. (1994) begin several fire diameters from the source where temperature variations are modest, where radiation can be ignored, and where the fire can be adequately characterized by release rates of heat and particulate matter. Although the computations involve the complete unsteady equations of conservation of mass, momentum, and energy, they are approximated by a two-dimensional time-dependent flow under the assumption that the component of the fluid velocity in the direction of the ambient wind is constant and equal to the wind speed. The calculations also do not extend to the smallest scales of the actual flow but are truncated by assuming a constant eddy viscosity that is three orders of magnitude larger than the actual viscosity of air. This limits small scale resolution to 5m to 15m, which is acceptable for the very large fire plumes considered in this study. Baum et al. (1994) should be consulted for other details concerning the model and the numerical method; the computer code is an adaptation of an approach used by McGrattan et al. (1994) to model enclosure fires.

The numerical simulations of Baum et al. (1994) were evaluated based on experiments of crude oil combustion in a crosswind by Evans et al. (1993). The experiment considered in the calculations involved a 204 MW fire source in a 4 m/s crosswind with an atmospheric lapse rate of -9.2K/km. Some typical results are illustrated in Figure 6 as plots of the measured (symbols) and predicted (solid line) center-line plume trajectory. The comparison between predictions and measurements is quite encouraging in view of the fact that these methods do not require the use of empirical turbulence modeling constants. This highlights the importance of the effects of large scale features on the mixing properties of buoyant turbulent plumes. Other examples of this and similar methodologies can be found in references cited by Baum et al. (1994), McGrattan et al. (1992), and Tieszen et al. (1996).

## BUOYANT TURBULENT DIFFUSION FLAMES

### Modeling Buoyant Turbulent Diffusion Flames

Modeling buoyant turbulent diffusion flames involves merging methods of finding the scalar properties of flames with methods for predicting the properties of noncombusting flows. Some typical approaches to this problem follow; methods of predicting flame radiation properties will be deferred for the present.

The most widely used methods of predicting the structure of buoyant turbulent diffusion flames exploit the k-e or k-e-g families of turbulence models (Bilger, 1976; Lockwood and Naguib, 1975). Bilger (1976) discusses the advantages of mass-weighted (Favre) averaged properties, although the quantitative effect of the averaging procedure is generally

quite modest for flames. Model constants are usually drawn from classical measurements for turbulent boundary layers and frequently employ gradient diffusion approximations that are known to be questionable for complex turbulent flows (Bilger, 1976; Gore and Faeth, 1988a, 1988b; Holen et al., 1991; Lockwood and Naguib, 1975). Calculations for more complex flows such as KAMELEON typically are based on the SIMPLEC method of Patankar and Spalding (Holen et al., 1991; Tieszen et al., 1996).

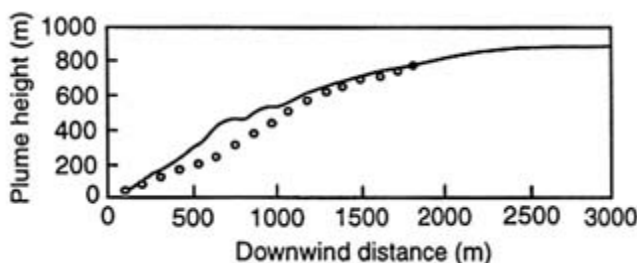


FIGURE 12-6 Measured and predicted trajectory of the center-line of a plume for a round 204 MW fire source in a 4 m/s cross-flow with a -9.2 K/km lapse rate. Symbols denote measurements and line denotes predictions. Source: Baum et al., 1994.

The two main methods for predicting scalar properties within buoyant turbulent diffusion flames are the conserved-scalar approach, and the eddy-dissipation or eddy-breakup approach. The conserved-scalar approach exploits state relationships for scalar properties, as discussed by Bilger (1976). The studies of Gore and Faeth (1988a, 1988b) represent typical examples of this approach for hydrocarbon-fueled buoyant turbulent diffusion flames. Concentrations of major gas species were found from state relationships obtained from measurements in laminar diffusion flames (discussed in connection with Figure 12-2). A state relationship for temperature was computed from this information while allowing for the relatively large fractions of combustion energy that are radiated from soot-containing flames. State relationships for soot concentrations were also used in these calculations, based on measurements in laminar flames, although later work shows that this procedure is questionable because of fundamental differences between soot processes in laminar and turbulent flames (see Faeth et al., 1989; Sunderland et al., 1995, for discussions of this issue). Finally, prescribed probability density functions of mixture fractions were used to compute mean and fluctuating values of mixture fractions found from solution of the governing equations; the results of Gore and Faeth (1988a, 1988b) used the clipped-Gaussian probability density function although the specific form of the function used does not seem to be very critical as long as it has at least two moments (Lockwood and Naguib, 1975).

The other main method for finding scalar properties in buoyant turbulent diffusion flames is based on eddy dissipation or eddy-breakup concepts. The studies of Holen et al. (1991) and Tieszen et al. (1986) represent typical examples of this approach. These methods involve the use of Burke/Schuman-like state relationships in conjunction with various approximations to treat finite-rate reactions, including the production and oxidation of soot. Unfortunately, current understanding of fuel-decomposition and soot reaction processes in diffusion flames is not highly developed, which severely limits capabilities for making reliable predictions of the structure of soot-containing flames. Thus, no method of treating the scalar properties of buoyant turbulent diffusion flames provides reliable estimates of soot concentrations, which are crucial for making accurate estimates of flame radiation properties.

### Turbulent Diffusion Flame Structure

Two examples of turbulent diffusion flames will be considered: a buoyant turbulent round jet diffusion flame, which provides a well-defined and readily reproducible flame configuration, and a pool fire in an enclosure, which is more representative of practical fire environments. The results include measurements and predictions, with the predictions involving both the conserved scalar and eddy-dissipation methods.

Representative measurements and predictions of properties along the axis of a soot-containing buoyant turbulent round jet diffusion flame by Gore and Faeth (1988b) are illustrated in Figure 12-7. Predictions of scalar properties are based on the conserved scalar approach and include both mass-weighted (Favre) and conventional time averages. As discussed by Faeth and Samuelsen (1986), the differences between these averages is not very significant for predicting scalar properties. The structure of mean properties in turbulent diffusion flames is only qualitatively similar to the structure of laminar diffusion flames (see Figures 12-1 and 12-7). For the turbulent flame illustrated in Figure 12-7, mean fuel and oxygen concentrations are smallest, and mean combustion product concentrations are largest, in a reaction zone (a flame-containing region) for dimensionless streamwise distances,  $x/d$ , in the range 60 to 90. Unlike the laminar diffusion flame in Figure 12-1, however, there is considerable overlap of mean fuel and oxygen concentrations. This overlap is caused by laminar flamelets shifting back and forth along the axis in the flame-containing region, i.e., although fuel and oxygen do not coexist at a point, they both appear because given locations in the flame-containing region have finite residence times in the fuel-lean and fuel-rich portions of laminar flamelets.

Measurements and predictions of mean properties shown in Figure 12-7 are in reasonably good agreement, including proper treatment of the overlap between fuel and oxygen and the presence of large concentrations of CO at fuel rich-conditions due to partial oxidation of the fuel. This behavior is typical of the performance of the conserved-scalar formalism

when combined with state relationships. The main deficiency of these predictions involves predictions of velocity fluctuations in the plume region of the flow beyond the flame-containing region. This problem is caused by deficiencies of the simple k-e-g turbulence model used by Gore and Faeth (1988b), which does not properly account for buoyancy/turbulence interactions in the plume. Unfortunately, existing advanced turbulence models offer little improvement of this deficiency (Dai and Faeth, 1995). As discussed earlier, relatively poor predictions of turbulence properties are typical of most turbulence models for buoyant turbulent flames and are a concern when these methods are used to treat complex flows where rates of flow development are strongly influenced by turbulence levels.

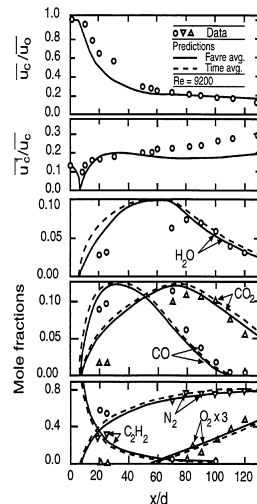


FIGURE 12-7 Measured and predicted properties of a round buoyant turbulent acetylene/air diffusion flame. Source: Gore and Faeth, 1988b.

Representative measurements and predictions of the properties of a diffusion flame in an enclosure, based on the eddy-dissipation approach of Holen et al. (1991), are illustrated in Figure 12-8. Results shown include measured and predicted mean temperatures at two conditions (averages for the floor and for the enclosure) as a function of time as the fire develops. The agreement between measurements and predictions for this rather complicated fire environment is quite good; predictions of other properties of the enclosure fire were also quite good. Nevertheless, many aspects of the model used for these predictions require additional study and more detailed evaluation than is possible using the comprehensive properties of enclosure fires.

### Modeling Flame Radiation

Flame radiation causes heating of materials in flame environments, which affects fire spread and growth rates. Radiation heat transfer is particularly important for soot-containing hydrocarbon-fueled flames because large fractions (as much as 60 percent) of the chemical energy release are radiated to the surroundings by a continuum of radiation from soot (Faeth et al., 1989). Current methods of modeling flame radiation are described next before representative measurements and predictions of radiation for buoyant turbulent diffusion flames are considered.

Reviews of available methods of predicting radiation in turbulent flame environments are presented by Faeth et al. (1989), Gore and Faeth (1988a, 1988b), Gore et al. (1987), and references cited therein. Naturally, information about the scalar structure of flames is a prerequisite for making radiation predictions, and it is assumed in the following description that the necessary properties, based on flame structure predictions that have already been discussed, are known. Issues that must be addressed include consideration of the spectral properties of radiation, the method used to estimate soot concentrations, and the treatment of turbulence/radiation interactions.

Practical flames exhibit significant effects of both gasband radiation and continuum radiation from soot. These effects are important because of the wide temperature variations of practical flames and the tendency of the largest soot concentrations to be associated with the highest-temperature regions of the flows. Predictions of soot concentrations in

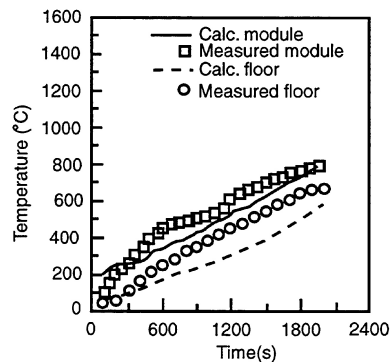


FIGURE 12-8 Measured and predicted temperatures for a rectangular liquid pool fire burning in air within an enclosure. Source: Holen et al., 1991.



flames have already been discussed. Current methods range from state relationships for soot volume fractions (Gore and Faeth, 1988a, 1988b) to empirical soot reaction expressions (Holen et al., 1991); neither approach is well established so that accurate estimates of soot concentrations in flames are probably the greatest limitation for making accurate estimates of flame radiation. Finally, buoyancy/turbulence interactions increase mean radiation levels as much as two to three times the estimates based on mean scalar properties in flames (Faeth et al., 1989); therefore, accurate treatment of these effects is also important. The radiation treatment by Holen et al. (1991) employs the gray gas approximation and uses mean properties as the basis of predictions while ignoring turbulence/radiation interactions, which is typical of the simplest models of flame radiation. At the other end of the spectrum, the methods used by Gore and Faeth (1988a, 1988b) are reasonably comprehensive and attempt to treat non-gray gas properties and the effects of turbulence radiation interactions; this approach is described next.

Predictions of scalar properties for the flames studied by Gore and Faeth (1988a, 1988b) have already been discussed in connection with Figure 12-7. As noted there, state relationships were used for all scalar properties, including soot concentrations, while a k-e-g turbulence model was used to find the distributions of mean and fluctuating mixture fractions. The prescribed clipped-Gaussian mixture fraction probability density function then yielded predictions of scalar property distributions following the conserved-scalar formalism (Lockwood and Naguib, 1975). Radiation predictions were made by first computing spectral radiation intensities for particular paths through the flames and then integrating these results over wavelength and direction in order to estimate radiant heat fluxes. These computations were made ignoring scattering, which is reasonable for typical soot particles and gases in the infrared portion of the spectrum of interest for flame radiation.

These predictions involved solving the equation of radiative transfer for given radiation paths, using the Goody statistical narrow-band model with the Curtis-Godson approximation for inhomogeneous gas paths. The computation considered the gas bands of CO<sub>2</sub>, H<sub>2</sub>O, CO, the fuel, and continuum radiation from soot (Ludwig et al., 1973). These calculations are straightforward when effects of turbulent fluctuations are ignored, based on mean scalar property predictions along the radiation path. Effects of turbulent fluctuations were also considered based on a stochastic method where distributions of mixture fractions through the flames were numerically simulated using classical statistical time-series methods. Scalar properties along the paths were then found from the state relationships and spectral radiation intensities were predicted as before for each realization of mixture fractions along the path. Sufficient realizations were considered to compute statistically-significant radiation properties (Faeth et al., 1989).

### Flame Radiation Predictions

Methods of predicting the radiation properties of buoyant turbulent flames have been evaluated with reasonably good success for a variety of soot-free and soot-containing flames (Faeth et al., 1989; Gore and Faeth, 1988a, 1988b; Gore et al., 1987). The results of Gore et al. (1987) are of interest for present purposes because they demonstrate capabilities of handling large-scale fires typical of post-crash fires. Present considerations will concentrate on the findings of Gore and Faeth (1988a) instead, however, because they illustrate radiation properties for flames with reasonably large soot concentrations, typical of liquid fuel fires.

Typical predictions and measurements of the radiation properties of round soot-containing buoyant turbulent diffusion flames (based on Gore and Faeth, 1988a) are illustrated in Figure 12-9. These conditions involve an ethylene/air flame at atmospheric pressure with a heat release rate of roughly 30 kW and a mean luminous flame height of roughly 500 mm. Spectral radiation intensities are shown as a function of wavelength for horizontal paths through the axis of the flame at various heights above the burner exit. The gas bands of water vapor and carbon dioxide can be seen, but the spectra are clearly dominated by continuum radiation from soot,

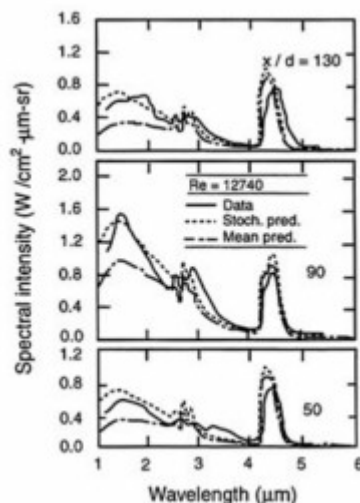


FIGURE 12-9 Measured and predicted spectral radiation intensities for horizontal paths through the axis of acetylene-fueled round buoyant turbulent diffusion flames burning in air. Source: Gore and Faeth, 1988b.



which reaches a maximum intensity near 1500 nm. Not surprisingly, radiation intensities also reach maximum values near the mean luminous flame height, although radiation levels in the plume are still reasonably large. Two predictions are shown, a mean property prediction and a stochastic prediction allowing for turbulence/radiation interactions. As noted earlier, turbulence/radiation interactions significantly increase radiation levels compared to estimates based on mean scalar properties. Nevertheless, differences between the two predictions are comparable to the uncertainties of estimates of soot concentrations and the levels of continuum radiation from soot. Thus, a limited understanding of soot processes in the buoyant turbulent diffusion flames is probably the greatest impediment to making accurate estimates of radiation from practical flames at the present time.

## TURBULENT SPRAYS AND SPRAY FLAMES

### Modeling Sprays

Sprays and spray flames are an important aspect of post-crash fires. Aircraft fuel is dispersed during crashes by ruptured fuel lines and fuel tanks, by aerodynamic effects due to the motion of the aircraft or wind relative to the aircraft over liquid-fuel streams created by ruptures, and also by splashing or drop formation due to turbulent primary breakup of liquid fuel spilling from ruptured fuel tanks onto aircraft surfaces or the ground. All these effects enhance mixing between the air and the liquid fuel, which creates regions capable of rapid combustion either as premixed flames or as intense spray diffusion flames. Naturally, fuel modifications that would inhibit the formation and mixing of liquid fuels as sprays will tend to enhance resistance to the initiation of post-crash fires. Thus, it is likely that consideration of fuel atomization and spray combustion will be an important aspect of the development of fuels with improved fire safety. Motivated by these considerations, the current understanding of turbulent sprays and spray flames is briefly reviewed beginning with a discussion of contemporary methods of modeling sprays, emphasizing processes in dilute sprays where liquid volume fractions are small, where processes of drop breakup have ended, and where the dispersed phase consists of polydisperse spherical drops. Primary and secondary drop breakup are then considered, prior to a discussion of spray structure and evaluations of predictions with available measurements.

The present discussion of the structure and modeling of sprays is brief, but more details can be found in articles by Chen and Davis (1964), Dai et al. (1997), Faeth (1983, 1987, 1996), Grant and Middleman (1966), Hsiang and Faeth (1992, 1993, 1995), Shearer et al. (1979), Ruff et al. (1991), Shuen et al. (1983), Solomon et al. (1985a, 1985b, 1985c), Tseng et al. (1992), Wu and Faeth (1993, 1995), Wu et al. (1992, 1995), and references cited therein. Some of the generic properties of sprays can be considered in a simple way by studying the properties of an ideal spray where spray atomization immediately yields infinitely small gas-and liquid-phase elements (small drops and bubbles). In these circumstances, the assumption that both phases have the same velocity and temperature and are in thermodynamic equilibrium can be adopted so that the flow can be analyzed using the locally-homogeneous flow (LHF) approximation of multiphase flow theory (Faeth, 1983). This implies that the multiphase flow acts like a single-phase flow but with a more complex equation of state. Then the flow can be analyzed using the conserved-scalar formalism combined with state relationships for scalar properties under the laminar flamelet concept.

Typical spray state relationships under the LHF approximation, providing scalar properties as a function of mixture fraction, are plotted in Figure 12-10. The results are for an n-pentane spray burning as a diffusion flame in air at normal temperature and pressure (NTP), drawn from Mao et al. (1980, 1981). The state relationships for sprays under the LHF approximation are qualitatively similar to state relationships for gas-fueled hydrocarbon/air diffusion flames, with maximum temperatures and combustion product concentrations at a flame sheet condition where the mixture is stoichiometric. The main difference between the state relationships for sprays and those for gaseous fuels involves the

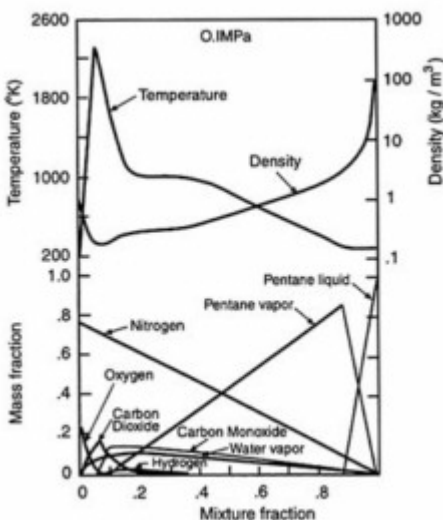


FIGURE 12-10 Predicted state relationships for major gas species for an n-pentane spray burning in air at atmospheric pressure. Source: Mao et al., 1980.

presence of liquid and the large density variation of the flow at large mixture fractions. The results illustrated in Figure 12-10 show that the presence of liquid is limited to mixture fractions of greater than 0.9 while combustion phenomena associated with the maximum temperature region are limited to mixture fractions of less than 0.1, which is typical of most practical combusting sprays. Thus, most spray phenomena occur at relatively cool conditions, remote from combustion phenomena, so that they can be studied without considering the effects of evaporation and combustion as a realistic first approximation—a practice that has been widely adopted by workers in the field (Faeth, 1996).

Although the LHF approximation is helpful for gaining insights into spray properties, numerous evaluations show that LHF models tend to overestimate the rate of development of sprays, indicating that the effects of separated flow are important (Faeth, 1983, 1987, 1996). Continuum formulations provide one approach to treating separated flow, but they are not used widely for sprays because of problems of computational efficiency for dilute dispersed flows.

Discrete-element formulations are probably the most popular separated flow treatments of sprays. These treatments typically involve a Eulerian formulation for the continuous phase, a Lagrangian formulation to track the motion and transport of representative drop groups through the flow, and terms from both formulations to treat interphase transport (Faeth, 1983, 1987). There are two main discrete-element formulations: deterministic separated flow (DSF) where dispersed phase (drop)/turbulence interactions are ignored; and stochastic separated flow (SSF) where drop/turbulence interactions are considered. The DSF approach is not very realistic, however, because drop motion is limited to deterministic trajectories prescribed by their initial conditions and mean gas properties throughout the dispersed flow field. As a result, DSF predictions exhibit unphysical laminar-like behavior where drops collect in low velocity regions.

The SSF methods involve treatment of gas-phase properties very similar to single-phase turbulent diffusion flames, using either the conserved-scalar formalism and state relationships as a function of gas-phase mixture fractions or eddy-dissipation (or eddy-breakup) methods to treat gas-phase scalar properties. Because of limitations on computational tractability, these models integrate over processes on the scale of drop sizes and assume a quasi-steady interphase transport of mass, momentum, and energy. Interphase transport typically involves consideration of particle inertia, drag forces, virtual mass forces, Basset history forces, body forces, Magnus forces, and Saffman lift forces (Faeth, 1983, 1987). The variation of drop properties (drop life histories) are computed for a statistically significant number of drops throughout the flow, and these results are used to provide the dispersed-phase source terms needed for computations of continuous-phase properties.

