Measuring fuel transport through fluorocarbon and fluorine-free firefighting foams

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ABSTRACT

A flux chamber was designed to measure the transient fuel transport through a foam layer before significant degradation of foam occurred. The fuel transport rate through AFFF (fluorinated foam) was much slower than through RF6 (fluorine-free foam) with break-through times being 820 s and 276 s respectively over n-heptane. The fuel flux through AFFF covering three fuel pools (n-heptane, iso-octane, and methyl-cyclohexane) was also measured. AFFF had the smallest flux over iso-octane with a break-through time over 1900 s and the highest flux over methyl-cyclohexane with a break-through time under 80 s even though the fuels have similar vapor pressures at room temperature. Despite the lack of aqueous film formation on an iso-octane fuel pool, the fuel vapor flux through AFFF was much smaller relative to the methyl-cyclohexane pool, which enables film formation due to its higher surface tension than iso-octane. Our measurements of transient fuel flux show that the foam layer is a significant barrier to fuel vapor transport. The data suggest a transient mechanism based on the suppression of fuel adsorption onto bubble lamellae surfaces due to the oleophobicity of fluorocarbon surfactants, which is consistent with fuel solubility data. This suggests that surfactants that suppress fuel adsorption and solubility into bubble lamellae surfaces may reduce fuel transport through foams.

1. Introduction

Liquid pool fires are suppressed by using aqueous foams in both military and civilian applications worldwide. Aqueous film forming foam (AFFF) is considered the most effective liquid pool fire suppressant because of its fast fire extinction and protection against re-ignition of the fuel pool [1]. Although the fire suppression capabilities of AFFF have passed stringent fire extinction requirements of U.S. Navy Military Standard (MilSpec) testing [2], foam solutions have been continuously reformulated to address U.S. EPA restrictions [3] due to the toxicity and environmental persistency of fluorocarbon surfactants contained in the foam solution used to generate AFFF. There is a definite need to eliminate the fluorocarbon surfactants from AFFF formulations to address their environmental impact while maintaining the high firefighting performance required by the MilSpec. Commercial fluorine-free foams such as RF6 resulted in significant loss of fire suppression during MilSpec testing [4]. Fire suppression occurs because the foam blocks the fuel vapor transport from the pool surface into the fire, thereby starving the fire to extinction [5]. In this paper, we quantify the relative permeation rates of fuel transport through commercially available AFFF and a fluorine-free firefighting foam containing only hydrocarbon surfactants. We also evaluate the role of

the "aqueous film" and the foam layer as barriers to fuel transport to assist in improving fire suppression performance of environmentally benign firefighting foams.

In liquid pool fires, the liquid fuel evaporates at the pool surface and forms vapor. The fuel vapor continuously diffuses away from the pool surface and feeds the fire above the pool. Foam solution is mixed with air to generate a foam with an expansion ratio (volume of foam/ volume of liquid contained in the foam) between 5 and 10 [1,2]. The foam is applied directly and continuously onto the burning liquid fuel surface until the fire is extinguished. As the foam deposits on the pool surface, it floats because its density is smaller than that of the liquid fuel. As the foam layer builds up to a small (1–2 cm) thickness, it spreads and covers the surface of the pool under the influence of gravity. The foam is exposed to fire radiation from the fire above as well as hot liquid fuel below, which can increase foam degradation, liquid drainage, and bubble coarsening in the foam, and influence the fuel transport through the foam [6]. Fuel transport is intrinsically time dependent especially in the time scale of fire extinction (30 s for MilSpec fire extinction test [2]). For the purpose of comparing the fuel transport characteristics intrinsic to foams containing fluorinated and fluorine-free surfactants, we generated the foams using an identical method and performed experiments under the controlled conditions of

the laboratory. We exposed the foams to fuel pools with comparable vapor pressures (at 25 °C) over a relatively short time period to accurately quantify the transient fuel transport rates, in the absence of a fire.

In addition to the foam layer, fluorocarbon surfactants in AFFF foam solution lower the surface tension (16 dynes/cm) of the foam solution and form an extremely thin "aqueous film" layer between the foam and pool surface despite the solution's higher density than the pool. Bernett et al. [7] and Moran et al. [8] demonstrated the formation of a 47 μm (average) thick "aqueous film" by placing the foam solution on an n-octane fuel pool (5 cm diameter) surface in the absence of a foam. Thicker than 47 μm films led to breaking and sinking of the films to the bottom of the pool. Studies comparing the relative contributions of the foam and "aqueous film" as barriers to fuel transport through AFFF have been lacking. This is important because "aqueous film" formation is very difficult to achieve without the use of fluorocarbon surfactants, and attempts to find fluorine-free AFFFs have had limited success to date [9]. It is also important in view of the widespread assumption that the "aqueous film" forms the main barrier to fuel transport relative to foam to explain the superior fire suppression of AFFF observed in numerous large scale tests [4,10–12]. The "aqueous film" has been deemed necessary for fast fire extinction, so much so that it is a requirement for U.S. MilSpec qualified firefighting foams.

