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Fluorine-free Foams with Oleophobic Surfactants and Additives for Effective Pool Fire Suppression

SERDP Project WP-2739

**Ramagopal Ananth, Arthur Snow (Emeritus), Katherine Hinnant,
Spencer Giles, John Farley
U.S. Naval Research Laboratory
and
Professors Jennifer Field and William Stubblefield, Oregon State University,
Corvallis, OR**

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Abstract

Objectives: The objective of our research program is to develop an environmentally-friendly, fluorine-free, firefighting surfactant formulation to replace AFFF by reducing the fuel permeation through foam and foam degradation and increasing surfactant oleophobicity. Conduct measurements of aquatic toxicity and biodegradation to assess the environmental impact of the fluorine-free surfactants in comparison to the fluorinated surfactants.

Technical Approach: We chose surfactant molecules based on hydrophobic and oleophobic balance. Commercial sources and chemical synthesis were used to obtain candidate surfactants. We pursued parallel efforts to quantify firefighting performance and assess environmental/health impact. Surfactants were down-selected by utilizing molecular dynamics simulations, and measurements of surfactant-solution properties. The first tier of evaluation was based on the measurements of the short-term acute toxicity using algae, invertebrates, and fish. The first tier also included the measurements of fuel transport through the foam, foam degradation, and foam spread rates. The second tier of evaluation included the measurements of chronic toxicity using algae, invertebrates, and fish. The second tier also included measurements of fire extinction dynamics. The final formulations' compositions were optimized at bench-scale prior to large scale MILSPEC testing.

Results: The chemistry of surfactants and oleophobicity play a very important role in controlling pool fires. A reference AFFF formulation containing a fluorocarbon surfactant, a hydrocarbon surfactant (alkylpolyglycoside, APG), and a solvent was shown to extinguish heptane and gasoline pool fires as quickly as a commercial AFFF at bench (19-cm diameter pool) and large (28 ft² pool) scales. By substituting different fluorine-free surfactants for the fluorocarbon and different hydrocarbon surfactants for APG in the RefAFFF, we found that varying the composition significantly affected the fire suppression. The bench scale measurements revealed that synergistic interactions between the siloxane and APG surfactants reduced foam degradation and fuel transport which caused the observed higher fire suppression performance.

In addition to the synergism, surfactant's amphiphilicity and polydispersity can affect fire suppression significantly. We synthesized trisiloxane polyoxyethylene surfactants with different distributions of oxyethylene head sizes with the average values ranging from 0 to 50. We quantified the effects of varying the oxyethylene head size of the trisiloxane surfactant on the degree of synergism, solution and foam properties, foam degradation rate, fuel transport rate, foam spread rate, and heptane-fire suppression. To obtain even larger improvement, we varied the glycoside head size with the tail size fixed, and varied the alkyl tail size with the head size fixed using monodispersed APGs. We found slight minima in fire extinction time as the head or tail size is varied. Varying head or tail size, one at a time, may have reduced amphiphilicity. Also, the lack of polydispersity of APG could have decreased the degree of synergism.

The work revealed a few general principles: (1) surfactant's chemical structure has a significant effect on foam's ability to suppress fires, (2) when varying surfactant's chemical structure, head's hydrophilicity should be balanced with tail's hydrophobicity to preserve amphiphilicity, which affects interfacial activity and fire suppression, (3) increasing synergism between two types of surfactants adsorbed at an interface is the key to enhancing fire suppression, (4) surfactant head structures that suppress surfactant extraction by fuel can increase fire suppression, (5) surfactant structures that decrease fuel permeation through foams enhance fire suppression, and (6) foams cool pool surface rapidly and reduce fuel vapor pressure leading to enhanced fire suppression for high flash point fuels, whose fire extinction times are close to their pool coverage times.

Biological endpoints were assessed to determine whether the mixture exhibited additive effects. The acute studies (toxicity based upon 48-hr or 96-hr survival) demonstrated that the mixture tested had additive or more-than-additive effects. In the chronic tests (72 h or 7 d), the scenario resulted in additive or less-than-additive effects. When comparing each species based upon measured mixture concentrations, *P. promelas* and *C. dubia* were more sensitive to chronic exposures versus acute exposures, while the algae, *R. subcapitata* was the least sensitive to the mixture tested.