Three main drop/turbulence interactions are of interest for SSF models: the dispersion of drops by turbulence; the modification of continuous-phase turbulence properties by transport from drops; and the modification of interphase transport rates by turbulence fluctuations. Current treatments of drop dispersion by turbulence have received significant attention; they involve numerical simulations of turbulence using a variety of approximate methods or, more recently, statistical time series techniques (Faeth, 1987). Given a simulation of the time-varying properties of the continuous-phase, corresponding predictions of drop life histories in this environment are straightforward. These methods also tend to compensate for the effects of turbulence fluctuations on interphase transport rates, at least for fluctuations at scales larger than drop sizes, which are generally the most important for combusting sprays. The earliest SSF simulations of drop dispersion were based on interactions between drops and a succession of uniform-property integral-scale-sized eddies, with eddy velocities found by random selections from the probability density functions of velocities, which were determined using *k*-*ε*-*g* turbulence model predictions. Subsequent work has been based on more sophisticated statistical time series simulations of continuous-phase flow properties although turbulence models are still most often used to find flow properties within complex turbulent combusting spray environments (Faeth, 1987, 1996).

In contrast to information about the effects of turbulent dispersion, current information about the modification of turbulence properties by drops is very limited. Fortunately, these effects do not have a large impact on the gross properties of dilute sprays. The effects of turbulence on interphase transport have received significant attention but are not very important compared to other uncertainties about analyzing sprays. Thus, a limited understanding of drop atomization, or breakup properties, is the greatest limitation for making accurate predictions of the properties of spray flames. This issue will be considered next before discussing overall predictions of spray structure.

### Drop Breakup

Processes of liquid atomization or drop breakup are important for reliable modeling of sprays. In particular, accurate estimation of drop breakup is crucial because these properties establish the initial conditions for the rest of the flow. In addition, spray processes tend to be quite sensitive to initial drop sizes (or atomization quality) because drop transport rates tend to be proportional to drop diameter squared (Faeth, 1983, 1987, 1996). Finally, recent work has confirmed traditional ideas that sprays involve the primary breakup of liquid columns and sheets to form large irregular ligaments and drops, which subsequently break up into smaller round drops by secondary breakup (Ruff et al., 1991). These two breakup mode will be discussed, in turn, emphasizing the mechanisms most relevant to sprays associated with post-crash fires.

Recent observations have highlighted the importance of flow properties at the beginning of atomization on the near-injector structure of sprays and the nature of primary breakup (Faeth, 1996; Ruff et al., 1991; Wu and Faeth, 1993, 1995; Wu et al., 1992, 1995). In fact, experiments with high velocity liquid jets injected into still air at atmospheric pressure have shown that the absence of vorticity and liquid turbulence at the jet exit entirely inhibits primary breakup and yields a stable liquid stream very similar to liquid cutting jets (Wu et al., 1995). Similar experiments show that the aerodynamic effects of liquid jets in still gases remain small for liquid/gas density ratios greater than 500 (Wu and Faeth, 1993). This behavior is logical because solid surfaces generate the liquid vorticity needed to produce drops by primary breakup more effectively than low density gases.

Past observations of primary breakup suggest that an important mechanism of primary breakup for post-crash fires involves the turbulent primary breakup mechanism. This mechanism has been studied for liquid jets injected into still air with fully-developed turbulent pipe flow at the jet exit (Wu and Faeth, 1993, 1995; Wu et al., 1992). These studies were intended to study practical pressure atomized sprays, but the primary breakup of liquid jets from ruptured fuel lines should be similar. More recent work has involved wall jets, where a turbulent boundary layer grows along the wall, the surface of the wall jet becomes roughened as it is approached by the outer edge of the growing turbulent boundary layer, and drop formation by the turbulent primary breakup mechanism begins once the kinetic energy of turbulent eddies near the liquid surface exceeds the surface-tension energy required by drops of comparable size (Dai et al., 1997). Past studies of the turbulent primary breakup of wall jets were motivated by the primary breakup in the bow waves of ships and hydrofoils. However, the mechanism is analogous to the primary breakup process of liquid fuels spilling along the surfaces of an aircraft or along the ground in connection with a post-crash fire.

Past studies of the turbulent primary breakup of free jets and wall jets have established criteria for the onset and end of drop formation at the liquid surface and for the variation of drop size and velocity distributions after turbulent primary breakup as functions of conditions along the liquid surface (Dai et al., 1997; Wu and Faeth, 1993, 1995; Wu et al., 1992). These studies have shown that drop size distributions after turbulent primary breakup satisfy the universal root normal distribution function with the ratio of the Sauter mean diameter (SMD) to the mass median diameter (MMD) equal to 1.2; therefore, this two-parameter distribution function is fully defined by the SMD alone. It was also found that mean and fluctuating drop velocities after turbulent primary breakup are independent of drop size and approximate local mean and fluctuating velocities near the liquid surface.

An example of the properties of turbulent primary breakup in a round liquid jet in still gases, with fully-developed turbulent pipe flow at the jet exit, is illustrated in Figure 12-11 (taken from Wu and Faeth, 1993). The SMD after turbulent primary breakup, normalized by the radial integral scale of

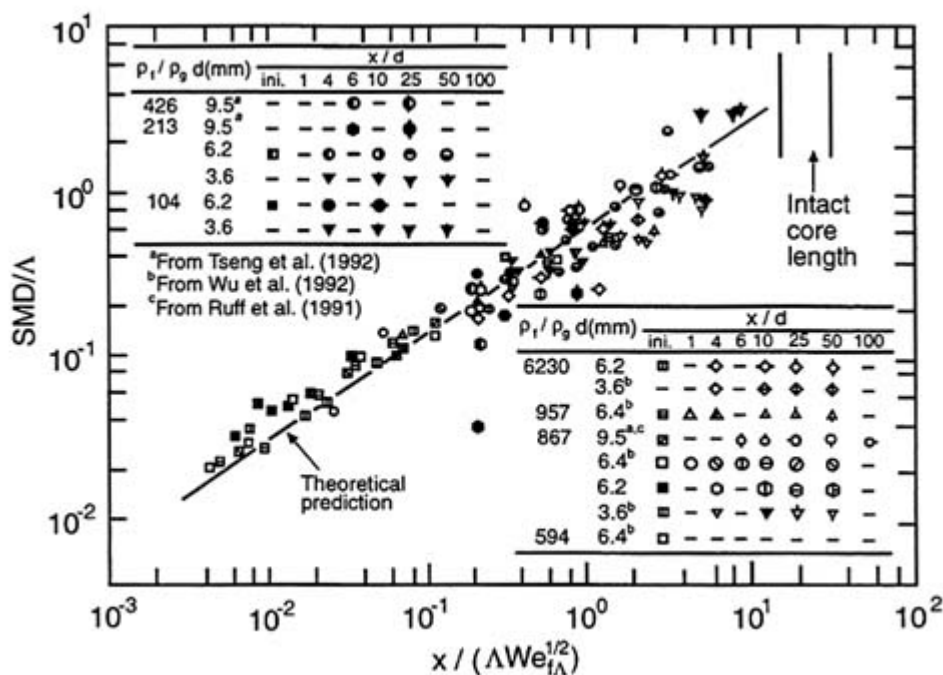


FIGURE 12-11 Measured SMD after turbulent primary breakup of round liquid jets in still air with fully developed turbulent pipe flow at the jet exit. Source: Wu and Faeth, 1993.

the liquid turbulence,  $\epsilon$ , is plotted as a function of distance along the liquid surface,  $x$ , and a characteristic Weber number,  $We_f$ . Measurements taken from Tseng et al. (1992), Wu et al. (1992), Ruff et al. (1991), and Wu and Faeth (1993) are plotted in the figure for a variety of liquid/gas density ratios,  $\rho_l/\rho_g$ , and jet exit diameters,  $d$ , along with a theoretical prediction based on a simplified phenomenological analysis of the primary breakup process. It is evident that an excellent correlation is achieved with good agreement between predictions and measurements; similar findings have been obtained for turbulent primary breakup in wall jets (Dai et al., 1997). These results also show that predictions of liquid jet intact lengths by Chen and Davis (1964) are a logical outcome of drop formation by turbulent primary breakup reaching the diameter of the liquid jet itself. In spite of this progress, however, information about the rate of drop formation by primary breakup, as well as effects of drops enhancing turbulent primary breakup by falling back into the liquid surface, are not well understood, which will limit capabilities to quantitatively model sprays formed by turbulent primary breakup during post-crash fires.

Other studies of nonturbulent and turbulent primary breakup processes have shown that dispersed phases near liquid surfaces actually are quite dilute, with liquid volume fractions less than 0.1 percent (Ruff et al., 1991; Faeth, 1996). This implies that well developed models of dilute dispersed-flows and sprays can be applied to so-called "dense-spray" regions near liquid surfaces. In addition, primary breakup by known nonturbulent and turbulent mechanisms yields drops that are intrinsically unstable to secondary breakup; therefore, secondary breakup clearly is an important factor in determining drop sizes in sprays.

Past studies of secondary breakup have been reviewed in several recent papers (Faeth, 1996; Hsiang and Faeth, 1992, 1993, 1995). Most existing studies of secondary breakup have been limited to drops subjected to shock-wave disturbances that simulate a step change of the local gas velocity relative to the drop; this condition is of interest because it approximates the environment of a drop after primary breakup. Most past studies of secondary breakup have been limited to liquid/gas density ratios greater than 500, which fortunately corresponds to drops in post-crash flames. In these circumstances, drop breakup involves bag, multimode, and shear breakup regimes, as drop Weber numbers increase. The jump conditions for these breakup regimes, giving drop size and velocity distributions, have been resolved (Hsiang and Faeth, 1992, 1993, 1995). Similar to primary breakup, the drop size distributions satisfy the universal root normal distribution function with MMD/SMD = 1.2, although drop velocity distributions are rather complex functions of drop sizes due to varying drop drag properties with drop size. The surprising feature of the findings is that drop sizes after secondary breakup are strong functions of liquid viscosity but are relatively independent of the surface tension. This behavior is the opposite of the behavior of drop sizes after turbulent primary breakup (Figure 12-11) where drop sizes are a strong function of surface tension but are relatively independent of liquid viscosity!

Although past work has supplied the jump conditions needed to estimate secondary breakup properties, these results suggest that secondary breakup should be treated as a rate process rather than by jump conditions, in some instances (Hsiang and Faeth, 1995). For example, secondary drop breakup times are  $t_b = (5-6)(\rho_l/\rho_g)^{1/2}d_0/u_0$ , where  $d_0$  and  $u_0$  are the initial drop diameter and relative velocity. Unfortunately, these times often are not small compared to drop residence times in dense spray regions. Secondary drop breakup processes can also extend more than 100  $d_0$ , which is also not small for practical sprays. This implies that secondary breakup should be treated as a rate process rather than by jump conditions in some instances. Unfortunately, available information about the rate aspects of secondary breakup is very limited, which limits capabilities for modeling this potentially important spray process (Faeth, 1996).

### Spray Predictions

Available models of simple turbulent dispersed flows are computationally tractable and reasonably effective. Numerous studies attempting to evaluate various models of nonevaporating, evaporating, and combusting sprays have been reported (see examples in Faeth, 1983, 1987, 1996; Mao et al., 1980, 1981; Ruff et al., 1991; Shearer et al., 1979; Shuen et al., 1983, 1985; Solomon et al., 1985a, 1985b, 1985c; Tseng et al., 1992; and references cited therein. A representative evaluation of spray models follows to illustrate the methodology.

The spray model evaluation to be considered involves a nearly monodisperse, round-turbulent-particle-laden jet, injected vertically downward, which was one of several examples considered by Shuen et al. (1983, 1985). The initial conditions of this flow were well documented to provide mean and fluctuating velocities of both phases and the mass flux distribution of the dispersed phase. Subsequent measurements of these properties were carried out over the flow field in order to evaluate the predictions. One model evaluated by the measurements involved using the LHF approximation in conjunction with the conserved-scalar formalism and state relationships analogous to Figure 12-10 to treat the multiphase flow. A second approach involved an SSF model with the turbulence structure approximated by random integral-sized eddies. In both cases, the continuous phase was treated using a conventional k-e-g turbulence model with standard turbulence model constants that had been well established based on measurements in turbulent single-phase flows.

A typical plot of the measured and predicted structure of the round-turbulent-particle-laden jets from Shuen et al.



(1985) appears in Figure 12-12. These results refer to spherical glass particles having an SMD of 0.119 mm and a ratio of the mass flow rate of particles to the mass flow rate of air, LR = 0.2, at a streamwise position of  $x/d = 20$ ; results at other conditions were similar. Parameters plotted on the figure include radial profiles of mean particle mass flux,  $G$ , streamwise particle velocity,  $\bar{U}_p$ , streamwise and cross-stream particle velocity fluctuations,  $\bar{U}'_p$  and  $\bar{V}'_p$ , and particle turbulence kinetic energy,  $k_p$ , with the subscript c denoting center-line quantities. Because separated-flow effects are important for the large particles present in this flow, the LHF predictions vastly overestimate the rate of development of the flow. Predictions of the SSF model, however, are quite satisfying, including good predictions of the fluctuating properties of the particles. Thus, the rather simple stochastic simulation of particle trajectories used by Shuen et al. (1985) appears to capture the most important particle turbulence interactions in this flow.

Evaluating models of sprays involving polydisperse effects, evaporation, and combustion becomes progressively more challenging as requirements for both measurements and model predictions increase. Some typical examples involving reasonably well-defined initial conditions include the results for round turbulent nonevaporating and evaporating sprays from Solomon et al. (1985a, 1985b, 1985c); however, there are numerous other examples in the literature (Faeth, 1983, 1987, 1996). It is generally agreed that the structure of sprays can be predicted reasonably well, given a good prescription of initial and boundary conditions, using typical contemporary spray models. Thus, the major limitation of this technology involves the proper definition of initial conditions, especially reliable definitions of atomization properties.

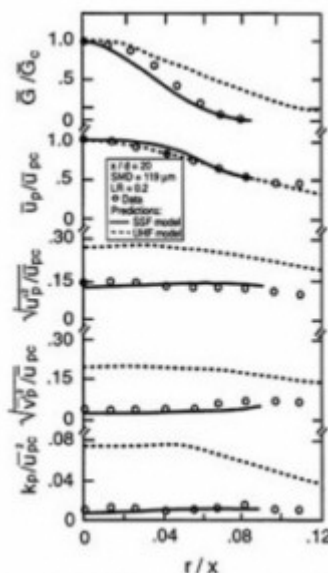


FIGURE 12-12 Measured and predicted mean and fluctuating particle properties in a round turbulent particle/air jet in still air at NTP. Source: Shuen et al., 1985.

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## 13

# Fundamentals of Fuel Ignition and Flammability

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### ABSTRACT

Three fundamental model configurations related to aviation fuel safety are discussed: flame spread above liquid fuel pools, the ignition of gaseous combustible mixtures by hot projectiles, and the ignition and flame propagation of fuel spray/air mixtures. Potential advantages of a two-fuel strategy are identified. The need for further research is identified.

### INTRODUCTION

The purpose of this paper is to outline aspects of ignition and flammability related to aircraft safety. The combustion characteristics of aviation fuels and other combustible liquids (e.g., hydraulic and lubricating fluids) will be analyzed in three configurations that could arise from accidents or hostile actions. Because aviation fuels are designed to ignite and burn easily in a combustor, their undesired ignition and burning in other configurations is very difficult to prevent, and makes them a significant fire hazard.

Three fundamental models are discussed below. First, flame spread above liquid fuels is discussed as a significant danger in accidents that result in liquid fuel forming a pool that can be ignited in various ways. Second, the ignition of gaseous combustible mixtures by hot moving particles is analyzed. Hot particles or fragments could result from a breakup of parts in an accident or from projectiles delivered for hostile purposes. Third, a ruptured fuel tank can release a fuel spray/air mixture, which can be easily ignited. In the final section, some potential advantages of a two-fuel strategy are discussed.

### IGNITION AND FLAME SPREAD ABOVE A LIQUID FUEL POOL

Figure 13-1 shows the important features of flame spread above a liquid fuel pool. For aviation fuels, the practical interest involves fuels below the flash-point temperature that must be preheated and vaporized before they will mix with oxygen and burn. In this scenario, the flame preheats the fuel. Heating and vaporization become a rate-controlling factor causing the flame to propagate much more slowly than it would through a premixed combustible gas formed from the same fuel.

Flames propagate faster over liquid fuels than solid fuels with similar thermal properties. Thermocapillary convection is the major reason for the difference. A surface shear stress results from the variation in surface tension (caused by the variation in surface temperature). This results in convective heat transfer ahead of the flame (Sirignano, 1972; Schiller and Sirignano, 1996; Schiller et al., 1996).

Understanding flame spread over a fuel pool is a complicated problem because this is an unsteady, multidimensional, multiphase phenomena with many length and time scales and exchanges of mass, momentum, and energy between the phases. The heat transfer results in temperature and density variations through both the liquid and gas phases. Consequently, buoyancy of air produces convection in both phases. The advancing flame causes local gas expansion producing another convective effect. The buoyant air flow and thermocapillary convection are opposed and tend to produce a recirculation zone. However, when the hot gas expands sufficiently, it can destroy any recirculation zone.

In the lower range of initial liquid temperatures ( $T_0$ ), the flame pulsates (alternately accelerates and decelerates) as it propagates. At higher initial temperatures, the flame propagates at a uniform rate. (See Figure 13-2.) The amplitude and period of the pulsations decrease as  $T_0$  rises. The domain size ( $\delta_{\text{flow}}$ ) for liquid motion ahead of the flame also decreases as  $T_0$  rises. The size of the gas-phase recirculation cell is directly related to the magnitude of  $\delta_{\text{flow}}$  and both become negligible in the uniform flame spread regime.

Figure 13-3 shows the pulsation cycle for a spreading flame. As the flame accelerates, the expansion of hot gas increases, destroying the recirculation zone. When the flame begins to decelerate because of the limited availability of fuel vapor, expansion of the hot gas expansion is reduced and the recirculation zone reforms. As the concentration of fuel vapor in the recirculation zone increases, the flame accelerates again, consuming the available fuel vapor and destroying

the recirculation zone. Analyses by Schiller et al. (1996) showed that many parameter variations besides  $T_0$  can change uniform flame spread to pulsating flame spread or vice versa. Essentially, the flame spread becomes pulsating as the flammability limit is approached and uniform spread can no longer be sustained. Average pulsating spread rates are lower than uniform spread rates.

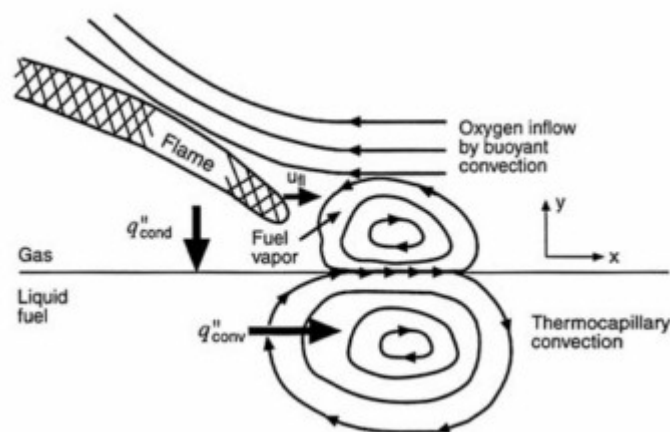


FIGURE 13-1 Basic configuration for flame spread above a liquid pool. Source: Schiller et al., 1996.

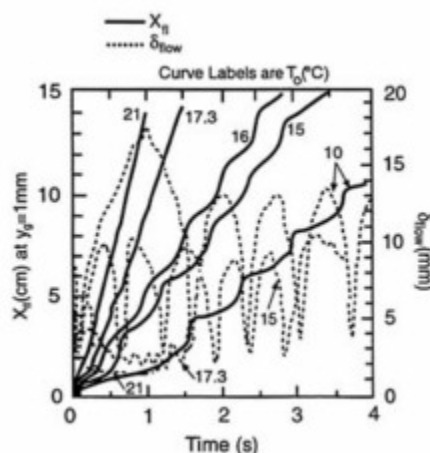


FIGURE 13-2 Effect of initial fuel temperature ( $T_0$ ) on spread rate and domain size ( $\delta_{flow}$ ) for liquid motion. Source: Schiller et al., 1996.

### IGNITION OF GASEOUS COMBUSTIBLE MIXTURES

A hot projectile moving through a combustible gaseous mixture has the same effect as a combustible gas flowing around a hot body. Heat is transferred by conduction to the gas; if the temperature rise is sufficient, oxidation rates result in ignition and the establishment of a flame. Figure 13-4 presents a schematic drawing of this phenomenon describing the local flow approximations employed. Namely, the viscous flow produces a boundary layer, and a wake is approximated using two zones: a stagnation flow region and a zero pressure gradient ("flat plate") region. The near wake is approximated using a mixing layer.

At issue is whether an element of combustible gas flowing past the hot body receives enough heat to cause ignition. The amount of heat received and the likelihood of ignition increase with increasing temperature and length of the projectile, and decrease with increasing relative velocity (residence time of the gas in the projectile vicinity). If the gas in the boundary layer over the projectile does not ignite, it might still ignite in the near wake, which can recirculate hot gases and sustain a flame.