The firefighting community developed a flux chamber to characterize a foam's ability to suppress fuel vapors by determining the rate of fuel transport through a specified thickness of foam covering a liquid pool surface over a long time period (steady-state), without the presence of a fire, at ambient, non-combusting, conditions [13–17]. Schaefer et al. [17], relying on previous designs [13–16], designed a flux chamber to compare the performance of fluorinated and fluorine-free foams, which were generated using a food blender. Schaefer et al.'s results revealed that fluorinated foams had a much smaller fuel flux than fluorine-free foams. They attributed this superior performance of fluorinated foams to both the transport resistance of liquid lamellae (bubble wall) separating adjacent bubbles and to the presence of an "aqueous film" [17].

At the U.S. Naval Research Laboratory, Moran et al. [8] developed a flux chamber to measure fuel transport through the "aqueous film" formed by an AFFF foam solution at different film thicknesses. Their work revealed that the presence of a 47 μm thick "aqueous film" suppresses the fuel vapor concentration by a factor of 20 relative to that over a bare fuel pool surface. We previously [4] reconstructed Moran et al.'s flux chamber but made fuel flux measurements from a foam layer covering an n-heptane pool instead of only the "aqueous film". We reported the steady state molar flux emanating from the foam surface for fluorinated and fluorine-free foams generated by using the same sparging technique and for different fuels [4].

In the present work, we adapt Moran et al.'s apparatus to measure the transient mass transport flux through a foam/film layer. The Naval Research Laboratory's flux chamber design and experimental method is an improvement over previous flux chamber designs in its ability to create a uniform foam layer without significant degradation for studying the transient fuel transport characteristics of the foams. We quantified fuel flux for AFFF over three fuels: n-heptane, methyl-cyclohexane, and iso-octane. AFFF foam solution was shown not to form a film on iso-octane unlike n-heptane and methyl-cyclohexane [4,8]. These three fuels have similar vapor pressures, but differ in surface tension and solubility in water. The transient fuel transport measurements suggest a mechanism for the surfactant's role in fuel transport through aqueous foams.

2. Approach

We generated AFFF (Buckeye 3%, Buckeye Fire Equipment Company, Inc.) and a fluorine-free foam (RF6 6%, Solberg®, formerly 3M Australia) at small flow rates using a sparging method suitable for

our bench-scale experiments rather than the pressurized nozzle used in U.S. MilSpec fire extinction tests. The commercial surfactant formulations were prepared from the concentrates supplied by the manufacturers following recommended procedures. The properties of the surfactant solutions, fuels, and foams were measured and are described below along with the experimental apparatus design and procedure. The gap between the foam surface and the nitrogen source is kept at 1 cm for all experiments to maintain identical stagnation flow mass transport conditions in the flux chamber. Measurements were conducted at room temperature (20 °C) with a relatively thick foam layer (4 cm) so that the changes in foam layer thickness due to degradation during the experiment are relatively small (< 0.5 cm). The two foams were characterized by composition, initial bubble diameter, liquid drainage beneath the foam, and initial expansion ratio all measured immediately after foam generation.

2.1. Foam solutions

The commercial AFFF foam solution used in our experiments has already been MilSpec qualified [2]. The foam solution was prepared by mixing the "concentrate solution" provided by the manufacturer with distilled water at 3% concentration by volume. The concentrate is a mixture of fluorocarbon, hydrocarbon surfactants, solvents, other additives, and water. The commercial fluorine-free surfactant solution, RF6, used in our experiments was approved by the International Civil Aviation Organization (ICAO). It was prepared by mixing RF6 "concentrate solution" provided by the manufacturer with distilled water at 6% concentration by volume. The concentrate solution is made of hydrocarbon surfactants, solvents, a polysaccharide thickener, other additives, and water. The composition of the foam solution is about 98% water for each foam with each foam solution having a surfactant concentration less than 1% by weight [18]. The properties of the solutions are given in Table 1 below. Both solutions have similar densities, but differ significantly in viscosity and surface tension with AFFF having a surface tension of 16.4 mN/m and RF6 having a surface tension of 26.4 mN/m at 25 °C. The surface tensions were measured using a DuNoy ring tensiometer at 25 °C. RF6 does not form an "aqueous film" unlike AFFF because of its higher surface tension.

2.2. Fuels

Three fuels, n-heptane, iso-octane, and methyl-cyclohexane, used in our experiments represent straight chained, branched, and cyclic compounds found in a jet fuel. The fuel properties for these three liquid fuels are detailed in Table 2. Table 2 shows that the vapor pressures differ by less than 15% from that of n-heptane. Iso-octane has the smallest surface tension among the fuels studied and does not allow film formation even for Buckeye 3% AFFF foam solution [4]. However, there is a significant difference in fuel solubility in water among the fuels studied especially between methyl-cyclohexane and iso-octane. The differences in solubility could be important because the fuel solubility is the driving force for fuel mass transport through a foam/film.

2.3. Foam generation and foam properties

Fig. 1 details the foam generation process. 400 mL of foam solution

Table 1
Measured foam solution properties at 25 °C.

Foam Solution	AFFF	RF6
Density (g/mL)	1.03	1.06
Viscosity (cP)	1.20	2.40
Surface Tension (mN/m)	16.40	26.40