Benefits: Further work is needed to improve the fire suppression of siloxane based formulation on gasoline and heptane. If successful, it has the potential to be a drop-in replacement for AFFF because of low viscosity and homogeneity of the 3% concentrate, unlike many of today's commercial fluorine-free formulations. The new surfactants and foams have the potential to be effective on different fuel-fires and meet MIL-F-24385F performance standards, and have acceptable persistence and aquatic toxicity.

Executive Summary

1. Introduction

Replacing fluorocarbon surfactant in Aqueous Film Forming Foams (AFFF) with fluorine-free surfactant will significantly reduce the environmental impact because of the elimination of extremely stable C-F bonds, which persist in the environment. In addition, the fluorine-free alternatives must meet the fast pool-fire extinction requirement, which is part of the MILSPEC and is critical for DOD applications. Even though many fluorine-free surfactants are available commercially, a foam with fire-fighting effectiveness comparable to that of AFFF has not been found during the last few decades despite the fact that fluoro-surfactants are very expensive relative to hydrocarbon surfactants. Furthermore, because of high viscosity of the concentrate, the commercial fluorine-free foam-solutions available on the market today would require expensive hardware-upgrades to generate the foams in field application.

Foam suppresses fires by forming a physical barrier between the pool and fire, blocking the fuel vapor transport from the pool surface to the combustion process. A foam layer contains a myriad of aqueous lamellae and air, forming a significant barrier to fuel transport. Fuel transport through the foam layer can occur as the fuel travels through the gas phase contained in the foam bubbles, through the liquid lamella (liquid layer between two adjacent bubbles or bubble wall) surrounding the bubbles, and through the plateau borders (liquid columns formed at the junction of three adjacent bubbles). Transport through liquids is much slower than transport through gases due to differences in diffusion coefficients between gases and liquids by four orders of magnitude. The foam solution composition may affect fuel transport because all surfactants adsorb at the lamella interface (bubble surface). Fluorocarbon surfactants in AFFF are unique in having both hydrophobic and oleophobic repulsions. The fluorocarbon tail repels a hydrocarbon fuel like n-heptane and suppress fuel dissolution into the liquid lamella and may impede the transport through the foam layer. Fluorine-free hydrocarbon surfactants are also hydrophobic, but the hydrocarbon tails do not repel the hydrocarbon fuel and are not as oleophobic as fluorocarbon surfactants. Fuel vapors can easily dissolve into the liquid lamella and move unimpeded by the hydrocarbon surfactant through the foam layer resulting in faster transport. Siloxane surfactants contain polar Si-O bonds in the tail and are different from the non-polar bonds contained in aliphatic fuels such as heptane. Therefore, the siloxane surfactants are more akin to the fluorocarbon surfactants due to their oleophobicity and are investigated in this report. Commercial siloxane surfactants are less common relative to commercial hydrocarbon surfactants and may require synthesis of novel materials.

2. Objectives

The objective of our research program is to develop an environmentally-friendly, fluorine-free, firefighting surfactant formulation to replace AFFF by reducing the fuel permeability through foam and foam degradation with increased surfactant oleophobicity as shown in Figure 1. Figure 1 shows that foam acts as a fuel vapor barrier and surfactants adsorbed at bubble surfaces interact with fuel vapors as they permeate through the foam feeding the fire. By increasing the oleophobicity of the fluorine-free surfactants, the fuel vapor permeation could be suppressed quickly to cut-off fuel supply into the fire.

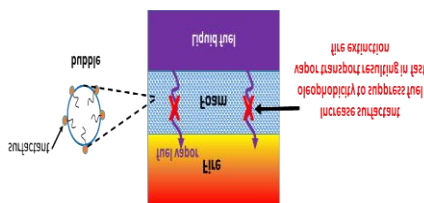


Figure 1. Enhancing fire suppression with surfactants by targeting the foam layer as a fuel vapor barrier rather than the aqueous film formation.

Our overall approach is to build on the research community's understanding and our own research experience on fire suppression mechanisms, laboratory experimental methods, and computational models at the U.S. Naval Research Laboratory (NRL) and environmental impact assessments of Oregon State University. In collaboration with Oregon State University (OSU), we conducted measurements of aquatic toxicity and biodegradation to assess the environmental impact of the fluorine-free surfactants in comparison to the fluorinated surfactants.