Figure 13-5 shows the limits for ignition. Ignition in the stagnation flow region requires higher temperatures and/or lower velocities than ignition in the zero pressure gradient region. If ignition does not occur in the boundary layer, it might occur in the mixing layer between the near wake with

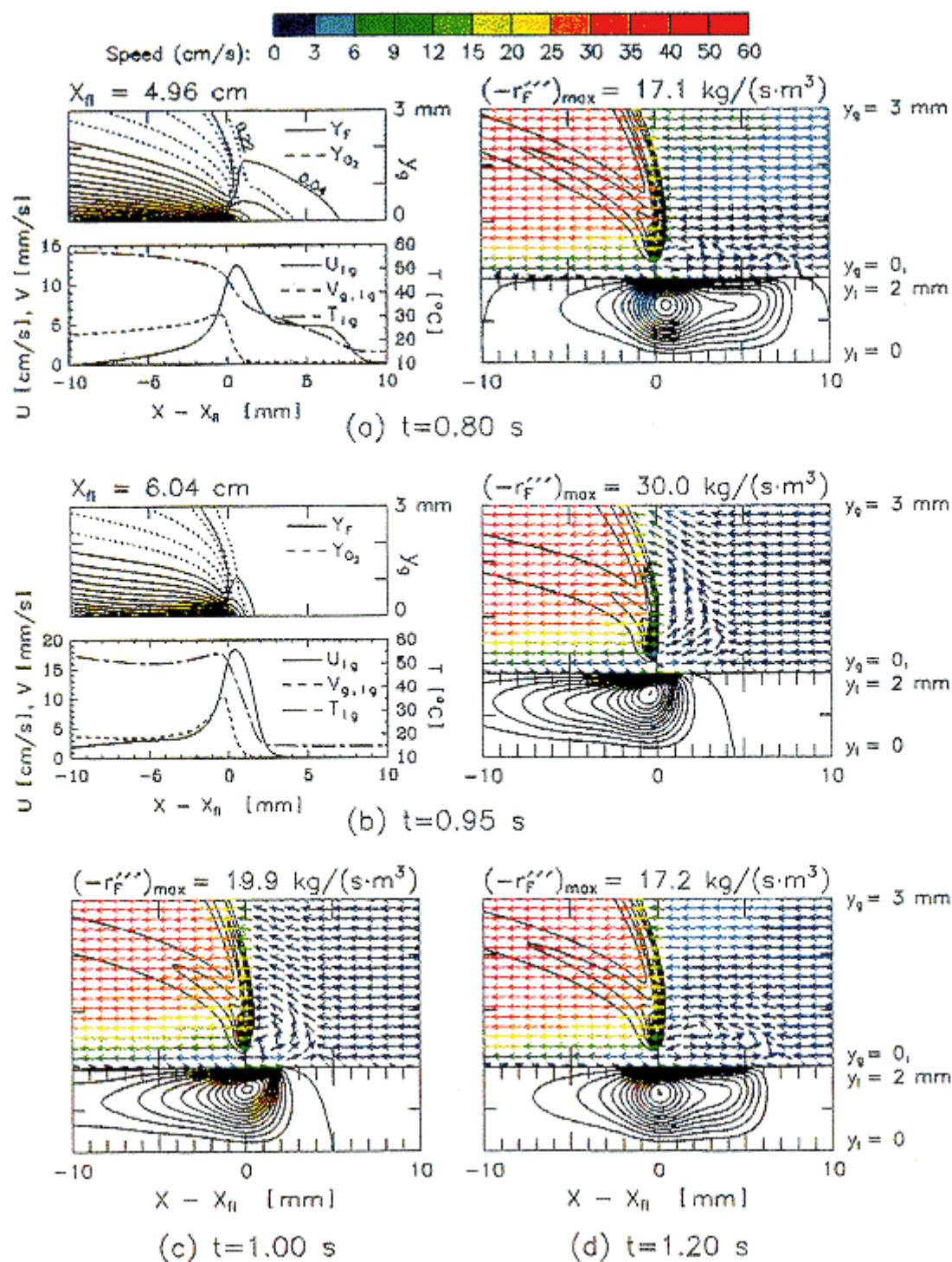


FIGURE 13-3 Pulsation cycle for flame spread above liquid fuel at low initial temperatures ( $T_0$ ). Source: Schiller et al., 1996.

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its recirculating hot gases and the external flow. Once ignition occurs, a flame is established that can spread through and consume the gaseous mixture.

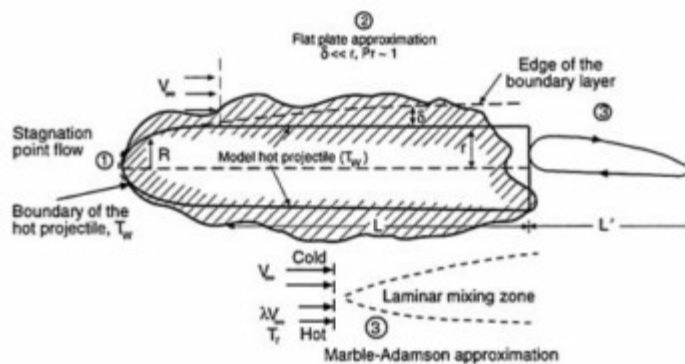


FIGURE 13-4 Schematic diagram of the flow field approximations used around a hot projectile ignition.

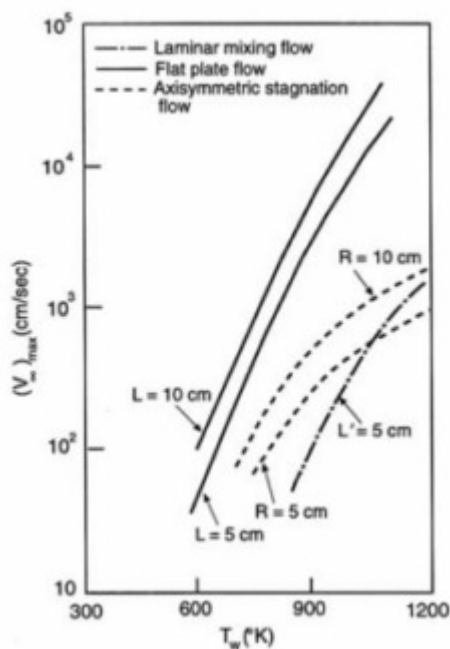


FIGURE 13-5 Variation along the limit of the relative velocity of the hot projectile with projectile temperature ( $T_w$ ) and projectile characteristics ( $L$  or  $R$ ) or near wake length ( $L'$ ). Source: Sharma and Sirignano, 1970.

### SPRAY IGNITION AND FLAME PROPAGATION

The ignition and flame propagation of fuel spray/air mixtures are substantially different from ignition of and flame propagation through gaseous combustible mixtures. The major factor for the differences is the fine structure associated with spatial variations in gas properties on a length scale as small as the distance between neighboring droplets.

Ignition and flame propagation each require heating and vaporization of the droplets and mixing of the fuel vapor with air before chemical reaction can occur. Intuition might indicate that ignition of or flame propagation through a spray always occurs at a slower rate when compared to a gaseous mixture at the same mixture ratio. For certain mixture ratios and for certain initial droplet sizes, however, ignition can be faster and/or flame speeds can be higher for the spray. The major factors causing this difference are variations in temperature and concentrations in the fine structure together, and the nonlinear dependence of the reaction rate on temperature and concentrations.

Figure 13-6 shows that the ignition delay does not always decrease as initial droplet size decreases. Ignition delay is plotted against a normalized mixture ratio (the equivalence ratio  $[E_r]$  equals unity for a stoichiometric mixture). At lean fuel conditions, the ignition delay is smaller for a certain, finite, initial droplet size than for a prevaporized, premixed gas. Therefore, creating larger initial droplets is not necessarily safer.

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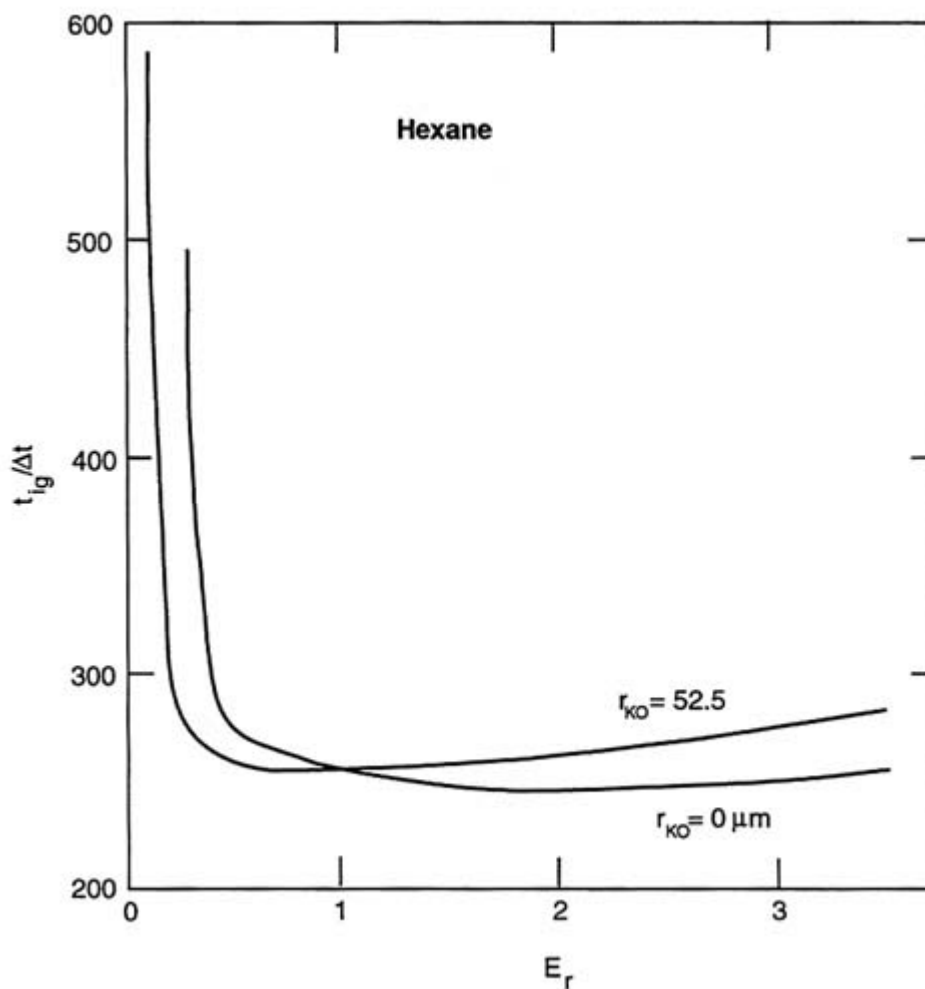


FIGURE 13-6 Ignition time delay versus equivalence ratio (normalized mixture ratio) and initial droplet radius. Source: Aggarwal and Sirignano, 1984.

In some situations (see Figure 13-7), the same type of nonlinearities and fine structure lead to a situation whereby the ignition rate may not increase as a droplet moves closer to an ignition source. In Figure 13-7, ignition energy ( $Q_{ig}$ ) and ignition delay are plotted against distance from a hot wall. Minima of those values are shown at specific, finite initial fuel droplet sizes.

In practical situations, a polydisperse spray has a distribution of initial droplet sizes. An average droplet size is used to represent the distribution;  $d_{32}$ , an average droplet diameter based on the ratio of volume to surface area, is a common choice. Aggarwal and Sirignano (1986) showed that  $d_{20}$ , an average based solely on surface area of the spray, was a better average value for predicting ignition. Figure 13-8 shows that the calculations based upon a monodisperse spray with the  $d_{20}$  value agree better with results for a bidisperse spray than calculations with the  $d_{32}$  value. Smaller droplets in the distribution tend to influence ignition more than larger droplets because they have more surface area per unit volume (or per unit mass).

A spray flame has a complex structure, with both diffusion flame characteristics and premixed flame characteristics. Some vaporization of fuel and mixing of the vapor with air can occur ahead of the flame; as the flame propagates, this gaseous mixture can be burned. However, sufficiently large droplets can pass through the flame and continue to vaporize and mix behind the flame. This can result in a fuel-rich gaseous mixture with fuel vapor that diffuses towards the flame region, where it mixes with oxygen and reacts.

Figures 13-9 and 13-10 show the results of the unsteady propagation of a spray flame. In Figure 13-9, the fuel vapor mass fraction ahead of the flame (traveling to the right) increases with time as a result of prevaporization. Because the calculation is for a closed volume, vaporization causes an increase in pressure and temperature ahead of the flame (see

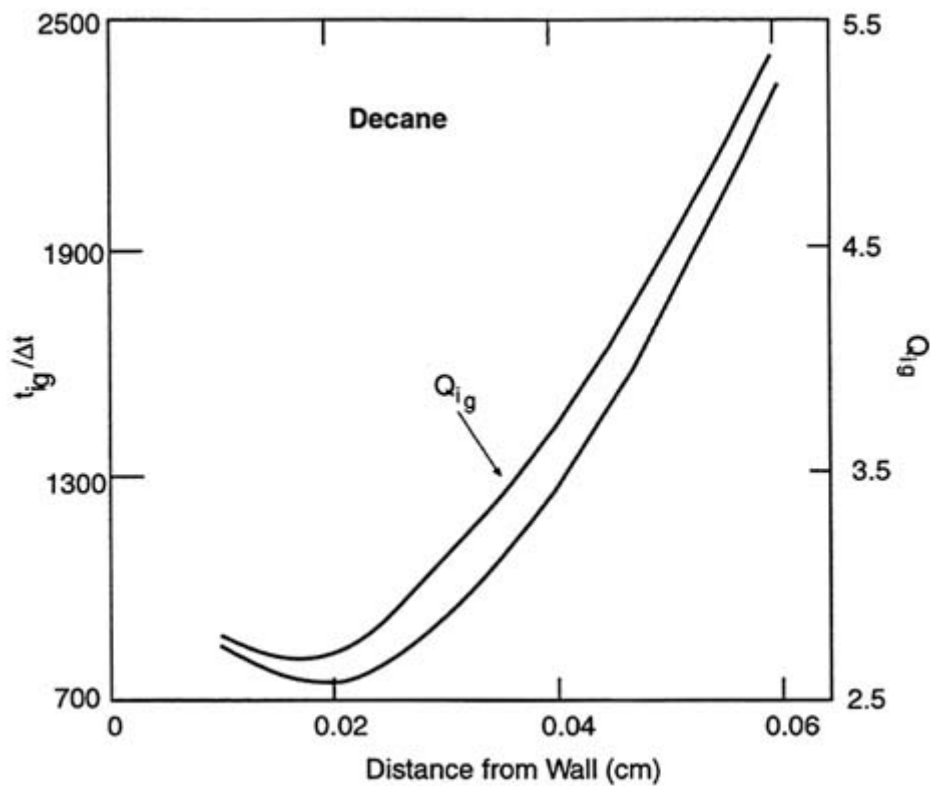


FIGURE 13-7 Ignition time delay and ignition energy ( $Q_{ig}$  versus distance from a hot wall. Source: Aggarwal and Sirignano, 1984.

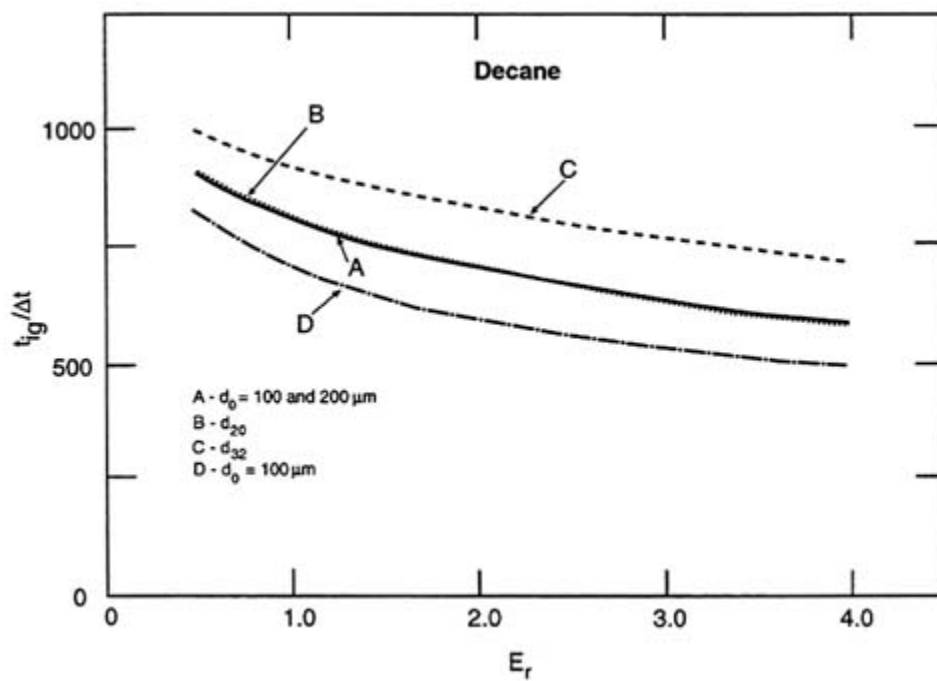


FIGURE 13-8 Ignition delay versus equivalence ratio for a polydisperse spray. Source: Aggarwal and Sirignano, 1986.

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Figure 13-10). The local peaks of fuel vapor mass fraction and minima of temperature occur at the discrete droplet positions as a result of mass and energy exchange between droplets and surrounding gas. A comparison of Figures 13-9 and 13-10 shows that fuel vapor mass fraction is largest well behind the flame-front (the region of a sharp increase in temperature) so that, to a large extent, burning occurs as a diffusion flame. However, because of prevaporization, the flame also has some of the characteristics of a premixed flame.

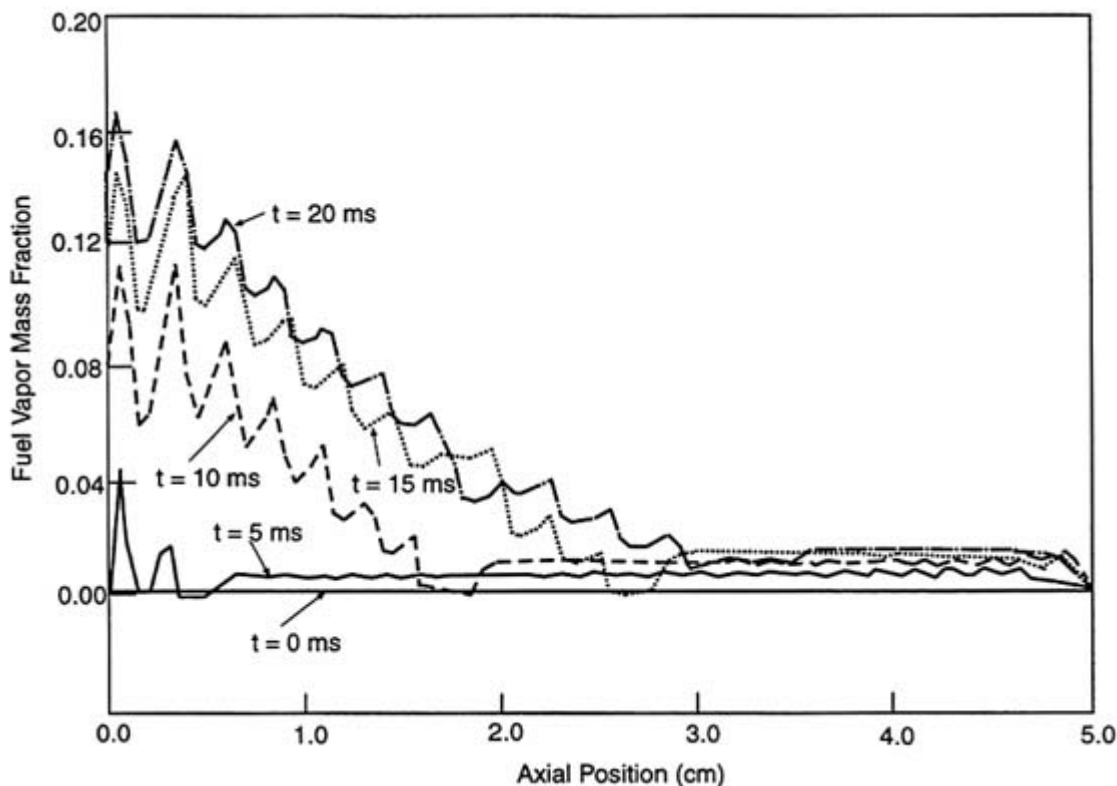


FIGURE 13-9 Fuel vapor mass fraction versus axial position at various times.  
Source: Aggarwal and Sirignano, 1985.

The nonlinear character of the reaction rate plus the fine structure in Figures 13-9 and 13-10 lead to the nonintuitive behavior of the flame speed, which does not continually increase as droplet size decreases. Instead, a maximum speed, which is greater than the premixed flame speed, is reached at a finite droplet size. (See Aggarwal and Sirignano, 1985.)

### TWO-FUEL STRATEGY

The challenge is to create a liquid fuel that burns very efficiently after injection into the engine combustor but burns considerably less efficiently when released accidentally. So far, no such fuel has been developed, but two new possibilities could be explored. One is a fuel with a strong pressure sensitivity that burns poorly at atmospheric conditions but extremely well at elevated pressure (personal communication from Thor Eklund, William J. Hughes Technical Center, FAA, June 1996). Another possibility is the development of a two-fuel (or multifuel) strategy.