3. Technical Approach

Figure 2 shows an overview of the technical approach we used to arrive at the final choice of surfactant for the fluorine-free alternative foam. In the first year, we used the insights and chemical intuition gained in our previous research to choose surfactant molecules based on an hydrophobic and oleophobic balance, as indicated by the first box at the top of Figure 2. We used a combination of literature evaluations and predictive models (such as EPA's EPIWIN models) to estimate the environmental fate of the molecules and to choose the surfactants to eliminate "show-stoppers". We used dual lines of commercial sources and chemical synthesis to obtain candidate surfactants. We began with more than 20 commercial surfactants and 8 surfactants for chemical synthesis. We pursued parallel efforts to quantify firefighting performance and assess environmental/health impact as shown on the right and left sides of Figure 2 respectively over the entire program. In the first tier of prescreening, we utilized molecular dynamics simulations, and measurements of surfactant solution properties to down-select surfactants. The second tier of prescreening in the first and second years of the program included measurement of short-term biodegradability and single lamella measurements along with modeling to down-select surfactants. In the latter half of the first year, we began the surfactant evaluation process. The first tier of evaluation was based on the measurements of the short-term acute toxicity using algae, invertebrates, and fish and on the measurements of foam dynamics including fuel transport through the foam, foam degradation, and foam spread. The second tier of evaluation beginning in the second year included the measurements of chronic toxicity using algae, invertebrates, and fish, and biodegradability, along with measurements of fire extinction dynamics. The two-tier evaluation lead to final surfactant formulations in the last year of the program. The formulations' compositions were optimized at bench-scale prior to large scale MILSPEC testing. We used NRL's custom-made foam formulation that passed both MILSPEC fire extinction and burn-back tests, and fuels (n-heptane, methyl-cyclohexane, and when safe, gasoline) to quantify the development of fluorine-free alternative surfactants.

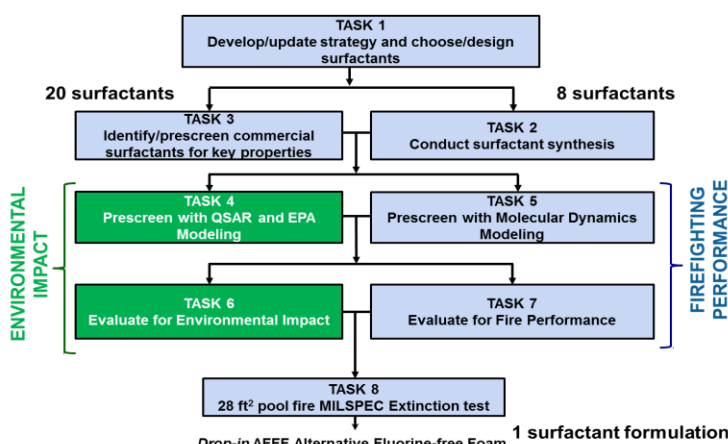


Figure 2. Technical approach and tasks.

Our first step is to develop a simple, well-defined, three component (two surfactants and a solvent) custom AFFF formulation with known molecular structures, and show its gasoline fire suppression matches that of a commercial AFFF. This is crucial because the compositions of commercial AFFFs are proprietary and subject to continuous changes. Known as the Reference AFFF, the fluorocarbon surfactant can be replaced with an alternative and the alternative's properties and performance can be evaluated against the fluorocarbon surfactant. This enabled us to empirically formulate cause-effect relationships which are used as the basis for changes due to the molecular structure of the alternative surfactants for improved performance.

A broad spectrum of commercially available siloxane and hydrocarbon surfactants are evaluated using bench scale methods as alternatives that are not necessarily designed for firefighting. Using bench scale methods, the surfactants are ranked and promising candidates are identified for large scale fire extinction testing. Novel surfactants are designed based on chemical intuition for increased oleophobicity and by performing molecular dynamics (MD) simulations to predict monolayer structures for surfactants at heptane-water and water-air interfaces. The novel surfactants are synthesized by chemical reactions at 10 grams scale using routes that are well established for

hydrocarbon surfactants but are established only to a very limited degree for the siloxane surfactants. Characterizations of the synthesized chemical structures are performed using NMR and LC/MS methods.