Some liquid fuel combinations burn better when they are blended before injection into a combustor than when they are injected separately into the same combustor, although many fuel combinations do the opposite. Previous studies (Delplanque et al., 1990; Delplanque et al., 1991) considered the advantages and disadvantages of blending fuel for incinerating hazardous waste. Some of those concepts might be applicable to aviation fuel. The goal is to find fuels that can be contained in separate tanks on board an airplane and blended on board at a limited rate before being injected into the engine. Delplanque et al. (1990, 1991), in studies of benzene (or toluene or monochlorobenzene) burned with hexane (or decane), found that improvements in overall burning efficiencies sometimes resulted from blending before injection.

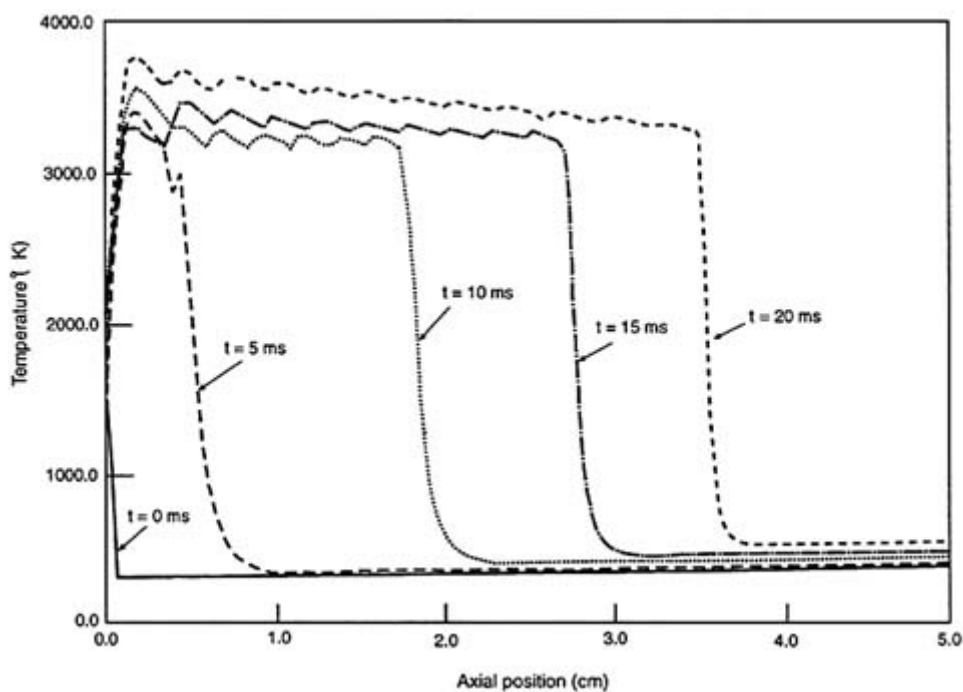


FIGURE 13-10 Gas temperature versus axial position at various times.  
 Source: Aggarwal and Sirignano, 1985.

### CONCLUDING REMARKS

The information presented herein does not lead directly to a practical solution of the very difficult aviation fuel safety problem. It is intended to provide fundamental scientific information, to encourage further research, and to provoke interest in improvements in safety.

In general, the models identified above have not been fully studied. Further study on the sensitivity of fuel to property changes might, for example, indicate a path towards improvements. The effects of inhibitors or quenching mechanisms could be added to the models to aid in the development of practical solutions. This author believes that notable improvements in safety will probably be generated by a combination of modifications rather than by a single engineering achievement. Therefore, a broad range of studies on the fuel safety problem must be initiated and sustained.

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## 14

# Post-Crash Fuel Dispersal

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### ABSTRACT

This paper is brief overview of work done over the last several decades in determining what happens to jet fuel in aircraft fuel tanks on impact with the ground. Fuel dispersal is discussed in terms of overall crash dynamics, and impact regimes are identified. In a generic sense, the types of flow regimes are identified, and general descriptions of the processes are given. Examples of engineering level tools, both computational and experimental, that are used for analyzing the complex environments are presented. Finally, the concept of risk-based decisions is discussed as a quick way of identifying requirements for developing preventive or mitigation strategies, such as antimisting agents.

### INTRODUCTION

Large energies are involved when an aircraft crashes into the ground. Gross take-off weights for large transport or bomber aircraft can be on the order of  $10^5$  kg. With flight velocities in the 10s to 100s of meters per second, the kinetic energy of impact ( $1/2mV^2$ ) can be on the order of  $10^9$  J. The fuel contained in the wing tanks of an aircraft can be in the  $10^4$  to  $10^5$  kg range. The typical energy in jet fuel that can be liberated on combustion is  $4.3 \times 10^7$  J/kg. Therefore, the amount of energy available is on the order of  $10^{12}$  J. These energies are substantial by almost any measure, and the energy available from combustion is potentially several orders of magnitude higher than the kinetic energy on impact.

Because of the energies involved, a crash can result in the destruction of both materials and personnel. Statistics show the magnitude of the effect (The Boeing Company, 1996). From 1959 through 1995, 65 percent of accidents that resulted in damage to the aircraft beyond economic repair also resulted in fatalities. Over the same period, less than 4 percent of accidents resulting in substantial but repairable damage resulted in fatalities. From 1991 to 1995, 71 percent of the fatalities were from loss of control in flight or controlled flight into terrain. Other statistics indicate that for "crash-survivable" accidents, 40 percent of deaths are caused by fire (20 percent of all fatalities) (FAA, 1991). Because of the high energy content of jet fuel and keeping in mind statistics that attest to the effect of fire, understanding the behavior of jet fuel in the post-crash environment is important, even in the presence of ground-based fuel in the impact area.

The role of fuel dispersal in the post-crash environment can best be described if the crash environment is viewed as a process, albeit an undesirable one. At the most abstract level, as shown in [Figure 14-1](#), the crash process can be thought of as a set of initial conditions (crash scenarios) that lead to a set of undesirable events (combustion modes), that lead to a set of unfortunate consequences (death and adverse environmental impact). Two generic strategies are available for interrupting these undesirable processes. These are prevention, keeping the undesirable event from occurring, and mitigation, minimizing the consequences of the accident.

In the context of the process shown in [Figure 14-1](#), fuel dispersal plays two major roles. The first role is within the process description itself. Jet fuel is a major source of combustible material in a crash environment and, therefore, must be tracked from the moment of impact until it is either consumed by fire or it has traveled sufficiently far from the aircraft that it no longer represents a significant hazard.

Because jet fuel is a major contributor to post-crash fires and fires are a major cause of deaths, it is only natural to seek a preventive strategy by changing the makeup of the fuel. Obviously, the ideal solution would be to have a fuel that burns with great vigor in an engine but absolutely will not combust anywhere else. Until someone creates this idealistic fuel, less effective fire prevention strategies must be employed.

Before one can begin to develop preventive or mitigative strategies for an undesirable process, one must first define the process to the extent that concrete design objectives for the preventive and mitigative strategies can be set. Although this statement is obvious, its importance cannot be overemphasized. The need to minimize costs places higher emphasis on fixing an undesirable process than on defining it. However, attempts to fix a process without a quantitative understanding of how the solution will affect the process can lead to higher overall costs and less than optimal results. Unfortunately, the more complex and nonlinear the process, the more difficult it

is to quantify it and, hence, the less likely it is that development of a preventative or mitigative strategy will be successful. Aircraft crash sequences are very complex, nonlinear processes.

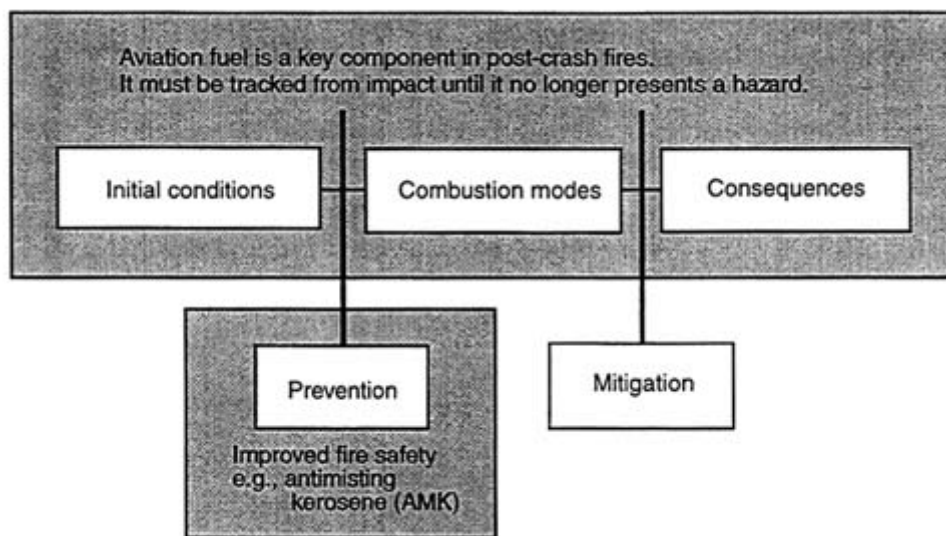


FIGURE 14-1 Dual role of fuel dispersal from a process perspective.

In general terms, fire prevention strategies attempt to separate one key element of fire from the other two. The three key elements are fuel, air, and an ignition source. Because air is ubiquitous, separating air from the other two elements is questionable, except in specific situations like the in-flight inerting of fuel tanks. Thus, either the ignition sources or fuel must be separated from the other two. An example of an ignition source strategy is to cover a runway with foam prior to landing if it appears that a crash is likely. However, not much can be done to eliminate ignition sources completely because hot running engines are required for aircraft flight, and hot brakes are likely in sliding accident. The separation of fuel from the other two fire elements has taken two general forms, improvements to fuel tank structural integrity (improving crashworthiness) and a long running attempt to develop an antimisting agent for jet fuel.

Fuel dispersal in the context of an aircraft crash is discussed in the next section (followed by qualitative descriptions of the processes involved in fuel dispersal). Tools for addressing fuel dispersal are then described, including engineering computational and experimental tools, followed by a description of risk-based decisions as applied to this problem. Because the flow regimes for fuel are numerous, the scope of this paper is limited to qualitative descriptions and the tools shown are meant to be representative, rather than comprehensive. Because of the broad nature of the flow regimes, it is not possible to cover the extensive fundamental research in fluid mechanics that underpins our understanding of them, and no attempt is made to do so in this paper.

### FUEL DISPERSAL IN THE CONTEXT OF A CRASH

Figure 14-2 shows an aircraft impact as a series of processes that are a function of time. These processes fit within the overall description in Figure 14-1. From the time of impact until the aircraft motion is terminated, tremendous energy is being dissipated. During a routine landing, this energy is dissipated into the brakes, tires, and, through thrust-reversers, into the air. In a crash, this energy can be further dispersed in abrasion of the fuselage or other parts that are skidding along the ground or in large-scale deformation upon impact with a solid object, all of which can produce either sparks or hot surfaces for ignition. If impact energies are sufficiently high, loss of fuel containment may result. For example, a fuel tank may fracture and begin to leak, resulting in fuel dispersal. The actual processes involved in fuel dispersal will be discussed in the next section.

Energy dissipation processes create the initial conditions for a fire (discussed with respect to Figure 14-1). The role of preventive strategies is to interrupt these processes. For a specified impact regime, such as a "crash-survivable" regime, the effect of preventive strategies is to prevent fire by preventing fuel, air, and an ignition source from occupying the same spot in space simultaneously.

If fuel vapor, fuel droplets, or sheets of fuel on the ground come into contact with an ignition source, then ignition can occur and fire can spread. In a general sense, fire spread can be thought of as a continuous ignition process with the existing fire acting as the ignition source. Thus, a large fireball that results from the ignition of a fine mist becomes a very strong ignition source for spread of the fire to discontinuous fuel segments via the radiative transfer of heat. Potential ignition sources range in duration and scale from a large fireball,

which would last for several seconds, to fragmenting engine parts and brakes, which can remain hot for several minutes, to small sparks, which may exist for just milliseconds (Tilston, 1989). Once the fire has spread, combustion continues until the fuel is depleted or effective firefighting measures are initiated. Combustion processes can take several modes depending on the state of the dispersed fuel. The modes range from a fireball to a fire above a continuous liquid pool, either stagnant (called a "pool fire") or replenished (called a "spill fire"), to a fire above soil saturated with fuel (called a "dirt fire").

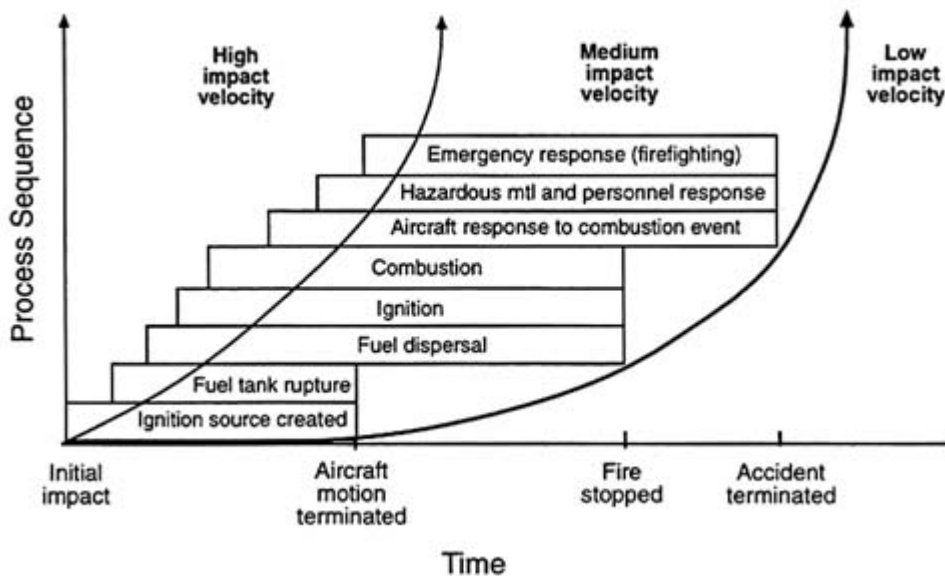


FIGURE 14-2 Processes involved in aircraft crashes as a function of time. The impact velocity regime are defined in Figure 14-3.

The ignition and combustion processes form the combustion modes for a fire. The role of mitigative strategies is to interrupt these processes in such a way that the spread of fire into the cabin area is blocked or the thermal/toxic consequences of the fire on humans and/or hazardous cargo (chemical, biological, or nuclear) is reduced. An example of a mitigative strategy is the use of fire- and smoke-resistant interior materials (National Research Council, 1995).

The consequences of a fire are both thermal and chemical (toxic). The aircraft provides some protection to occupants inside depending on the damage and the environmental conditions, such as wind. In general, the consequences of a crash can be impact trauma, thermal trauma, or both. The term crash-survivable typically means that humans can survive the impact trauma. Crash-survivable conditions for hazardous material containers or for nuclear weapons are usually much broader than for humans. Therefore, the term can be confusing unless the object to which it applies is specified.

Regimes can also be categorized by considering the character of the basic process as a function of impact velocity. This method of categorization is shown in Figure 14-3. While this categorization yields less insight on the ratio of impact to thermal survivability, it yields more insight on physical processes that occur in an accident. Accidents can be broadly characterized as "sliding out" accidents or "augering in" accidents (Kuchta and Clodfelter, 1985; Tieszen, 1995) depending on their "normal" impact velocity, the velocity perpendicular to the surface. At low normal impact velocities, a plane lands safely. Above a certain normal impact velocity, in the case of landing gear failure, for example, the plane crosses into the medium impact velocity regime. At medium normal impact velocities, a crash can be characterized as a slide-out, i.e. the plane slides along the ground. The fuel tanks can be damaged in this regime but are not fragmented. Fuel dispersal results from leakage from the damaged tanks. Ignition may result in a small to moderate fireball. After the aircraft comes to rest, pouring fuel can cause a long duration spill fire. At higher impact velocities, the plane and fuel tanks are fragmented as the plane augers in. The fuel disperses in a large splash, and ignition results in a large fireball. Fuel remaining on the ground burns as a pool or dirt fire.

The distinction between medium and high impact regimes is somewhat arbitrary. However, for reference, Wittlin (1987) concludes that a distributed-load wing impact (such as striking a low hill or mound with the wing) between 60 and 72 m/sec will devastate the wing fuel tanks. For concentrated loads (such as a telephone pole), the velocity at which the wing tanks will be destroyed is even lower, 33 to 41 m/sec, depending on the type of obstacle. Because jet flight speeds are well above this range, any impact into the side of a steep

mountain or building can be considered a high velocity impact. Airports are increasingly being surrounded by the growth of cities, in part because of the commercial opportunities near airports. Considering that almost 50 percent of fatalities already occur during landing and take off (The Boeing Company, 1995), a significant increase in vertical surfaces (i.e., buildings) may mean a significant increase in high velocity impacts. The ratio of ground to aircraft fatalities may also increase with time.








| Model     | Impact velocity regime  |   |   |
|-----------|---|---|---|
|           | Low   | Medium  | High  |
| Impact    | Safe landing<br> | Slide-Out<br> | Auger-In<br> |
| Dispersal | None  | Leakage<br>    | Splash<br>   |
| Fire      | None  | Spill<br>     | Pool<br>     |

FIGURE 14-3 Classification of crashes by impact velocity.

The impact velocity regimes shown in Figure 14-3 can be qualitatively mapped onto the timing of the crash processes shown in Figure 14-2. The higher the impact velocity, the sooner each process begins.

### Fuel Dispersal Processes in Medium Velocity Impacts

The crash-survivable regime for humans is wholly within the medium velocity impact range. The principal study of this regime has been the long running FAA program on the development of antimisting kerosene, which ended in 1986 (Yaffee, 1986). The program conducted a dozen full scale tests between 1965 and 1984. The structural damage to fuel tanks and the efficacy of crash resistant designs can be found in Nissley and Heid (1964), Buckson, et al. (1965), Schauerman (1971), Hackler (1972), and Wittlin (1987). Studies characterizing antimisting fuels can be found in Ahlers (1970), Miller and Wilford (1971), Russell (1971), Rockow and Shaw (1972), Faul (1978), Salmon (1981), Mahood and Talley (1982), and Parikh, et al. (1983). Other programs to evaluate crashworthiness have also been conducted within the Department of Defense community (see for example, Shaw [1971] and Johnson, et al. [1989]).

Only a small number of direct measurements of fuel dispersal without an antimisting agent are available. A summary of the data directly related to the physical processes involved in fuel dispersal can be found in Tieszen (1995). The processes involved in fuel dispersal in the medium impact velocity regime are shown in Figures 14-4 and 14-5.

Figure 14-4 shows the dispersal stages prior to ignition of the fuel. Initially, upon impact with the ground, the fuel in the tank is subject to inertial loads because of rapid deceleration of the aircraft on impact (in addition to the gravitational force). The fuel sloshes around in the tanks to adjust to the time-varying inertial force. Because the fuel mass is usually many times the wing mass, the inertia of the fuel and its compressibility are important in determining the impact dynamics of the fuel tank and influenced the damage from the impact. If a fuel tank is punctured or torn, inertial and gravitational forces create a flow out of the tank. The rate of leakage will be proportional to the damage (hole area) and the forces present.

The next stage of dispersal occurs as the balance of forces on the fuel emerging from the tank changes. The fuel stream is subject to a free pressure boundary just outside the damaged tank. During a slide-out accident, there is relative motion between the aircraft and the surrounding air. As a result, the



total pressure against the fuel stream changes rapidly as it traverses the boundary layer between the tank surface and the free stream. Because of the destabilizing processes of aerodynamic drag and because of turbulence within the fuel itself, a sequence of breakup processes begins that results in the atomization of some fraction of the fuel. Initially, drops are shed from the liquid column. Under certain flow regimes, the whole column can break up into sheets, ligaments, and drops. Surface tension is the primary force resisting breakup. However, the breakup process occurs in the presence of regions of high spatial and temporal gradients, so rate dependent forces, such as viscosity, which retards breakup, can affect the outcome. The process by which a continuous liquid jet becomes atomized is called primary breakup.

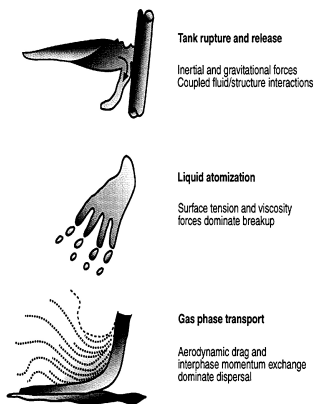


FIGURE 14-4 Stages of pre-ignition fuel dispersal in the medium-impact velocity regime.

An in-depth description of breakup processes can be found in Lefebvre (1989). Recent studies showing the effect of turbulence in the liquid phase can be found in Wu, et al. (1992), Wu and Faeth (1993), Wu, et al. (1995), and Wu and Faeth (1995). The two distinct flow streams in this stage of dispersal are airborne droplets, which result from the primary breakup, and the residual fuel stream, which continues to fall until it reaches the ground.

The next stage of dispersal of the airborne droplets involves secondary breakup and interphase momentum exchange with the air. Secondary breakup occurs if the drops are large and the velocity difference between the drops and the gas is high. The secondary breakup process has traditionally been viewed as a balance between inertial forces and surface tension. If there are many small drops, then they can coalesce into larger droplets.

The final size distribution of drops is important because it affects the rates of interphase momentum exchange, which occurs continuously from the time drops separate from the fuel stream. The momentum transfer distance can be quite short for small droplets; larger droplets can travel many meters. Given sufficient travel distance without impacting a solid surface, droplets eventually reach an equilibrium velocity relative to air as a result of gravitational acceleration. Although the transfer of momentum from the fuel stream to the air is dissipative, it does not imply a total loss of momentum. Rather the air acquires the momentum and transports the drops. As a result of interphase momentum exchange, a spray can be transported via turbulent air motion over large volumes of space.

Depending on the amount of damage to the fuel tank and the slideout velocity, the fuel flowing from the tank may not be atomized to the point that it is significantly deflected by the air. The fuel stream, both as a continuous column and as discontinuous, partially atomized segments, can continue to fall under the influence of gravity until it reaches the ground. Not all of the fuel that reaches the surface as a liquid stream remains on the surface. Some droplets may splash off the surface back into the air, depending on the impact velocity and liquid turbulence levels (Errico, 1986; Lienhard et al., 1992; Bhunia and Lienhard, 1994a, 1994b; Tieszen, 1995).

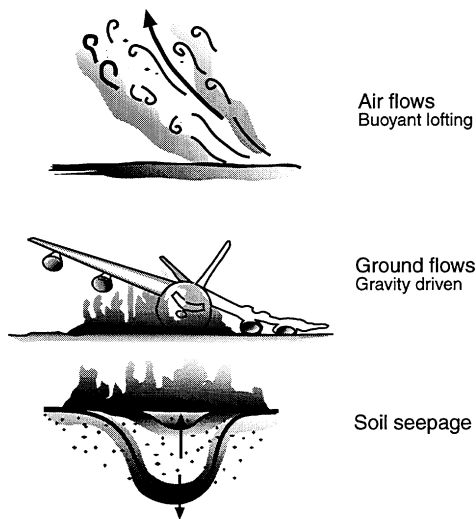


FIGURE 14-5 Stages of post-ignition fuel dispersal in the medium-impact velocity regime.

Depending on the velocity of the fuel stream hitting the ground, the flowing liquid can be either faster than the gravity wave speed on the free surface, i.e., supercritical, or slower than the gravity wave speed, i.e., subcritical. If it is supercritical, a hydraulic jump will follow, which reduces the velocity to subcritical. The subcritical fluid will continue to spread over the terrain. At this point, the fuel spread rate is governed by several factors, including gravity, the slope of the terrain, inertia of the existing fluid, and viscous drag on the solid surface (Didden and Maxworthy, 1982; Huppert, 1982; Lister, 1992). Soil porosity will also affect the spread rate and size of the spill.

Fire can only occur in the presence of fuel, air, and an ignition source. A criterion for ignition can be thought of as the instantaneous overlap of the geometric regions for which ignition energies are present and for which an ignitable spray volume or liquid fuel stream is present. Viewed in this manner, determining ignition requires time-dependent, spatial tracking of energy sources and fuel streams for simultaneous co-location (and accounting for action-at-a-distance mechanisms, such as radiative heating). Determining the ignition of spray requires tracking the concentration and size of drops, which must be sufficient to initiate ignition and propagate flames. The key parameter for the liquid stream is spatial distribution. If ignition sources and fuels can be kept separate for all points in space and for all points in time during the accident transient, then there will be no fire.

Figure 14-5 shows the stages of fuel dispersal after ignition of the fuel. Ignition of the mist can result in a fairly sizable fireball that results in radiant heating of nearby fuel surfaces. Fireballs radiate energy for anywhere from a few seconds to tens of seconds, depending on the mass (Dorofeev et al., 1991). Because of the buoyancy induced by combustion, the fireball will rise, and the combusting mist will be elevated with it. In this manner, fireballs quickly consume fuel. However, they also provide a large ignition source for fuel that might not otherwise be ignited. In addition to radiative heat transfer, a fireball can spread flames back along the fuel mist to the fuel source, if the fuel mist has no discontinuous or nonflammable regions. The flame can then anchor onto the spill point on the aircraft.

Depending on the amount of damage to the fuel tank and the amount of fuel in the tank at the time of the accident, fuel may continue to drain long after the aircraft comes to rest. If ignition occurs in the fuel on the ground, flame spread can result in the propagation of flames back to the source, if the fuel spill has no discontinuous or nonflammable regions. The flame can then anchor onto the spill point on the aircraft.

After the aircraft comes to rest, the flow of liquid from the tanks will primarily be gravity driven. However, fire induced heating of the tanks may produce residual pressures that can contribute to the rate at which the fuel leaks from the tank. The size of the fire will be limited by the balance between the rate of evaporation caused by the fire and the spill rate (Cline and Koenig, 1983).

Besides flowing over the ground, fuel can flow into the ground, if the ground is porous and if the pores are not saturated with water. In addition to gravity, fuel is pulled into porous ground by capillary pressure that is a function of pore size. Because of capillary pressure, fuel that has flowed into the ground is not necessarily safe from being evaporated by and contributing to the fire. In this case, evaporation from the fire dries the surface of the soil and fuel under the dry layer is pulled up against the force of gravity by capillary forces to evaporate and feed the fire. Very long duration fires can be sustained this way.

### Fuel Dispersal Processes in High Velocity Impacts

The high velocity impact regime has received less attention than the medium velocity regime. The lack of interest in this regime is not due to a lack of accidents occurring in this regime but to the fact that human survival in this impact regime is problematic. The primary source of data for this regime has been U.S. Department of Defense studies, the most recent of which is the Defense Special Weapons Agency (DSWA) Fuel-Fire Technology Base program, which has sponsored studies of post-crash fuel dispersal (Tieszen, 1995; Tieszen and Attaway, 1996) and fires in post-crash environments (Gritz et al., 1995, 1996; Nicolette et al., 1995; Tieszen et al., 1996b). The primary goal of these studies is to characterize the post-crash environment to the extent that it affects nuclear weapon safety. Rather than trying to develop preventive engineering measures as the FAA has done, the DSWA program was intended to increase understanding of the crash process so risk-assessment compatible models could be developed. Risk assessments place significant time constraints on models because tens of thousands of scenarios are often run to establish statistical significance. As a result, the models focus only on dominant physical mechanisms.

The primary difference between the medium impact velocity regime and the high impact velocity regime is that aircraft tend to slide out in the medium velocity regime and auger in the high velocity regime. The dividing line between the regimes is continuous and therefore somewhat arbitrary. Figure 14-6 shows examples near the boundary between the regimes. On the medium velocity impact side of the regime, damage to the fuel tanks increases as impact velocity increases. For example, a heavily damaged wing may separate from the fuselage and tumble down range, leaking fuel in the process. This type of accident begins to be indistinguishable from the high-speed impact in which the wing is fragmented on impact, and the fuel and fragments are thrown forward from the impact.



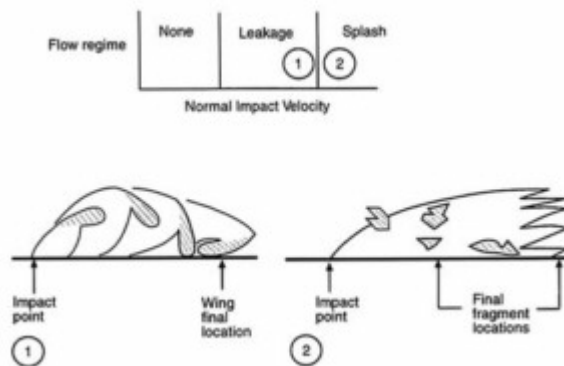


FIGURE 14-6 Transition from medium- to high-impact velocity regimes. A tumbling wing splashing fuel forward of an impact point becomes indistinguishable from a fragmentation impact.

Figure 14-7 shows the stages of fuel dispersal in the high impact velocity regime. In many respects, the flow regimes are not qualitatively different from flow regimes in the medium impact velocity range, although there are quantitative differences. Note that in many cases, the angle of impact, not just the velocity, determines whether or not the impact is of the high normal impact velocity type. The impact of any aircraft at any flight speed against the side of a steel building will result in fragmentation of the aircraft and augering in to the building.

Upon initial impact with the ground, the fuel in the tank will be subject to inertial loads caused by the rapid deceleration of the aircraft on impact. The compressibility not only of the fuel mass but also of the surface that is impacted is important. If the surface is sufficiently hard, such as a concrete runway, there may not be craters. If the surface is sufficiently soft, such as a plowed field, then there will certainly be craters. Studies have shown (Tieszen, 1995; Tieszen and Attaway, 1996) that there is a distinct difference in the dispersal characteristics of crashes into cratering and non-cratering surfaces. This difference illustrates the effect of inertial coupling and compressibility on the problem.

The next stage of dispersal occurs as the fuel emerges from the ground surface or crater. Just as in the medium impact velocity regime, the fuel stream in the high velocity regime is subject to a free pressure boundary. Because of the destabilizing processes of aerodynamic drag and turbulence within the fuel itself, breakup processes begin, which results in complete atomization of the fuel leaving the surface. Surface tension is the primary force resisting breakup. However, the breakup process occurs in regions of high spatial and temporal gradients, so rate dependent forces, such as viscosity, which retards breakup, can affect the outcome. The fuel that leaves the surface is likely to be completely atomized because of the large scale and high velocity associated with the impact

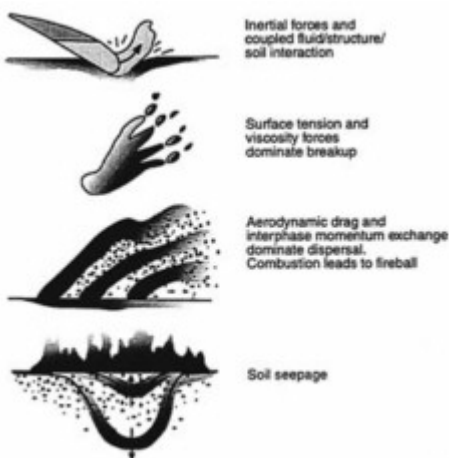


FIGURE 14-7 Stages of fuel dispersal in the high-impact velocity regime.

(Tieszen and Attaway, 1996). However, not all the fuel in the tank leaves the surface in an accident that involves craters. More than 50 percent of the fuel can remain in the crater, depending on the angle of impact (Tieszen and Attaway, 1996).

As a result of the energies involved in impact and the intermixing of aircraft fragments with fuel, ignition is very likely in cratering impacts. In the high velocity regime, it is very difficult to employ any mitigative strategy to prevent ignition by maintaining physical separation of the fuels and ignition sources. Given ignition, the airborne fuel spray causes a large fireball and is consumed. In the medium impact velocity regime, the presence of the fireball significantly increases the probability of ignition and, in this sense, is considered to be detrimental. In the high impact velocity regime, when ignition is virtually guaranteed by intermixing, the fireball is a quick way of burning off the fuel. Often hazardous cargoes are sufficiently hardened so that fireball heat lasting seconds to tens of seconds will not damage the cargo.

Long duration fires present a more serious consequence and can be of two types. If the fuel in the crater is in the form of a continuous liquid pool, then the fire will be a pool fire. If the fuel pool is or becomes discontinuous as a result of seepage into porous soil, then the fire can be sustained off the evaporation from the soil and is a dirt fire. The location, intensity, and duration of this fire relative to hazardous cargo containers has been the principal concern in this type of accident.

### Engineering Tools for Post-Crash Fuel Dispersal

Computational and experimental tools that have been applied to fuel dispersal problems are briefly addressed in this section. The purpose is not to be comprehensive but to give the reader a feeling for the types of tools and their uses. As has been discussed, the range of multiphase flow regimes that can result from fuel dispersal is extremely broad. For this reason, space does not permit a discussion of fundamental research tools and results. Tools and issues for four stages of dispersal are briefly covered, tank damage/destruction, fuel atomization, interphase momentum exchange, and ground flows.

The initial stage of fuel dispersal involves tracking the fluid out of the tank. Typically, compressibility is important. Computationally, the tool of choice for many years for this type of problem has been the transient, multidimensional hydrocode. An example of the use of the CTH computer code on a fuel dispersal problem is given in Gardner (1990). A new approach has recently been developed that can easily be coupled to standard finite-element based approaches, which are now the norm for structural dynamics (Attaway et al., 1994). The new approach is called "smooth particle hydrodynamics" (SPH). Although SPH has not yet been completely accepted for general fluid mechanics work, it has many advantages for short duration, high strain rate impacts (such as a gridless formulation that allows large mesh deformation without entanglement).

Figure 14-8 shows a sample two-dimensional calculation (Tieszen et al., 1996). Shell elements representing the wing

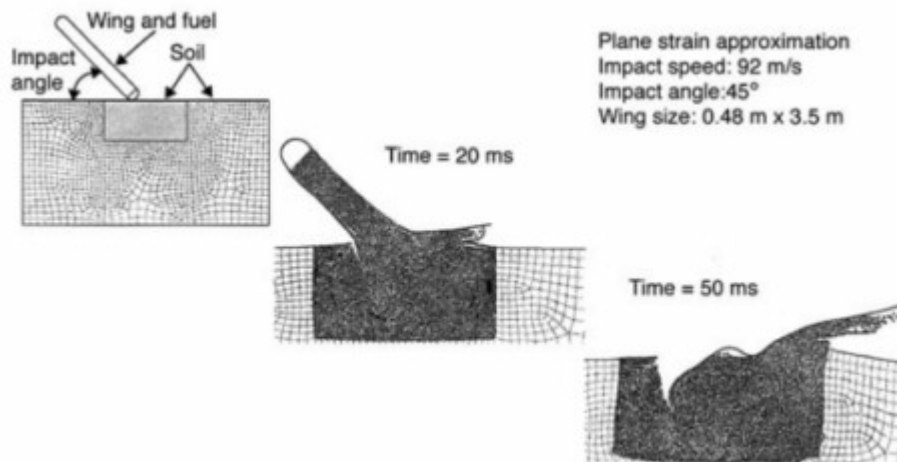


FIGURE 14-8 Example of numerical simulation tool for the impact stage of dispersal. Example of two-dimensional SPH calculation. Source: Tieszen et al., 1996a.

skin can be used in the same formulation as the gridless integration points. Both the fuel in the wing and the soil in the near impact region employ the smooth particle integration points. Although SPH allows for differing formulations of equation of state, the time step must be very short to take into account the effects of compressibility. For this and other reasons, SPH is not particularly suitable for tracking fluid beyond the impact and breakup of the tank into the atomization regime.

Figure 14-9 is a photograph of a small gas gun that was used to test the suitability of the SPH approach for liquid/soil impacts (Tieszen and Attaway, 1996). The facility depicted is representative of the facilities in federal laboratories used to study impacts. Very few of these facilities have been used directly for dispersal studies, but many could be modified to cover the range needed for investigating dispersal. The U.S. Department of Defense (all services), the U.S. Department of Energy, and the U.S. Department of Transportation also have impact facilities, ranging in size from several feet long (Figure 14-9) to large sled tracks that run for miles (for example, at White Sands Missile Range, at Naval Air Warfare Center-China Lake, and at Sandia National Laboratories). Most facilities use high-speed cinematography and can record high-speed digital data, such as data from strain gages. The author knows of no transient measurements of the characteristics of fuel leaving the tanks in any tests.

The second stage of fuel dispersal, atomization, is still not understood sufficiently to have been examined computationally at relevant scales and velocities. The principal reason for the lack of an engineering computational tool for this stage (in the author's opinion) has been the differences in length scales. The minimum cross-sectional diameter of a wing, near the wing root, is a significant fraction of a meter. To capture fuel tank breaks and liquid flow from the tank, length scales on this order are required. At the same time, surface tension acts over submillimeter length scales (as evidenced by the distribution of drop sizes from simple pressurized atomization, which range down into the hundreds of micrometers in diameter). Therefore, to be relevant to the engineering problem and to resolve the range of surface tension forces, a spectrum of at least four orders of magnitude (from submillimeter to meter) for each spatial dimension must be run. In three dimensions, this would require  $10^{12}$  grid points, a very large number by any standard, particularly for a transient, multiphase flow problem.

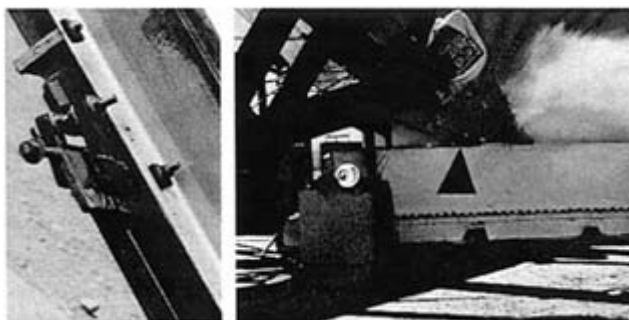


FIGURE 14-9 Example of impact facility for studying the impact stage showing liquid impact into soil to determine dispersal. Model wing chord is 0.084 m and impact at 45<sup>1</sup> and 64 m/s. Source: Tieszen and Attaway, 1996.

In many situations the length scale problem can be resolved by placing dense grid points only in regions that require it. This strategy may be used to solve the present problem as well, but as the fuel surface begins to break up, the regions that require high grid density will quickly grow, and the location of break up will change as a function of time. To the author's knowledge, no computational tool directly addresses the problem. Perhaps with the new "teraflop" level of computing hardware, it will be possible to modify existing tools to conduct two-dimensional simulations of the breakup process. It is anticipated that fully transient problems with  $10^8$  grid points will be within the capability of the early teraflop level machines.

In an experimental sense, substantial progress has been made in the commercialization of hardware that can characterize drop size. Commercial hardware vendors include Malvern, Insitec, Dantec, and Aerometrics.<sup>1</sup> Available instruments can characterize drop size and, in some cases, velocity. Unfortunately, they are most applicable in flow regimes near the end of the primary breakup stage and into the interphase transfer stage. For various reasons, they have increasing trouble in the primary breakup stage. Experimental diagnostics in the primary breakup phase is still being investigated at the laboratory scale, and, in the author's opinion, this situation will continue. Even though engineering scale tests could be conducted in the impact facilities mentioned above, the relevance of the tests would be limited by the level of diagnostics that could be brought to bear.

The third stage of fuel dispersal, interphase momentum exchange, has even broader length scale ranges than the breakup stage. However, as the overall density of the fuel phase decreases relative to the gas phase, it is possible to treat the liquid phase as dispersed within the continuous gas phase. Computationally, the drops are treated as subgrid models by size classes, allowing for breakup, coalescence, and interphase momentum exchange, in an engineering sense. Figure 14-10 shows a sample calculation of a dispersal of decane droplets (Glass, 1990). The computational tool is a modification of the KIVA-II code, one of several products of the T-3 group at Los Alamos National Laboratories that can be used for this application.

<sup>1</sup> Respectively, Malvern Instruments, Inc., 10 Southville Road, Southborough, MA 01772; Insitec, Inc., 2110 Omega Road, Suite D, San Ramon, CA 94583; Dantec Measurement Technology, Inc., 777 Corporate Drive, Mahwah, NJ. 07430; and Aerometrics, 777 N. Mary Ave., Sunnyvale, CA 94086.

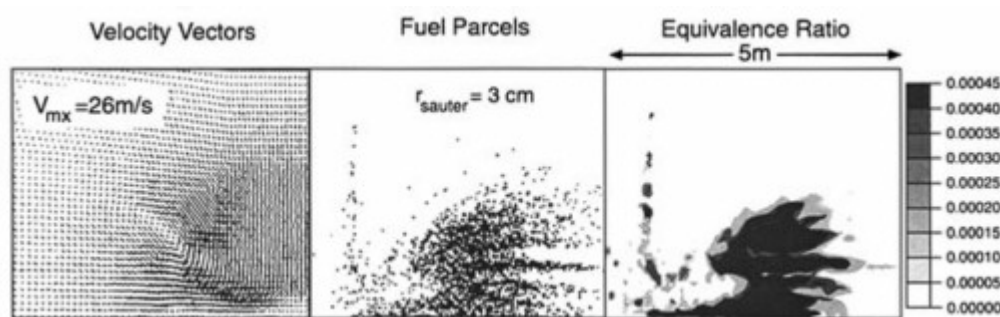


FIGURE 14-10 Example of a numerical simulation tool for the study of the interphase momentum exchange stage using a modified version of the KIV A-II code. Source: Glass, 1990.

Experimentally, the interphase momentum exchange can be studied in engineering environments in the impact facilities mentioned above. Figure 14-11 shows a test from a medium-scale study of an impact on a runway in which the fragmentation of the airframe was ignored (Tieszen, 1995). Drop size diagnostics were not used in the study, but the footprint of the spray was determined by mass collection as a function of position from the point of impact. The mass was collected by rapidly deploying absorbent media. All of the commercial drop size measurement devices work well in the interphase momentum exchange regime.

Tools are available for the study of ground-based flows in the final stages of dispersal prior to ignition. Computationally, commercial tools like Flow 3D<sup>2</sup> can be used to track slow moving free surface flows over terrain. Experimentally, flows can be measured at any number of university hydrology laboratories at the appropriate scales.