A number of bench-scale experiments are used. A single lamella is formed with the surfactant solution and its dynamics of rupture was studied; lamella is a representation of a bubble wall. Solution and foam properties, foam degradation, fuel transport through a foam layer, foam spread, and fire extinction are measured at bench scale to evaluate the surfactants. The surfactants are evaluated for heptane, jet fuel, and gasoline fire suppression. Bench scale experiments have two purposes; (1) to screen and rank fluorine-free surfactants and the top-ranked surfactants are then subjected to large scale testing, (2) to guide the design of new surfactant molecular structures by varying the experimental parameters under well controlled conditions to establish cause-and-effect relationships. Because, the bench scale tests use tens of grams of surfactant to vary a parameter (e.g., vary foam application rates by a factor of 20, three fuels, many surfactant compositions) rather than 100s of grams needed for a single large scale test, they are the most appropriate tool to understand the effects of surfactants on foam dynamics and fire suppression unlike the large scale tests. The bench scale experiments are the only convenient choice for synthesized surfactants that are available only in small quantities. The bench-scale experiments also allow for more detailed measurements unlike the large scale tests. But, the bench scale experiments are not a replacement for the large scale tests. Therefore, we also conducted large scale, 28 ft² heptane and gasoline pool fire extinction and burnback tests at varied foam application rates to a very limited degree.

Solution properties such as surface tension and critical micelle concentrations are measured. Foams are generated using a sparging method and are characterized by measuring expansion ratio. Foam stability and fuel vapor permeation through a foam layer play critical roles in fire suppression by aqueous foams. Therefore, they are measured in separate experiments in the absence of a fire for each of the surfactant formulations. These measurements help understand the fire extinction results. The foam degradation experiment involves generating a foam from a surfactant formulation by air aspiration. A 4 cm height of foam is collected from the foam generator into a 100 mL beaker containing 50 ml heptane liquid, which is preheated and maintained at 60°C using hot water bath. The foam thickness is monitored as a function of time. Foam degradation is also measured on gasoline fuel which is heated to 35°C because of its higher volatility than heptane. The fuel transport experiment characterizing permeation through an initial 4 cm thick layer of foam was conducted on foams prepared in an identical manner to those in the degradation experiment, but contained in a specifically designed fuel transport container rather than a beaker. After deposition of the foam over 60°C heptane liquid and closing the container, the increase in heptane vapor in the headspace of the container is monitored by a slow purge through an IR gas cell. Bench scale fire extinction tests were conducted using a 19-cm diameter pools of heptane and gasoline at different foam application rates. Previously, we showed that fluorine-free foams are sensitive to aromatic and aliphatic premix solution is prepared and is used to conduct fire extinction up to ten foam application rates for a given formulation and fuel.

Environmental impact of the fluorine-free alternatives was evaluated by measuring aquatic toxicity. The conduct of the study of acute and chronic Toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK, and their mixture to the cladoceran, *Ceriodaphnia dubia*, the fathead minnow, *Pimephales promelas*, and the green algae, *Raphidocelis subcapitata* was reviewed for compliance with OSU AquaTox Standard Operating Procedures (SOPs). Analysis and documentation for the study were carried out in the spirit of U.S. EPA and OECD Good Laboratory Practice (GLP) standards. The testing reported herein was conducted to evaluate the potential acute and chronic toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK, and a mixture designed to represent an end-use product, to the cladoceran, *Ceriodaphnia dubia*, fathead minnow, *Pimephales promelas*, and the green algae, *Raphidocelis subcapitata*. Accompanying the toxicity tests were measurements of DOWSIL™ 502W Additive and Butyl Carbitol of exposure concentrations, while exposures for Glucopon® 225 DK are reported as nominal concentrations due to the lack of an analytical method. Where applicable, the test methodologies followed U.S. Environmental Protection Agency (USEPA) and Organization of Economic Co-operation and Development (OECD) guidance as described throughout this report. Analysis and documentation for the study were carried out in a manner consistent with U.S. EPA and OECD Good Laboratory Practice (GLP) standards. The toxicity tests were performed at the Oregon State University Aquatic Toxicology Laboratory (OSU AquaTox, Corvallis, OR, USA) and the analytical verification was performed at the OSU Field Laboratory (Corvallis, OR, USA). All data related to this study will be maintained in the OSU AquaTox archives for 10 years. All culturing and testing with the fathead minnow is regulated and approved by the Oregon State University Institutional Animal Care and Use Committee (IACUC) under an approved animal care and use protocol (ACUP).

4. Results and Discussion

Commercial AFFF solutions contain numerous proprietary components preventing us from isolating the effect of a surfactant on fire extinction from other components in the solution. We need a simple, well-characterized, and known chemical structures to constitute a Reference AFFF formulation to establish baseline properties and performance. We demonstrated that a simple four-component Ref AFFF formulation matches the small and the large-scale fire extinction performance of a commercial AFFF [44]. This Ref AFFF formulation is prepared by mixing 0.2 % Glucopon 215 CS UP (poly-D-glucopyranose with octyl and decyl alkyl chains), 0.3% Capstone 1125 (tridecafluorooctyl sulfonamide alkylbetaine), 0.5% DGBE (diethyleneglycol monobutyl ether) by volume in distilled water.