Post-ignition flows are very difficult to model computationally. The author is not aware of any computational fire models that couple free-surface flow solutions simultaneously with the fire. Computational fire models with fuel spray models are being developed but to the author's knowledge they had not been quantitatively demonstrated at the time of this paper. There are numerous fire test facilities in the U.S. Department of Defense (all services), the U.S. Department of Energy, and the U.S. Department of Transportation. However, the environments are so difficult to work in that the quantitative measurement of fuel dispersal characteristics during fire transients has received very little attention.

### RISK-BASED DECISION

Given the current state of knowledge and the available tools, one may ask how one can design a preventive or mitigative strategy to minimize the consequences of fuel fires in the post-crash environment in a cost-effective manner. The answer involves work in two areas. For a given strategy, such as the strategy pursued by the FAA for antimisting kerosene, one must first develop design criteria and then develop the strategy to meet them.

The development of design criteria implies that the post-crash dispersal process is sufficiently understood to permit quantitative assessment. However, from the previous discussion it is obvious that although the dispersal processes in the post-crash environment are qualitatively understood, there is not enough information to predict the effect of a preventive strategy (say a fuel viscosity change) on the dispersal characteristics. This lack of knowledge implies that fundamental work must still be done to characterize the post-crash dispersal environment.

The goal of a risk-based decision is to produce design criteria based on risk reduction targets (Bohn, 1992). The methodology is very similar to probabilistic risk assessment (PRA) methodologies. In a PRA the goal is to analyze an existing process to determine the overall risk and the major contributors to that risk. PRA is based on data from three sources, historical data, deterministic subprocess models, and expert elicitation. A risk-based decision differs in that the process to be studied is new. One of the strengths of a risk-based decision is that it can be used (1) to define the physical processes that need to be understood to make changes at the system level, (2) to identify the uncertainties in the process models and sensitivity to uncertainties at a system level, and (3) to conduct cost-benefit analyses to determine the trade-offs for a given preventive or mitigative strategy.

For a risk-based decision, historical data, such as accident frequency, can be used as inputs to the process (provided, of course, that the frequency of accidents is not modified by the process modification), but the sequence of events that occurs with a preventive or mitigative strategy in place (say a modified-viscosity fuel) must be specified by one or more deterministic models. The deterministic models must be designed

<sup>2</sup> Flow Sciences, Inc., 1325 Trinity Drive, Los Alamos, NM 87544.



so that the effects of the new design strategy can be propagated through the model to the consequence of interest, say passenger deaths from fire. For example, for a modification of fuel viscosity, there might be one model for the effect of viscosity on drop size distribution of the atomized spray, one for the effect of drop size distribution on the size and location of the combustible spray cloud, one for the effect of the cloud size and location on ignitability, and so forth to passenger deaths. The models must be valid over the range of crash parameters for which they will be exercised (medium and high impact regimes).

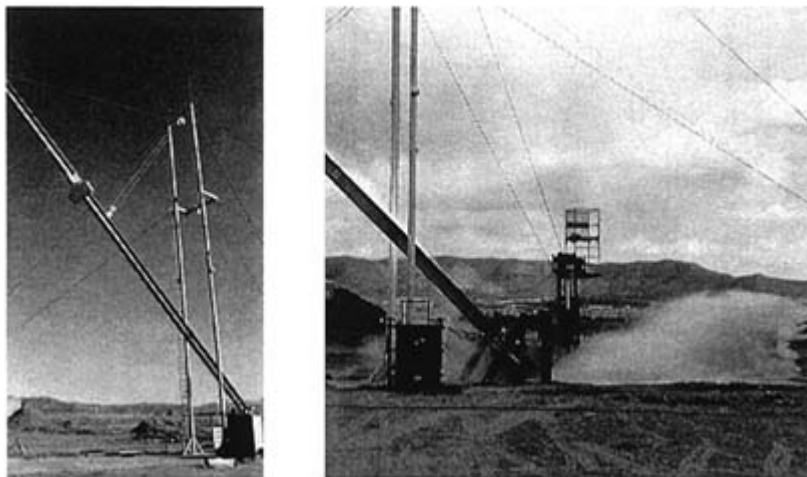


FIGURE 14-11 Example of impact facility for studying the impact stage showing liquid impact into a runway.  
Source: Tieszen and Attaway, 1996.

In an ideal world with perfect knowledge of all physical processes, this type of strategy would not be difficult to implement. However, in practice it is very difficult. For example, some of the physical processes may not have been quantified or may be very difficult to quantify. Under these conditions, it is not possible to design deterministic models for physical processes without additional fundamental research to describe the physics, which requires considerable time and resources.

Historically, in the absence of a clear physical description of the physical processes involved, engineering judgment has been based on the best available knowledge. The risk-based decision process can be used to focus such expert judgments along the lines of the required models. Engineering judgment from individuals with relevant expertise can also be used to estimate effects, based on the best available knowledge. The initial estimate of the effects could be used to guide the development of experiments and models.

This development path, although initially tenuous because of the engineering judgments, would lead to design criteria on a system-wide level. As the process is better understood from the data and models, the estimate of effects would become stronger and more defensible, i.e., less engineering judgment-based and more science-based. The process could be continuously refined to reduce engineering judgment until a satisfactory level of scientific defensibility is reached. At all stages of refinement, uncertainty estimates could be tracked, including uncertainty estimates based on the expert judgment.

In the author's opinion, this would be the most cost-effective way of determining the necessary fundamental research to complete a study, and would allow the most resources to be focused on the development of specific preventive or mitigative strategies. Once all processes are known, the risk based decision process can also be used to decide if a preventive or mitigative strategy makes sense on a cost-benefit basis. To make this decision, cost estimates for research, development, and implementation must be generated, as well as estimates of the expected savings based on the number of deaths prevented (from insurance data, for example). Cost-benefit analyses for different strategies can be conducted without insurance data.

Using a systems strategy, such as a risk-based decision process, the effect of a preventive measure can be tracked throughout any defined process. For example, if a modification in viscosity could be made to the fuel just before impact, only the postcrash environment would need be considered. If the modification was made as the fuel was pumped onto the aircraft, then the effect of the change would have to be tracked through all processes the fuel is used for, from lubrication to combustion. In this way, the positive effects of the modification in the postcrash environment could be balanced against negative effects in other processes.

## CONCLUSIONS

Much has been learned about post-crash fuel dispersal processes in the last few decades, both from programs directed at understanding this environment and from fun

damental research in fluid mechanics. In general terms, the processes of fuel dispersal can be qualitatively described, but in many cases, quantitative predictions of effects are beyond our capabilities. Tools, both experimental and computational, have been developed and applied to the dispersal problem and will continue to be developed and improved with time. In designing a preventive or mitigative strategy, the crash process must be understood well enough to develop quantitative design criteria. Risk-based decisions represent one approach that might achieve this goal. However, quantitative descriptions will not come easily because the postcrash environment involves a myriad of complex, coupled, and nonlinear processes that are, by their very nature, difficult to describe quantitatively.

### ACKNOWLEDGMENTS

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## Appendices

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## Appendix A

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## Appendix B

### **New Concepts in Fuel Fire Research: Final Summary Report of Short-Term Advisory Services (STAS) Team**

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<sup>1</sup> The views, opinions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

### Executive Summary

This report describes the consensus of results and opinions reached by a STAS team review of proposed development strategies for a new fire-resistant fuel for use in Army vehicles. It was concluded that one of the most limiting issues of previous efforts has been the consideration of fuel and vehicle related modifications as separate issues, and future work should be proposed and carried out on a systems (fuel, fuel system, engine system, deployment) basis. Furthermore, fundamental/engineering issues which are important to optimizing the various methods available for fire hazard mitigation remain unanswered. Future programs should take a more balanced approach (than demonstrated by previous programs) in providing sufficient fundamental knowledge to guide the development of optimum approaches.

Constraints for previous research goals were not suitably defined in advance of development or deployment-oriented efforts, and those stated for future program development are unrealistic. Specific, acceptable, and realistic criteria for the program solution must be made before any new program or program continuation is initiated. A critical part of deriving these criteria is a conservative cost-benefit ratio analysis of changes in vehicle performance, range, costs, retrofit, deployment, etc. with fire hazard reduction. Acceptable vehicle/fuel systems modifications criteria need to be established because they are in themselves important and sometimes synergistic to modifications in fuels for reducing fire hazard.

In reviewing the proposed approaches the program phase plan for future work, it was concluded that the disadvantages produced for operating combustion systems by the presence of halons outweigh fire hazard advantages which would result from their addition. Techniques to remove additives prior to combustion are limited, and four year development of a successful system based on any use of halons other than in approaches currently under development for compartment deluge on M-1 tanks appears unlikely. Furthermore, implementation as a fuel additive would appear to involve substantial logistics difficulties and performance degradation.

An 18-month decision point on the proposed approaches is unrealistic because sufficient fundamental information on which to judge their viability is lacking. In fact, there is such a substantial lack of fundamental understanding available for association polymers that it is unrealistic to consider this approach as a serious candidate for four year development and deployment. Long term fundamental research on both conventional and association antimisting polymers is needed on the physical behavior of these compounds under shear before even a decision point for development research can be made.

Recommended additional approaches which are believed to hold potential for development and deployment include fuel flash point modification, fuel cooling, halon compartment deluge, and line closure systems. These approaches are all based on established technology, have significant fire hazard reduction potential, are compatible with the addition of other approaches which involve fuel modification, and do not result in (what appear to be) unacceptable performance or logistics penalties. With fuel cooling and suitable fuel systems modifications, conventional antimisting agents may have some potential for reducing aerosol formation, but again fundamental information to guide successful development is lacking. Techniques to derive liquid/vapor interface dilution such as micro-emulsions and/or co-solvent formulations have substantial promise for producing fire-resistant fuel formulations and should be pursued. Fundamental phase diagram development work is critical to evaluating these approaches and deriving optimum formulations.

### Preface

Extending over the past twelve years, the U.S. Army has been involved in several research programs, all of which have been directed at reducing the fire threat resultant from required fuel supplies carried aboard combat vehicles (both air and ground). Both mechanical and vehicular design changes as well as modifications of the fuel itself have been considered.

Most recent efforts on fuel modification have been devoted to development of a fire-resistant fuel (FRF) based on water-in-fuel micro-emulsion technology. During the last two years, major difficulties have surfaced in this program, particularly with regard to potential field introduction of the FRF formulation brought forward from this research. At the U.S. Army Materials Development and Readiness and Command level, all research on the current FRF formulation was terminated because of logistical, technical, and organizational problems which would result from field introduction. Subsequently, the Fuels and Lubricants Division has been requested to develop an unconstrained plan that would place a new FRF formulation into the field within four years from initiation of the program. In order to aid the Materials, Fuels and Lubricants Laboratory and the staff of the U.S. Army Fuels and Lubricants Research Laboratory in developing the framework for this new plan, both the Coordinating Research Council Ad Hoc Fire-Resistant Fuel Advisory Group and a Short-Term Advisory Services (STAS) team of eleven academicians and scientists were asked to give assistance in reviewing those approaches which are to be proposed and/or recommending alternatives that might assist in this effort.

This summary report describes the consensus of results and opinions reached in a two day working session held by the STAS team on May 8-9, 1984 at the Army Fuels and Lubricants Research Laboratory, Southwest Research Institute, San Antonio, Texas. In addition to ten of the team members, Dr. D. Mann of the U.S. Army Research Office, Mr. F.W. Schaeckel, Chief of the Fuels and Lubricants Branch of the Materials, Fuels, and Lubricants Laboratory (Fort Belvoir), and six researchers from the Army Fuels and Lubri

cant Research Laboratory (A.A. Johnston, S.J. Lestz, W.D. Weatherford, Jr., B.R. Wright, G.E. Fodor, and M.D. Kanakia) were present to brief and assist the team. The team expresses its gratitude for the briefings given and the clarifications offered by these individuals during the meeting. We also thank Southwest Research Institute for the hospitality shown the team members during the meeting. Finally, the team leader expresses his gratitude for the material contributed to and draft review of this summary report by the team members.

### Introduction

As part of the work statement (TCN 84-047) under which the STAS team operated, the task objective of the team was to review the proposed development strategy for the new fire-resistant fuel and to recommend any additional approaches and/or concepts having potential merit. More specifically, the team was charged to:

1. Review the pertinent background information summary on the research and development activities completed to date on fuel fire reduction.
2. Review the different approaches for a new fire-resistant fuel being proposed for consideration within the new draft plan and assess the merits of each approach being considered.
3. Recommend any additional approaches for the development of a new fire-resistant fuel not addressed in the plans above.
4. Assess the potential for success within each approach; that is, based upon the existing technology, what is the opportunity for achieving the specific goal.

In meeting these charges, the team first spent considerable time in attempting to define the technical aspects of the problem, particularly, the scientific fundamentals, and the systems interactions which are relevant to reducing fire hazard. Summaries of the team discussions on the technical issues and on the various methods for reducing fire hazard are presented in the second section (on technical issues) and third section (on methods for producing fire-resistant fuel properties) below. These sections provide the background for the specific task discussions on the above charges which appear in the fourth section.

### Technical Issues

#### Fire-Resistant Fuel, The Problem Definition

The fire problem associated with liquid fuels stored in vehicles can be fundamentally viewed in terms of the following three principal, but not entirely separable, phenomena:

##### *Fuel Spillage*

The compartment (or compartments) which store the fuel, and/or the fuel delivery system on the vehicle are somehow damaged allowing the fuel to escape. If the fuel is under pressure or the impact which causes the malfunction is severe, the spillage initially results in a fuel aerosol cloud, often followed by further spillage which yields a fuel pool in the vicinity of the vehicle.

##### *Ignition*

The presence of hot surfaces or incendiary fragments in the vicinity of the fuel aerosol cloud and/or fuel spill lead to ignition.

##### *Flame Propagation and Pool Ignition*

Flame propagates through the aerosol cloud, and formation of a large "flame ball" ensues. The diffusion/mixing limited character of this flame ball yields large amounts of gas phase soot formation and results in substantial continuum radiative heat transfer. For combat scenarios, it appears that the flame ball alone may result in irrevocable consequences to both vehicle and operating personnel. Further, the intensity of radiation is typically severe enough to further involve any fuel pool spill which has occurred, thus causing additional damage from the sustained burning in the vicinity of the vehicle.

Tantamount to the fire evolution is the ignition process. If the source of ignition can be effectively removed or the ignition process otherwise inhibited, no fire would follow. There are, however, essentially two "ignition" processes: that which leads to the formation of the flame ball, and that of the spilled pool. Elimination of the flame ball ignition process would be more effective as a hazard control method since the flame ball typically causes severe damage. Furthermore, the flame ball is the more likely ignition source of the pool spill.

If ignition of the fireball cannot be prevented, the issue becomes one of controlling the "size" of the flame ball. The "size" is not only a volumetric issues, but is related to the time-integrated radiative heat evolved in comparison to that which will result in harm to personnel, or, more likely, to that which will result in secondary ignition of any fuel pool spill which has resulted.

Finally, if neither the aerosol ignition nor flame ball size can be controlled, one must consider prevention of the ignition of the fuel pool spill, or the containment of the pool fire to a small area by limiting the region over which the fuel is spilled or the rate at which the flames spread over the fuel spill.

The occurrence of these phenomena are inter-related through the actual fire scenario, the mechanical design of the vehicle, fuel storage, and fuel delivery systems, as well as through the physical and chemical properties of the fuel.

Furthermore, the choice of the propulsion system (spark ignition, diesel, turbine) and the fuel storage and delivery system design provide certain limitations in the acceptable ranges over which these fuel properties may vary. These property ranges may be contrary to those which would optimize fuel fire resistance.

In order to fully clarify the analysis given in the third section of this report, it is important to summarize here the principal effects of these interrelationships. The bibliography in the fifth section (and the references contained within the literature cited) serve as a reasonable basis from which to derive these interactions. It is appropriate to consider the effects of the base fuel properties first.

### Effects of Base Fuel Physical Properties

One of the most important properties of the fuel is the "flash" point. Fundamentally, the flash point of a fuel is that liquid temperature which results in sufficient fuel vapor pressure at the liquid/air interface to produce a flammable mixture of fuel vapor and air over the surface. Thus, for pure liquids, if one knows the lean flammability limit of the material (i.e., the minimum fuel content in air which will sustain a pre-mixed flame) and the vapor pressure-liquid temperature relationship of the material, a "theoretical" flash temperature can be calculated. In lieu of knowing the flammability limit and in order to account for non-ideal vapor pressure-liquid temperature relationships, particularly for multi-component mixtures such as real fuels, various experimental techniques have been developed to measure the flash point. As a result of diffusive transport near the liquid surface and the positioning as well as the type (flame, spark, etc.) of ignition source used to test for flammable mixture conditions, these techniques typically produce experimental values for the flash temperature which are somewhat higher (a few to 5°C) than values calculated for pure liquids or (even ideal) mixtures.

In some cases, the flame produced by passing an ignition source over the surface of a liquid heated to its experimental flash point does not sustain itself after propagating over the surface (hence the term "flash" point). However, if the liquid temperature is raised a few degrees Celsius higher, both flame propagation and sustained combustion result. The liquid temperature at which this condition occurs is termed the "fire" point. It is really this condition which is of interest in terms of fire hazard analysis of liquids, but the flash point serves as a conservative approximation which is more easily measured and interpreted. Fire points for conventional fuels may differ from the reported flash points by as much as 20 to 30°C due to the difficulty in retaining the light ends of the fuel during these tests. It is principally the light volatile fraction of the fuel which determines both of these properties.

The flash temperature of a fuel in relation to the ambient temperature is important in identifying what controls the ignition and flame propagation process. If the flash temperatures of a fuel is much lower than the ambient temperature, then even at ambient conditions, a flammable mixture will result over an open spill after a very short time. This time is governed by convective/diffusive transport and evaporation kinetics. Ignition and flame propagation will be controlled entirely by gas phase chemical and physical processes. In fact, open spills will sustain flame propagation (with no turbulence effects) over their surface up to nearly five times the laminar flame velocity (approaching several meters per second) because of the stratified fuel/air mixture which exists over the pool. For low flash point fuels, the ignition process will be dominated by requirements for chemical initiation, and aerosol flame propagation will be found to be relatively independent of the aerosol particle size (although there may be some dependence on particle number density).

In the case of liquids which have flash points well above the ambient temperature, the liquid must receive heat in order to create a flammable mixture over the liquid surface. Ignition will require sufficient heat to first generate the flammable mixture and then sufficient energy in the form of enthalpy or radicals to cause chemical initiation of flame. In the case of aerosols, the droplet surface must be heated to near the flash point before a flame can be established. This characteristic "heating time" influences the rate of flame propagation through the aerosol by causing significant dependence on droplet size and number density. Indeed, if droplets are large enough and/or the heat available is insufficient, no flame ball will result. Obviously, the minimum droplet size will be a complex function of the amount the liquid is subcooled below its flash temperature, etc., but unlike the case of low flash temperature fuels, aerosol flame ball development may be inhibited by controlling aerosol formation.

Finally, the ignition of a pool spill will require heating of the pool surface to produce flammable conditions, and subsequently, ignition of this flammable mixture. Without significant heating of the pool surface by radiation from the flame ball, propagation over the pool surface will be limited to velocities lower than about 0.1 meters per second. This is because the major method through which the region ahead of the flame is heated to temperatures exceeding the flash point is through liquid-phase convection. Indeed, if the surface on which the fuel is spilled is porous and/or the pool is not sufficiently deep for convection to occur, the flame spread rate may be lower than 0.01 meters per second! It will be seen below that the fuel flash point in relation to ambient conditions (or fuel circulation/compartments storage temperature) will dictate the effectiveness of various methods for producing a fire-resistant fuel.

### Typical Fuel Systems/Engine Systems Encountered

The primary reason for carrying fuel in an Army vehicle is to provide propulsion for the vehicle through combustion.

Thus any changes in the fuel properties or the fuel/engine system in the interest of fuel fire safety must also consider the effects of these proposed changes on vehicle performance, range, and environmental operating constraints (ambient temperature range, etc.).

Most Army vehicles currently use diesel (D-type) or turbine (JP-type) fuels. Jeep vehicles currently powered by gasoline type fuels are to be gradually replaced by attrition as newer, diesel-fueled jeeps are added to the fleet. With the exception of the M-1 armored tank which uses turbine type fuels, all other tactical ground vehicles use diesel grades of fuel and diesel engines. Typical fuel properties for such fuels are shown in [Table B-1](#).

Currently, the diesel engines used are either water- or air-cooled with much of the cooling of the fuel injection nozzle itself provided by circulating up to as much as twice to three times the actual fuel required through the nozzle. The excess fuel is then returned to the fuel storage compartment(s). Steady state, recirculated fuel temperatures typically far exceed the flash points shown in [Table B-1](#) and approach or exceed the fire point of the fuel used. Engines with considerably higher operating temperatures and much lower total heat rejection are under development. However, these engines actually make greater use of both lubricating oil and fuel circulation for cooling purposes than earlier designs. It appears that direct cooling, at least of the fuel, through some sort of air-cooled or refrigerated intercooler will be necessary to prevent fuel degradation and nozzle tip deposits.

Fuel is often stored in more than one fuel compartment on the vehicle, and thus the susceptibility of the fuel storage compartments to combat damage ranges from uncontrolled to something less than minimized.

### Methods for Producing Fire-Resistant Fuel Properties

There are several potential approaches which separately or together might be used to produce fire-resistant fuel characteristics. These include:

- antimisting agents
- use of higher flash point fuels/fuel cooling
- liquid/gas interface dilution
- halon suppressants
- gelling agents
- combinations of these methods

The use of these methods may require certain design modifications in the fuel system, engine, or vehicle structure. Each of these approaches and their interactions are briefly discussed below, and the STAS team positions taken on these approaches are detailed.