We evaluated fire suppression of a number of commercial siloxane and hydrocarbon surfactants by preparing aqueous solutions of surfactants only and surfactant mixtures (formulations). These evaluations lead to identification of siloxane surfactants as promising fluorine-free alternatives to AFFF. The formulations were prepared by replacing Capstone1157 in the RefAFFF composition with the fluorine-free candidate. We selected a group of five non-ionic siloxane surfactants with identical trisiloxane tails and closely related head groups of different average length (a distribution of lengths exist). They are Silwet L77 from Momentive Inc., GelestSiH6185 from Gelest Inc., and 67A, 501W, and 502W from Dow-Corning Inc. 67A and 502W have poly oxy-ethylene head groups with hydroxyl terminal unit. Silwet L77 and 501W also have poly oxy-ethylene head group but have methyl terminal unit. The other three are grafted siloxane surfactants, and have multiple siloxane tails and heads. They are 193A from Dow-Corning Inc. and SilsurfJ208 from Siltec Inc. The eighth surfactant, SilphosJ208, is similar to SilsurfJ208 but is anionic. Similarly, three hydrocarbon surfactants with an alkane tail of similar lengths (six to twelve carbons) but different polar head groups; Alpha Foamer (Stepan Inc.) has an oxy-ethylene connected to the sulfonate head group unlike sodium dodecyl sulfonate (SDS, Aldrich Co.), and Glucopon215UP (BASF) has a glucoside head group having numerous hydroxyl units, which are non-ionic. The other hydrocarbon surfactants have different number of oxyethylene head groups and different hydrocarbon tails; Tergitol 15-S-7 (Dow Chemical) has two alkane tails and Tergitol TMN6 (Dow Chemical) has pendant methyl groups on the two tails. The surfactants can be ranked based on the values of foam flow rate at which the extinction time becomes relatively long. The smaller the foam flow rate needed for a 30 s extinction time, the more efficient is extinction. This identified a siloxane-glucopon215 formulation as one of the more effective at suppressing heptane pool fires and was chosen for further development.

Figure 3 compares heptane-fire extinction times for the fluorine-free siloxane-glycoside foam identified above with two fluorinated foams (Buckeye 3% and RefAFFF). Foams were generated using sparging method. In the mixture siloxane-glycoside formulation, Glucopon 225 DK was used instead of the Glucopon 215UP in a mixture with siloxane (Dowsil502W additive) for improved fire suppression. Figure 3 presents time-lapse images of this fire suppression over a 19 cm diameter heptane pool fire using a foam application rate of 1000 mL min⁻¹[50]. At 0 seconds, the foam is introduced to the pool fire surface after the pool has been burning for 60 seconds. The siloxane-glycoside foam takes slightly longer times to fully extinguish the flame. These results are consistent with MilSpec testing on a 6ft-diameter heptane pool fire at 2 gallon per minute solution flow rate. The large scale testing also showed the extinction time for the Siloxane-glycoside foam is 1.5 times longer than that for RefAFFF.

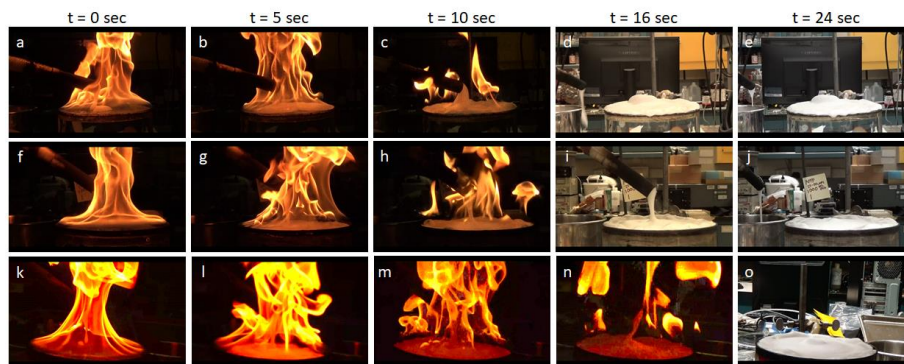


Figure 3. Time lapse images of 19-cm diameter heptane pool fire suppression by Buckeye 3% (top row), RefAFFF (Middle row), and Siloxane-glycoside foam (bottom row) at 1000 mL/min foam application rate.