#### Antimisting Agents

When added to the fuel, so-called antimisting agents tend to resist the ligament breakup of fluid sheets (and sometimes even the formation of the liquid sheets) during shear atomization of a fluid, and thus they inhibit the formation of small aerosol droplets. All of the products currently used are proprietary so that little can be said of their actual chemical structure except that they are long chain hydrocarbon and sulfur based polymers with molecular weights in excess of one million. One to two percent added to high flash point aircraft fuels have shown them to be extremely effective in eliminating the fireball hazard which arises from wind shear and ground crash impact of aircraft. Tests have also shown them to be ineffective when used with low flash temperature fuels such as JP-4. This fact clearly establishes that the operating mode of these materials is through formation of aerosol drops too large to be heated to flash point conditions by the available heating/ignition sources. In the case of low flash point fuels, aerosol drops already provide flammable vapor concentrations at the environmental temperature.

Antimisting agents show no effect on flame propagation over fuel spills for either low or high flash temperature fuels once the pool fire is initiated. However, for high flash point fuels, pool fire initiation can be prevented by using antimisting agents to inhibit or eliminate the occurrence of a fireball. But modification of the fuel atomization characteristics such that it is difficult to form very small fuel droplets is also detrimental to the fuel combustion properties. The formation of a combustible mixture in the diesel engine cylinder is directly related to the droplet formation from the fuel injector. Thus, the antimisting agent must be degraded before the fuel is injected into the engine. It has been found that high shearing rates existing in either the engine fuel pump and/or the engine fuel injectors reduces the chain length of the polymer. However, this results in fuel recirculated to the fuel storage no longer having antimist character, and any fire-resistant fuel qualities are quickly lost.

There are essentially three potential ways to solve this problem and retain the fuel antimisting properties. They are listed here in order of the team-evaluated current technical feasibility.

#### Engine/Fuel System Retrofit

Since current engine designs require fuel recirculation to cool the injectors, modify the fuel circulation system such that no fuel is returned to the fuel storage tanks. This modification might include nozzle changes and/or some refrigerated intercooling of the circulation loop (see later discussions in next section). The STAS team does not believe that such system modifications should necessarily eliminate this approach from consideration.

TABLE B-1 Reference Fuel Properties

| Property (Fuel Code)   | (No. 7225)          | (No. 8821)                | (FRF of No. 8821) <sup>a</sup> | (No. 9295)     |
|--|---------------------|---------------------------|--------------------------------|----------------|
| Specification Type   | MIL-F-46162A(MR)-II | Fed. Spec. VV-F-800b-DF-2 |                                | VV-F-800b-DF-A |
| Gravity, API at 15.5°C                                       | 36.1                | 35.2                      | 30.4                           | 0.795          |
| Density, g/ml at 15.5°C                                      | 0.844               | 0.848                     | 0.874                          | 45(113)        |
| Flash Point, PMCC, °C(°F)                                    | 60(140)             | 72.(161)                  | None                           | —              |
| Fire Point, °C(°F)   | 91(196)             | 84(183)                   | —                              | -52 (126)      |
| Cloud Point, °C(°F)  | -21 (-6)            | -1 (30)                   | —                              | -56 (133)      |
| Pour Point, °C(°F)   | -24 (-11)           | -10 (14)                  | —                              | 1.2            |
| Kinematic Viscosity, cSt at 40°C                             | 2.2                 | 3.2                       | 5.3                            | —              |
| Accelerated Stability (ASTM D 2274), mg/100mL                | 0.6                 | 2.7                       | —                              | —              |
| Total Acid No., mg KOH/g                                     | 0.01                | 0.03                      | 1.12                           | —              |
| Steam Jet Gum, mg/100 mL                                     | 3.9                 | 3.2                       | —                              | 0.0            |
| Sulfur, wt pet   | 0.35                | 0.47                      | 0.36                           | —              |
| Nitrogen, wt pet   | —                   | —                         | -0.32                          | 1A             |
| Copper Strip Corrosion (ASTM D 130)                          | 1A                  | 1A                        | —                              | —              |
| Carbon, wt pet   | 86.8                | 86.7                      | 75.06                          | —              |
| Hydrogen, wt pet   | 13.2                | 13.3                      | 12.66                          | —              |
| Heat of Combustion (Gross), J/kgx10 <sup>-6</sup> , (Btu/lb) | 45.1 (19,427)       | 45.7 (19,670)             | 39.29 (16,893)                 | 46.1 (19,810)  |
| Heat of Combustion (Net), J/kgx10 <sup>-6</sup> , (Btu/lb)   | 42.5 (18,283)       | 42.8 (18,450)             | 36.47 (15,679)                 | —(—)           |
| Hydrocarbon Types, saturates                                 | —                   | 69.1                      | —                              | 87.3           |
| FIA, vol pet aromatics                                       | —                   | 29.4                      | —                              | 10.8           |
| Hydrocarbon Types, saturates                                 | 72.5                | 74.1                      | —                              | —              |
| HPLC, wt pet aromatics                                       | 27.5                | 25.9                      | —                              | —              |
| Aromatic Ring Carbon, mononuclear                            | 7.1                 | 7.5                       | —                              | 5.5            |
| UV, wt pet dinuclear   | 11.5                | 6.5                       | —                              | 2.4            |
| trinuclear   | 0.3                 | 0.4                       | —                              | 0.0            |
| total  | 18.9                | 14.4                      | —                              | 7.9            |
| Cetane No.   | 48                  | 51                        | —                              | 51             |
| Distillation (ASTM D 86), °C(°F)                             | 166 (331)           | 183 (362)                 | —                              | 164 (328)      |
| Initial Boiling Point  | 219 (426)           | 225 (437)                 | —                              | 178 (353)      |
| 10% Distilled  | 244 (471)           | 282 (539)                 | —                              | 191 (376)      |
| 50% Distilled  | 296 (565)           | 331 (628)                 | —                              | 214 (418)      |
| 90% Distilled  | 358 (676)           | 361 (682)                 | —                              | 252 (485)      |
| End Point  | —                   | —                         | —                              | —              |

<sup>a</sup> 10 vol pet in 84/6 (v/v) base fuel/surfactant mixture.



*Rapid Addition of Antimisting Agent to Fuel Tank During Fire Hazard Period Only*

In this scenario, some system would be retrofitted to the fuel storage compartment to rapidly disperse antimisting agent in the fuel on fuel system rupture. The team concluded that either the approach of jacketing the storage compartment or of rapidly injecting antimisting agent directly into the tanks do not appear to be practicable designs.

*Association Polymers*

It has been suggested that another class of polymers, so-called "association polymers," might be substituted for the material conventionally used as antimisting agent to eliminate the shear degradation problem. In this type of polymer, a very high molecular weight is achieved by linking smaller polymer units, which are not shear degraded, by means of hydrogen or ionic bonds, as shown in Figure B-1. The assumption here is that, while shear might temporarily disrupt the bonds, the bonding would reform rapidly. Critical points in judging the utility of such compounds, if they do exist, would be the determination of the range of shear energy under which the bonding would be destroyed (without destroying the bonding of the smaller polymer units) and the time required for the association bonding to reform. For the polymer to be effective, it would likely have to have re-association times the order of milliseconds (if not microseconds), and such short association times might also interface with fuel injector atomization. The possibility of the future use of association polymers was considered by the team to be highly speculative. (See later discussion of similar designs for halon addition to the fuel).

It should be pointed out here that there is apparently a lack of fundamental information, even for the behavior of current antimisting polymers. While it is clear that these compounds shear degrade, little quantitative information as to the minimum shear that such polymers can sustain is available. The aerosol-forming shear created by impact of an incendiary round is likely to be far greater than that produced by wind shear or impactation during aircraft failure, and it is unclear the level to which antimisting agents perform under such combat-related situations. Indeed, the team was led to believe that antimisting performance in tests under such conditions with high flash point fuels may not have been equal to that achieved in aircraft tests. The team therefore concluded that additional fundamental testing of antimisting agent behavior when subjected to varying shear conditions should be obtained before further consideration of their use is made.

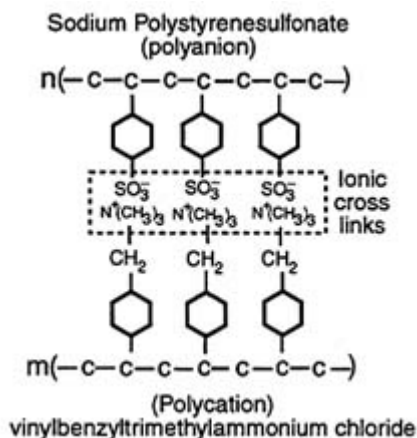


FIGURE B-1 Hypothetical structure of an "association" polymer.

**Higher Flash Point Fuels/Fuel Cooling**

Without being in the high flash point regime, there is essentially no way of eliminating the fireball hazard if an aerosol is formed and even weak ignition sources are available. Further, any flame propagation which would occur over a fuel pool spill would typically be gas-phase controlled and extremely rapid. Ignition of the fuel pool would also be facilitated by the combustible vapor cloud which would immediately form over the pool. Using a fuel with a flash point well above the range of ambient temperatures to be tolerated is a prerequisite for fuel spills to remain in the high flash point regime over long periods of time.

Furthermore, if the fuel is used as a cooling medium for the fuel injectors, (see discussion above), it is clear that keeping the fuel circulation and storage temperatures well below the flash point would be beneficial to fire hazard mitigation. If the circulation temperature approaches the flash and/or fire point of the fuel, then aerosol and spilled fuel fire phenomena will again be gas-phase controlled. In fact, the lower the fuel circulation temperature is kept relative to the flash point, the stronger the ignition phenomena will have to be to initiate the flame ball, and the more intense the fireball must be to ignite a pool fire. Such fuel cooling will have little or no effect in terms of diesel engine performance or vehicle range. Substantial cooling of the fuel could be accommodated with existing technology by placing a refrigerated inter-cooler in the fuel recirculation system or fuel tank(s). As mentioned above, inter-cooling will in any event probably be required in new engine designs, but in the absence of fire considerations, air-cooled systems might be adequate. Refrigerated systems would divert some available engine power, but estimated magnitudes would appear to produce relatively small reductions in range. Furthermore, such systems could be modulated during tactical maneuvers requiring maximum power, and therefore, there would be effectively no degradation in vehicle performance. Finally, increasing fuel flash point and cooling recirculated fuel are approaches which are also compatible

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with not returning circulated fuel to the fuel storage compartments, a requirement for using current antimisting agent (see previous section). The consensus of the STAS team was that some vehicle modifications will likely be required with almost any effective approach to improving fire-resistance of the vehicle (and fuel), and such modifications should not completely eliminate potential approaches. The relevant question is what level of vehicle modification would be acceptable on a cost-benefit basis.

### Liquid/Gas Interface Dilution

The more recent work on the development of fire-resistant fuels has dealt primarily with the formulation of clear to hazy surfactant stabilized emulsions of small percentages of water-in-diesel fuel. The FRF candidate rejected by the U.S. Army Materials Development and Readiness Command was a mixture of 10 percent (by volume) water, 6 percent surfactant, 6 percent co-solvent (for the surfactant) in diesel oil. This formulation diminished (but did not eliminate) the ability of the base diesel fuel to produce a fireball, and completely prevented pool fires.

The mechanism by which the material reduced the fireball problem is apparently through an increase in fuel viscosity and thus a reduced capacity to form small aerosol droplets. It appears that the mechanism through which the pool fire issue is mitigated is through the dilution of the fuel vapor layer over the liquid surface by evaporating water. This liquid surface blanketing with water vapor leads to suppression of chemical initiation (pool fire ignition) as well as provides sufficient heat sink effect to extinguish any existent flame. These effects essentially manifest themselves as a nonflammable mixture of water and fuel vapor over the liquid fuel surface. A minimum neat fuel flash point is defined (about 70°C for the current FRF candidate) above which no flame can be established over an FRF formulated from that fuel until all of the water in the FRF formulation has been depleted by evaporation. These mechanisms of action have been experimentally established in recent work at Southwest Research. The findings are contrary to previous work elsewhere which suggested a mechanism of limiting the fuel liquid surface temperature to the boiling point of water. This hypothesis was based upon the premise that the components of an immiscible mixture such as an emulsion vaporize independently of one another. However, the vapor pressure of FRF micro-emulsions were found to be substantially less than would be predicted for classical water-fuel immiscible mixtures.

FRF-type blends containing 6 vol pct surfactant and between 2 and 10 vol pct water as micro-emulsions appear to behave similarly as far as liquid vapor pressure-temperature relationships are concerned, but a formulation containing 6 vol pct surfactant, 6 percent co-solvent to solvate the surfactant in aromatic diesel fuel, and 10 vol pct water was chosen as the prototype FRF composition. These large amounts of materials added significant procurement costs, caused substantial deployment difficulties (since the material was to be prepared in forward supply areas), and reduced the performance and range of the vehicles tested. Stability was also substantially affected by the purity of the water used in the formulation. However, minimal water/surfactant concentrations required for fire-resistant behavior were apparently never defined previous to proposing deployment. Finally the formulated FRF showed difficulties in filter plugging at low ambient temperatures.

Part of these difficulties may have been the result of too little fundamental research and development before the selection of the micro-emulsion component structure itself. Micro-emulsions represent a state of matter in which one immiscible liquid is dispersed in another, the particle size of the dispersed phase being of the order of 100 to 200 A.U. The presence of a stabilizer (i.e., surfactant or emulsifier) is required to produce stability of the structure. In the case of micro-emulsions, this surfactant is usually a binary mixture of an appreciably water-soluble surfactant (e.g., sodium dodecyl sulfate) and a less-soluble co-surfactant (e.g., pentanol). The composition of the micro-emulsion (oil/water ratio, surfactant concentration, surfactant/co-surfactant ratio, etc.) is usually critical with regard to maintaining stability over any appreciable range of environmental conditions (e.g., changes in temperature). This is in contrast to macro-emulsions which are characterized by much larger particle sizes, and where the composition is much less critical. On the other hand, micro-emulsions are considered to be thermodynamically stable (similar to true solubilized systems), while macro-emulsions are thermodynamically unstable. From this point of view, micro-emulsions can be viewed as an extension of solubilized systems while macro-emulsions represent a totally different state of matter.

The relation among composition properties and the existence of micro-emulsions is best understood in terms of a ternary (three component) phase diagram. This is illustrated in [Figure B-2](#) where the micro-emulsion exists only in the shaded regions (S = surfactant; E = water; H = oil). In this figure, surfactant concentration corresponds to the concentration of surfactant mixture and the surfactant/co-surfactant ratio is constant. A different phase diagram for this system would be engendered by a change in S/co-S ratio.

It is also to be noted that the diagram is defined for a specific mixture temperature and would be different for different mixture temperatures. [Figure B-3](#) illustrates the kinds of changes in phase diagram which can occur with change in mixture temperature, in this case from 30 to 40°C. A single region of existence has been transformed to two separated regions, and even more drastic changes can occur for larger changes in mixture temperature.

The problem involved in formulating a micro-emulsion fuel is obviously to ensure that the chosen formulation is one which will remain stable over the range of mixture

temperatures which will be experienced. In the military diesel range, these might range from 0°C to about 80°C. Clearly, if the micro-emulsion FRF used was at times cloudy or clogged filters, stability problems had occurred. Particle sizes the order of 100 to 200 A.U. would not result in such phenomena. Apparently the FRF micro-emulsions used were not formulated properly for stability over the temperature range and diesel fuel property and water purity variations of interest. The STAS team believes that achieving suitable results with a single formulation is not a trivial nor highly probable matter.

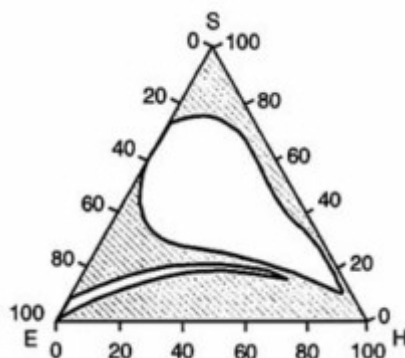


FIGURE B-2 Micro-emulsion system water/K oleate/l-hexanol/hexdecane. S/CS ratio: 3/5. (S = surfactant; E = water; H = oil).

On the other hand, liquid/vapor-interface dilution could also be accomplished through the use of true solution techniques. Such solutions are likely to be less sensitive to water purity. True solutions are stable to shear forces, are not subject to separation on storage, can have wide ranges of solubility and be maintained over wide ranges of mixture temperature, and can easily be produced in the field. Examples of such systems are shown in the ternary diagram of Figure B-4 for several hydrocarbon-water-alcohol co-solvent systems. Apparently, the existence of diesel fuel-water-co-solvent mixtures and their flammability characteristics have not been previously investigated.

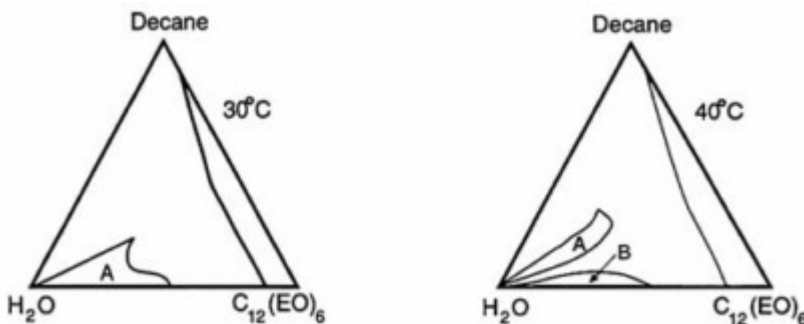


FIGURE B-3 Effect of temperature. At 30°C, micro-emulsions exist in area A; at 40°C, the micro-emulsion region has split into two regions, A and B.

It is likely that the same flammability characteristics as those observed for micro-emulsion FRF could be generated with such solutions. Furthermore, it is likely that co-solvent alcohols of higher molecular weight than ethanol could be found. Finally, other types of co-solvents such as ketones may also exist.

It appears that liquid/vapor interface dilution is itself a feasible technical approach which should be further considered before it is abandoned. Limited storage life and operating temperatures are compelling reasons for rejection of candidate systems, but the STAS team concluded that lower energy content and cetane number of candidate mixtures have less serious impact. Decreased energy content has two implications: the logistics of the fuel supply are made more difficult, and there may be a consequent reduction in engine power (and, for existing vehicles, a reduction in vehicle range). Most fuel injector have some reserve capacity, and furthermore, increased fuel volume requirements do not automatically eliminate a system from consideration if other benefits are perceived to be of sufficient importance (as is evidenced by the adoption of the M-1 tank with a 30 to 100 percent greater fuel consumption than previous designs). Likewise, moderate decreases in cetane number are also tolerable, since starting aids are already required and present. At moderate to full load, turbocharged diesels are relatively insensitive to cetane number and future mini-cooled diesel engines will be even less so once they are at operating temperature. If proper micro-emulsion formulation or co-solvent approaches could lead to appropriate stability characteristics, and amounts of co-solvents and/or surfactants as well as water were held to minimums, the fire safety benefits of this approach might outweigh other performance and range degradations.

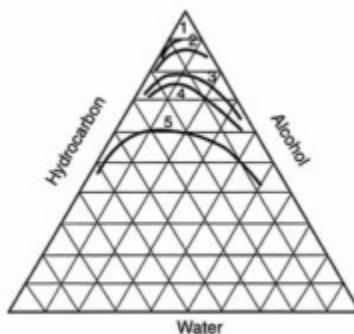


FIGURE B-4 Ternary water-alcohol-hydrocarbon solutions.

- (1) Water-methanol-heptane.
- (2) Water-methanol-hexane.
- (3) Water-ethanol-heptane.
- (4) Water-ethanol-hexane.
- (5) Water-ethanol-toluene.

Source: International Critical Tables.

### Halon Suppressants

Halons are compounds which contain carbon, various combinations of halogens (fluorine, chlorine, bromine, or iodine), and, occasionally, hydrogen. For convenience, a system of numbering has been devised for halon compounds which consists of four numbers. The first denotes the number of carbon atoms, the second, the number of fluorine atoms, the third, the number of chlorine atoms, and the fourth, the number of bromine atoms. Iodine has not been included in this numbering system since it has only rarely been considered in the construction of halon compounds. (However, iodine atoms are slightly more effective in fire suppressant character than bromine atoms). The amount of hydrogen atoms contained in the compound is determined by the number of remaining valence bonds needed to saturate the number of carbon atoms. There is a considerable body of literature, both fundamental and practical, on the use of halons for ignition and flame inhibition as well as fire extinguishment. There are also a considerable number of formulated halons of varying physical and chemical properties from which to select.

The most often employed halon is currently halon 1301, i.e., trifluoro-bromo-methane ( $\text{CF}_3\text{Br}$ ). According to the briefings received, the Army already has considerable experience in using halon 1301 as a fire suppressant applied as a deluge surrounding the vicinity of fuel compartments (on the M-1 tank). The briefings described a triggering mechanism which released halon 1301 into the compartment surroundings upon shell impact so rapidly that, although an aerosol cloud of fuel is formed by the impact, no fireball ignition (formation) occurs. These systems are currently reaching the deployment stage, and apparently further work is under way to develop (implement?) systems which would operate under multiple impact conditions (on the M-1).