The reason for relatively good fire suppression performance of the Siloxane-Gluc225 formulation is the synergism between the Siloxane and Glycoside surfactants. Figure 4a depicts heptane-fire extinction time versus foam application rate for the siloxane-Glucopon mixtures and for the individual components. It shows synergism where the siloxane-Glucopon surfactant mixture extinguishes the fire much faster than the individual components. Figure 4b shows similar synergism in foam stability when foams are exposed to fuel vapors. Glucopon is a commercial polydispersed alkylpolyglycoside (APG) surfactant; Glucopon 600UP, 215UP, and 225DK have varying average head and tail sizes. Figure 4 also shows the effects of varying mainly the size of the glycoside head group of the APG surfactant (Glucopon 600UP, 215UP, and 225DK). Figure 4c shows that a 3% concentrate of the siloxane solution has a long shelf-life as indicated by a thermal stress test, where the concentrate is held at 65 °C for 10 days and was used to show that the bench scale fire extinction was unaffected.

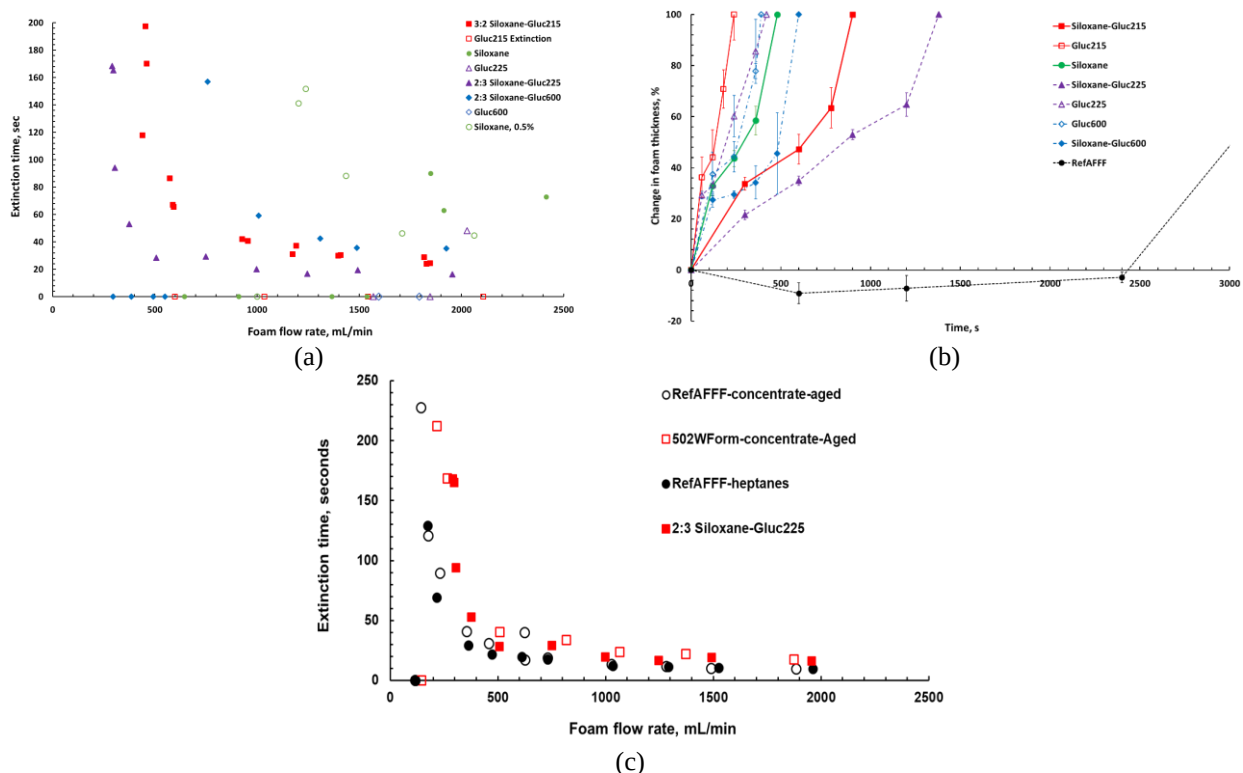


Figure 4. Enhanced fire suppression and foam stability with a mixture siloxane-glycoside relative to the individual components in (a) heptane-fire extinction time versus foam application rate, and (b) % foam degradation by fuel vapors versus time when a 4-cm foam layer is placed on a hot (60 °C) heptane pool surface. Also shown (a) and (b) is the increased synergism with increased average glycoside-head-size among Glucopon600 (1.4 units glycoside head size) Glucopon 215UP (1.5 units), and Glucopon 225 DK (1.7 units). (c) Extinction time profile before and after subjecting a 3% concentrate of the siloxane-Glucopon225DK and RefAFFF formulations to 65 °C for 10 days in an oven; the concentrates are diluted to make premix solutions, which are used for generating the foams.