This approach to fire suppression can be accomplished via retrofit on other vehicle systems, and the method does not require modification of the engine/fuel system. As such, no degradation of performance or range should result to the extent that the mass/volume of the fire suppressant system offers unacceptable constraints. The STAS team is fully supportive of additional efforts to further evaluate such possibilities. If the fireball formation can be eliminated, one of the major sources of ignition for any fuel pool spill will have been removed.

Compartment environment inerting as described above is very effective in preventing ignition of flammable fuel/air mixtures. Inerting through the use of halons probably results from several fundamental effects. Halons have large specific heats and therefore are very effective absorbers of sensible enthalpy. Second, halogen materials, particularly bromine, scavenge radicals which can lead to ignition. Finally, local oxygen concentrations are decreased by the addition of halons and chemical reactions leading to rapid oxidation will be slowed.

The order of 1 to 5 percent concentration of halon in the surrounding air is sufficient to prevent ignition and to extinguish small fires (e.g., smoldering cigarettes, etc.). This concentration of halon 1301 in air also causes no distress to human respiratory systems. However, if a vigorous fire is already present when the halon is added, thermal decomposition of the halon can lead to species which are not only extremely toxic, but actually accelerate the rate of burning. Toxic gaseous products and copious amounts of particulates (soot) are produced. Compartment inerting could also be accomplished using carbon dioxide or nitrogen purges which would not lead to any toxicity difficulties. However, there is no direct chemical inhibition which results from these materials, and much larger dilution ratios are required to be effective. Any rapid admission of fresh air would result in loss of effectiveness sooner in the case of these latter materials.

Halons might also be used as fire suppressing agents in ways other than through localized atmospheric inerting. These include:

#### *Addition to the Fuel Itself*

Presence of the halon material in the fuel itself could add an additional mechanism for fire safety protection, i.e., liquid/vapor interface inerting (see discussions above). To obtain this benefit, a halon (or mixture of halons) with the appropriate volatility characteristics in comparison to the fuel must be chosen. Initial investigations of the combustion properties of fuel formulations containing halon 1301 in engines



by the Army showed that the combustion products derived from the halon were so corrosive as to severely damage the engine in less than 50 hours of operation. Thus the halon component would have to be removed from the fuel previous to injection into the engine. While this removal is probably technically possible through absorption processes, such approaches may not be feasible for this particular application. It is also highly unlikely that a halon type compound could be derived which would not produce engine corrosion problems.

#### *Injection and Mixing in the Fuel Compartments After Impact*

In this approach, upon threat of a fire incident, i.e., shell impact, etc., halon would be rapidly injected and mixed with the liquid fuel within the fuel compartments. Such a technique would not only require very rapid response systems, but designs which would result in almost instantaneous dispersal within the fuel tank. It should be remarked that the fuel-halon mixture will cause rapid degradation of the engine hardware. While several of the STAS team believed that at least some further conceptual studies of the problem might be worthwhile, the majority opinion was that the success of this approach was unlikely.

#### *Jacketing of the Fuel Tank*

In this approach, the fuel compartments themselves would be constructed in some double-jacketed design with halon in the outer shell. The concept here was that any penetration of the fuel compartments would yield a mixture of halon and fuel leaving the point of penetration. The apparent drawbacks are that the fuel supply system to the engine remains unprotected, the rate of ejection and mixing with the fuel at the point of penetration are uncontrolled, and the system is essentially restricted to protecting a single penetration event. Because of these issues, the fire hazard reduction achievable with this technique is unknown.

#### *Liquid Halon Deluge of Fuel Spill*

The STAS team could not envision any method through which such an approach could be implemented since there is no knowledge as to where the impact will occur nor where the spill will result.

In summary, the most appropriate method for using halon fire suppressant technology today appears to be to control ignition of the fireball in the vicinity of the fuel compartment penetration. This will not reduce the possibility of igniting the aerosol produced at locations remote from this region. However, if the flame ball can be prevented, the opportunity to prevent serious pool spill burning is substantially improved.

### **Gelling Agents**

Gelling agents were one of the earliest methods investigated by the Army for fuel fire hazard reduction. The basic premise of using gelling agents was to achieve performance similar to antimisting agents as well as contain the region of post-impact fuel spillage. All previous formulations studied have had serious manufacturing difficulties (in terms of reproducibility of the gel properties), and performance problems (poor filtering ability, substantial difficulty in emptying fuel ullage, high resistance to pumping, poor thermal stability). Indeed, so many difficulties were identified in previous work that those team members who were aware of the research were surprised by the suggested revival of this approach. There appears to be few benefits which can not be achieved through the other methods reviewed above with much less difficulty and fewer performance effects. The STAS team did not place much promise on the possibility of success of any further work on this method.

### **Combinations of These Methods**

Some of the above discussions assume certain combinations of the various approaches that were described. For example, the use of antimisting agents is only effective in reducing flame ball formation if a high flash point (relative to ambient) base fuel is used and circulation temperature of the fuel is kept well below the flash temperature. However, combinations of two or more of the types of approaches discussed above may result in synergistic improvements. The STAS team devoted some discussion to combinations of not only fuel modifications, but fuel system/vehicle accessories to reduce fire hazard. In these discussions, priority was given to those areas where existing technologies would be used first, and those technologies which required least developmental work would be combined with them.

Systems modifications and base fuel modifications fell in the first category of items. The highest priority issue appears to be retrofit of compartment halon deluge systems similar to those already devised for the M-1 tank, and the addition of fuel line closures which activate upon fuel line fracture. The former modification would eliminate the fireball ignition in the vicinity of a ballistic impact itself, and multiple impact designs should be considered. The latter modification would address much of the fire hazard issue arising from fuel supply system line fractures. Clearly, increasing the base fuel flash point and decreasing the fuel circulation and storage temperature (relative to ambient operating requirements) would in all cases benefit the fire hazard issue. Flame ball and pool spill flame initiation should become more difficult, and pool spill flame spread rate might be reduced to a value such that if the vehicle could still maneuver, it might remove itself from the vicinity of the pool before being enveloped. Indeed, the

consensus was that halon compartment deluge and refrigerated cooling would be of greater benefit in fire hazard reduction than the costs in additional accessory power requirements and vehicle retrofit issues. Full scale testing will be required to determine if these methods in themselves suitably control the fire hazard issue, but these steps would only be further benefited by those appearing below.

The added use of conventional antimisting agents and fuel vapor interface dilution techniques require additional fundamental questions to be answered, as well as some vehicle design modifications, logistics decisions, and fuel cost procurement decisions to be made.

In the case of antimisting agents, the minimum shear required to degrade the agent in comparison to shears experienced under ballistic impact needs to be quantified rather than qualitatively determined. In this regard, association polymers will require considerable fundamental research and development and were therefore given both a very long required lead time and a high risk research rating. Finally, a fuel system modification which would not return circulated fuel to the fuel storage compartments would be required. This may cause the need for some redundancy in fuel inter-cooling systems if both the fuel stored as well as the fuel recirculated needs to be cooled. (The team endorsed the refrigerated cooling of stored fuel to permit modulation of the cooling power during strategic power conditions, but air cooling of the small volume of fuel recirculated might be adequate to provide sufficient injector cooling designs which do not return fuel to storage).

The added use of liquid/vapor interface dilution, from either micro-emulsion or co-solvent approaches requires additional fundamental work to determine the optimum formulation(s) with regard to thermal stability. The use of this technology could substantially benefit the pool fire problem. If thermal stability is achieved, no filtering problems will be experienced. This research should also determine the minimum quantities and purities of materials that can be used to obtain successful dilution of the interface. Logistic and cost/benefit results must be quantified, i.e., it is impossible to use these technologies without some additional logistical and/or fuel costs being incurred. Indeed, no technique can meet such inflexible criteria, and acceptable levels must be defined. Finally, in the case of both antimisting agents and liquid/vapor interface dilution, the possibility of formulations defined for specific climates should be further investigated. Such an approach is compatible with existing climatic formulations of diesel fuel itself.

Methods which add halon type compounds to the fuel, either by injection on impact or as a supplied fuel component, appear to be long term, high risk approaches. The possibility of protecting engine components from the corrosive compounds which result from combustion of halons under further engine operation is speculative at best, directing and controlling halon dispersal in the region of ballistic impact also seems unlikely.

Finally, the use of fuel gelling technology appears to add more technical complications than benefits derived in addition to those available from other techniques.

### Specific Task Discussions

On the basis of information, analysis and commentary appearing in the previous two sections, this section briefly summarizes the collective opinions of the STAS team on the specifics of the tasks appearing in the work statement detailed above.

### Background Review Summary

**Future work should be proposed and carried out on a systems (fuel, fuel system, engine system, deployment) basis.** One of the principal issues which the team believes has caused considerable difficulty in reaching a successful result is that previous work has concentrated separately on the formulation of a fire-resistant fuel and vehicle modifications as separate approaches to reducing fire hazard. A "successful" FRF was developed, but the implementation phase uncovered shortcomings, most of which would have been evident much earlier in the program if an integrated approach had been taken.

**Fundamental/engineering issues which are important to optimizing the various methods available for fire hazard mitigation have remained unanswered. Future programs should take a more balanced approach in obtaining sufficient fundamental knowledge to guide development of optimum approaches.** For example, in the case of the recently formulated FRF, the team was briefed that no research was devoted to defining the minimum additive package which would yield effective dilution of the liquid/vapor interface. Yet it was because large amounts of additives were required that substantial deployment difficulties resulted. Clouding and filtering difficulties of the FRF indicate thermal instability of the formulation, but no fundamental research apparently ensued from the point of developing simple phase diagrams for the formulation. Another example is that after substantial work, it appears that there is no quantitative definition of what shear leads to degradation of conventional antimisting agents.

**Constraints for previous research goals were not suitably defined. Specific, acceptable, and realistic criteria for the program solution must be made before any new program or program continuation is initiated.** Specific, acceptable, and realistic criteria which bound the possibilities for solution of the fire hazard issue should have been defined in advance of any development-or deployment-oriented



efforts. Fundamental research should have proceeded at some level to identify controlling parameters influencing the effectiveness of various approaches, but applied development efforts had little chance of success without this guidance.

**A conservative cost-benefit ratio for changes in vehicle performance, range, costs, retrofit, deployment, etc. And fire hazard reduction is needed to guide selection of appropriate program criteria.** It is neither useful nor realistic for DARCOM to state that any approach to reducing the fire hazard issue must:

- not degrade performance, range in particular
- not generate additional procurement cost
- contribute significantly to fuel survivability
- have worldwide use capability
- be compatible with fuel handling and distribution systems

Tests and quantitative definitions must be provided for such issues if a successful program is to result. For example, the STAS team consensus was that possibly a range degradation of 10 percent and a maximum power degradation of 5 percent might be accommodated, since these are comparable to effects derived from changes in altitude, alternate base fuels, temperature, etc. In fact, declutching might result in no power degradation at all. With regard to logistics, worldwide use compatibility equivalent to current military diesel fuel classifications might be considered. Similar approaches could be taken in reframing fuel supply/distribution and stability requirements. Finally, an acceptable procurement adjustment (and vehicle retrofit level) must be identified. These suggestions are meant only to exemplify the kind(s) of guidance this development program must have in order to not repeat the recent problem with FRF.

**Acceptable vehicle/fuel systems modifications criteria need to be established.** Even minor vehicle modifications such as fuel filter heating might have eliminated some of the difficulties encountered with the current FRF. Furthermore, the simple addition of line closure mechanism to close fuel lines upon fracture could substantially reduce any hazards arising from fuel line rupture. As detailed in the previous sections of the report, the STAS team thought certain vehicle modifications can be as important as, and synergistic with, modifications to the fuel in mitigating the fire hazard problem.

### Review of Proposed Approaches for New Program

The commentary below specifically addresses the proposed approaches and program phase plan appearing as [Table B-2](#) and [Figure B-5](#). In each case, the merits of each

TABLE B-2 Plan for "New" Fire-Resistant Fuel (FRF)

Three parallel approaches to be considered during initial phase of program

Addition of halon compounds (i.e., low molecular weight compounds containing chlorine and bromine) to diesel fuel.

Addition of associated polymers (i.e., metal-containing organo-complexes) to diesel fuel

Addition of both halon compounds *and* associated polymers to diesel fuel.

Selection of candidate fuel approach and major decision point will occur at first milestone (i.e., after 18 months from program initiation)

Interim milestone at ninth month will establish selection criteria for major decision point

Plan consists of three phases:

laboratory investigations

full-scale engine/system and field tests

specification development and user's guide

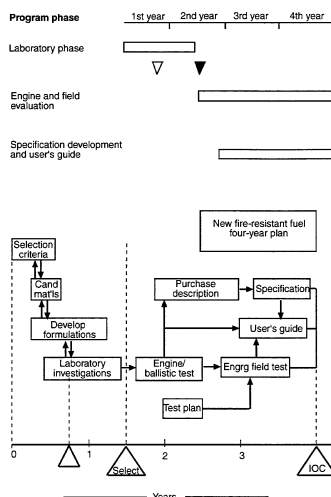


FIGURE B-5 Plan for "new" fire-resistant fuel (FRF).

approach are summarized, and the potential for success within the time requirements is given.

#### *Addition of Halon Compounds to Diesel Fuel*

- **As a Fuel Component.** The disadvantage produced for operating combustion systems by the presence of halons in the fuel presently outweigh fire hazard advantages which would result from the addition. Co-additives to eliminate the formation of acidic combustion products which are highly toxic and corrosive to engine systems does not appear to be possible. Furthermore, techniques to remove the additive prior to combustion are relatively limited, and successful development of an operating method is doubtful. It is also likely that halons added to the fuel could actually aggravate fireball conditions if the fireball were to be ignited. Four year development of suitable techniques appears unlikely, and implementation will involve logistics difficulties, and performance degradation which must be addressed.
- **By Post-Injection.** Post-injection of halons (or surfactant-water) into the fuel storage compartments upon initiation of a fire hazard condition will also result in fuel which has similar combustion difficulties to the fuel which would originally contain the additive. In addition, the response time required for injection/dilution in the stored fuel is unknown and is probably system compartment-geometry dependent. The method will probably be ineffective for fireball mitigation, but would involve little logistics problems, and performance degradation only upon activation. Four year development appears unlikely.
- **Post-Deluge of Spilled Fuel.** Post-deluge of spilled fuel, either with halons or halon/surfactant/water mixtures does not appear to be a plausible approach. While the use of compartment jackets to contain the mixture would orient the fuel spill and deluge direction, rates of ejection and mixing would be very difficult to control. Other methods appear to be entirely unacceptable since the spill rate/direction will be scenario dependent. Large amounts of additives are likely to be required for this approach, and fuel storage volumes may be significantly reduced. Successful development of an effective system within a four year period appears unlikely.

#### *Addition of Association Polymers to Diesel Fuel*

There is such a substantial lack of fundamental information available for this approach that it is difficult to consider association polymers seriously even for long range development (10 years). No fundamental guidance is available for the physical behavior of such compounds under shear, and none is available concerning the dynamics of their degradation or re-association. The team considered successful development of this approach unlikely.

#### *Co-Addition of Halons and Association Polymers*

The limitations and inadequacies of such a proposal are adequately covered in the discussions appearing in sections on addition as a fuel component and by post injection above.

### **Milestone Plan and Phases**

**An 18-month decision point to choose among the proposed approaches is unrealistic.** In the cases for which any potential for success exists, fundamental information on which to judge their viability is missing. Based upon the emphasis of previous Army research programs on this subject, it is also likely that too little emphasis will be placed on obtaining such information from laboratory research prior to full scale systems and field tests in future programs.

### **Recommended Additional Approaches**

On the basis of earlier discussions, this section briefly summarizes the STAS team consensus on other potential approaches to mitigating the fire hazard problem.

- Fuel flash point reduction, fuel cooling, compartment inerting by halon deluge, and line closure systems can all be approached on the basis of existent technology, and are therefore all suitable candidates for a four year development-to-implementation program. The potential success of these collective approaches in reducing the fire hazard are substantial, they are compatible with other approaches considered here which might be added at a later date, and they do not result in (what appear to be) unacceptable performance or logistic penalties. It is recommended that the existing program of studying the effect of vehicle fuel system temperature on fires be accelerated and emphasized so as to provide a better technical basis to define trade-offs for advanced vehicle fuel cooling systems. There is a need to immediately do a design study of several existing vehicles using cooling system computer modeling to determine the hardware requirements, complexity, energy requirements, ambient temperature effects, cost, etc. to cool the fuel in the lines and compartments.
- With fuel cooling and circulation system modifications, conventional antimisting agents may have some poten

tial for mitigating the aerosol formation problem. Additional fundamental information on shear energy effects are apparently required before further development should be considered. The technology here is nearly fully developed, is applicable to high flash point fuels, and does not impose large performance penalties or logistics difficulties. Fuel cooling effects may also be synergistic with the addition of antimisting agents. With the system design modifications and fundamental questions answered which were mentioned above, the development of an antimisting fuel package in an intermediate time (5 to 8 years) is plausible.

- Techniques which have been derived for producing liquid/vapor interface dilution do not currently meet suggested criteria constraints. However, optimization of micro-emulsion technology for this application appears to have been incomplete, and co-solvent approaches have not been investigated. Four year development and deployment of these techniques were viewed as unlikely because of the current lack of fundamental understanding needed to guide such efforts. One of the team members has revised his assessment since the meeting, and he now considers the probability of successful derivation of a suitable micro-emulsion formulation to be possible in the suggested four year period. In fact, the entire STAS team believes that these methods hold sufficient long term promise such that continued effort should be given to mechanisms for producing liquid/vapor interface dilution. Initial work should be on a fundamental level to identify stability issues based on phase diagram analysis, and to better define minimal additive requirements. Additional systems evaluations should not be contemplated without promising results at this research level.

### Success Potential

The success potential of the various methods has been considered in the sections above.

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1. Summary listings of reports completed to date on Fuel Fire Research.
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4. Briefing films on FRF performance and shaped charge issues.

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## Appendix C

# Biographical Sketches of the Committee Members and Technical Consultant

### Members

**John J. Wise** (chair) is retired from his position as vice president of research at the Mobil Research and Development Corporation after 44 years with the company. His division conducted research and development in exploration, production, refining, and products, including aviation fuel chemistry. He holds a B.S. in chemical engineering from Tufts University and a Ph.D. in chemistry from the Massachusetts Institute of Technology. He is a member of the National Academy of Engineering.

**James B. Day** is a private consultant in the air-breathing propulsion industry. He is a retired civilian engineer from Wright-Patterson Air Force Base, Ohio, with more than 34 years in jet engine research and development. During his career, he had major responsibilities in the development of engines for Air Force fighter, bomber, and transport aircraft, including the F-15, F-16, B-1, and B-2, and F-22. He was chief engineer for USAF engine development for 10 years and holds a B.S. and M.S. in mechanical engineering from the University of Kentucky.

**Frederick L. Dryer** received a B.S. in aerospace engineering from Rensselaer Polytechnic Institute and a Ph.D. in mechanical and aerospace engineering from Princeton University. He is currently professor of mechanical and aeronautical engineering at Princeton University. His research interests include fundamental combustion science, high-temperature chemistry of hydrocarbons, and fire-safety-related phenomena.

**Peyman Givi** is a professor of mechanical and aerospace engineering and director of the CFD Laboratory at the State University of New York at Buffalo. He received a B.E. degree from Youngstown State University and a Ph.D. from Carnegie-Mellon University. His current research interests include turbulent combustion, computational fluid mechanics, analytical methods, and stochastic processes.

**Richard H. Hall** received a B.S.Ch.E. from Case Institute of Technology and an M.S. and Ph.D. in chemistry from the University of Delaware. He worked as a chemist for the Dow Chemical Company for 39 years before retiring in 1992. Since then he has worked as a technical consultant for Imbibitive Technologies. His expertise is in petrochemical processes with an emphasis on additives, and he has been involved in a research program investigating gellants for crash safe fuels. He holds more than 100 patents in 17 countries.

**Syed Qutubuddin** is professor of chemical engineering and macro-molecular science at Case Western Reserve University. He holds a Ph.D. from Carnegie-Mellon University. Colloids, interfacial phenomena, and polymers constitute his basic research interests. Currently, he is involved in the study of polymer solutions and surfactant systems, particularly micro-emulsions, using rheological, laser light scattering, electrochemical, and other techniques. He has developed novel polymer blends and nanocomposites using colloidal approaches. Qutubuddin is a recipient of the Presidential Young Investigator Award and the LaMer Award of the American Chemical Society.

**Elizabeth J. Weckman** is an associate professor of mechanical engineering at the University of Waterloo, Ontario. She received a B.A.Sc., M.A.Sc., and Ph.D. in mechanical engineering from the University of Waterloo. Her expertise is in experimental combustion, ranging from fire measurements to application of advanced laser diagnostics for detailed characterization of burner flames. Her research has been particularly related to the behavior of pool fires and full-scale structural fires.

### Technical Consultant

**Thor I. Eklund** is a consulting engineer specializing in aviation technology with primary focus on fire safety. He received a B.S.E. in aerospace and mechanical sciences from Princeton University and a Ph.D. in fluid mechanics from Brown University's Division of Engineering. He previously was manager of the Federal Aviation Administration's (FAA) Fire Research Branch, and his past research experience includes fuel flammability, fire resistant materials, fire modeling, fire detection and suppression, and smoke control in aircraft. He played a pivotal role in developing overall aviation safety plans for the FAA, in areas such as fire research, aging aircraft, security, and free flight.