Molecular dynamics (MD) models are developed for monolayers of surfactants adsorbed at air-water and heptane-water interfaces. The models predict a number of interfacial properties such as a surface tension, area per molecule or packing density, interface thickness, Gibbs elasticity of the interface, hydrogen bonding for surfactant components and mixtures. Figure 5 shows that the area per molecule decreases when an APG surfactant is added to the trisiloxane-oxyethylene surfactant when compared the trisiloxane surfactant alone. This is because the large glycoside-head of the APG aligns with the large trisiloxane-tail of the trisiloxane-oxyethylene surfactants adsorbed at water and fuel sides of an interface respectively forming a bi-layer. This geometrical alignment allows the two types of molecules to occupy less area per molecule compared to adsorption of the two surfactant without such geometrical alignment.

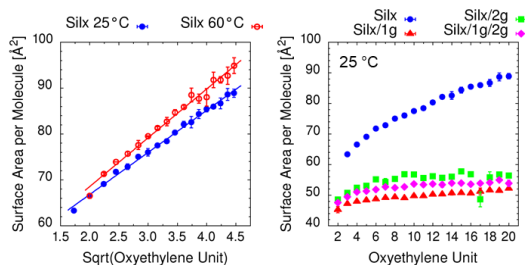


Figure 5. Molecular dynamics model predictions for area per surfactant molecule adsorbed at heptane-water interface for siloxane only and for siloxane-glycoside surfactant mixture.

We conducted large scale pool fire testing of NRL's drop-in siloxane502W formulation, which is the 2:3 Siloxane-Gluc225 composition listed in Table 19. Tables 53a and 53b compare 28 ft² pool fire extinction performance for heptane and gasoline fuels. They show that the siloxane formulation is much more effective on heptane than on gasoline fire.

Table 1a. Large scale heptane fire extinction.

	Drop-in Requirement	28 ft ² Heptane Pool Fire	
	3% concentrate viscosity cP	Extinction Time (s)	Burnback Time (s)
Ref AFFF	4.7	30	981
NRL's Drop-In Siloxane Formulation	7.4	51	338
Commercial Fluorine-Free Foam	16,120	42	778

*28 ft² heptane pool fire at 2 gpm foam solution application rate

Table 1b. Large scale gasoline fire extinction.

	28 ft ² Gasoline Pool Fire	
	Extinction Time (s)	Burnback Time (s)
MilSpec Criteria	< 30	> 360
Ref AFFF	24	759
Drop-in 502W Formulation	> 60, no extinction	N/A

To understand the causes for this difference among fuels, we studied the composition of gasoline that differentiates it from heptane, and conducted a series of bench scale experiments with siloxane formulation as well as other commercial fluorine-free formulations [65]. We found that the AFFF formulations are relative insensitive to the identity of the fuel, but the fluorine-free formulations display a significant divergence in extinction capability between these two fuels with the gasoline fire being the more difficult to extinguish. Using the NRL's siloxane formulation, twelve major components of gasoline from the *n*-alkane, *iso*-alkane, *cyclo*-alkane, aromatic and olefin categories were examined to determine a source for this difference in extinction capability. We found that it is the aromatic components category that caused the divergence in performance. Within the aromatic components this effect substantially increased with the number of methyl substituents (trimethylbenzene > xylenes > toluene > benzene) as shown in Figure 6. The mechanism involved was investigated by an experiment monitoring the aqueous surfactant solution – fuel interface for the crossing of surfactants and fuel with the finding that the surfactant was extracted by the fuel. The degree of extraction of surfactant into the fuel correlated with the effect of the fuel component on extinction, particularly within the aromatic components (trimethylbenzene > xylenes > toluene > benzene). As a simple two-component simulant for gasoline, a trimethylbenzene/heptane mixture is proposed and supported by foam degradation and fuel vapor transport through the foam characterization [65].

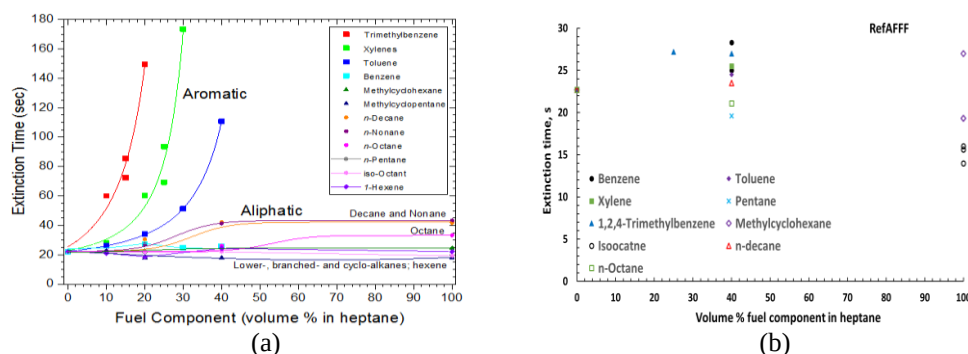


Figure 6. Fire extinction time at 1000 mL/min foam application rate for heptane doped with aliphatic and aromatic components of gasoline with (a) Siloxane-Glucopon225DK formulation and (b) RefAFFF formulation

To further improve heptane-fire suppression with siloxane-glucopon225DK surfactant mixture, we varied the chemical structures of the siloxane and glycoside surfactants. A systematic variation of the average oxyethylene head length of the polydispersed trisiloxane-polyoxyethylene surfactant can only be achieved by synthesizing “homologous” (polydispersed) series of the siloxane molecules. A single step hydrosilylation reaction between bis(trimethylsiloxy)methylsilane and the allyloxy-poly(oxyethylene) reagent catalyzed by chloroplatinic acid in isopropanol was conducted at 20 grams scale as depicted in Figure 7a. The catalyst reactivity is sensitive to the oxyethylene chain length. Reaction conversion was monitored by ^1H NMR. The polydispersed products are characterized by ^1H NMR and other analytical techniques. Figure 7b shows integrated NMR analyses of the ratio of head to tail protons versus average oxyethylene length. The dashed red line corresponds to theoretical calibration derived from chemical structure with head and tail proton counts.

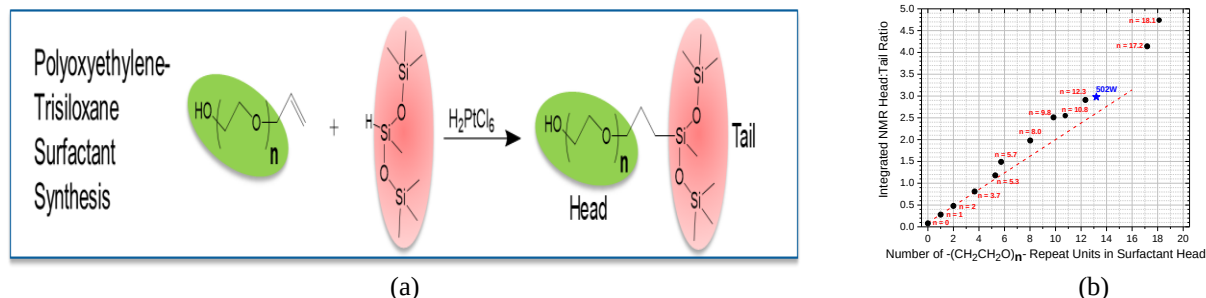


Figure 7. (a) Synthesis of trisiloxane poly(oxyethylene) (BHMTS-OEn) surfactants with homologous head lengths, average n , (b) calibration plot of integrated H:T proton ratio as a function of oxyethylene chain length (n). Dowsil 502W commercial siloxane surfactant used in siloxane-Glucopon225DK formulation is shown in (b).

Formulations containing 0.2% synthesized trisiloxanes, 0.3% Glucopon225DK, and 0.5% DGBE in water by weight were prepared. Variety of solution, interface, and foam properties, and heptane-fire extinction were measured. Figure 8a and b show the effect of oxyethylene head length on foam properties when the foams are exposed to heptane vapors. Figure 8a shows time for complete degradation of a 4-cm thick layer of foam placed on hot (60 °C) heptane pool and 8b shows fuel permeation through the foam layer. Figure 8b shows time at which heptane vapor flux at the top of the foam layer reaches 5.3×10^{-9} mole/cm²s corresponding to the lower flammability limit (1.1 mole%). They both show a maximum near oxyethylene length of 12 units, which correlates with the minimum in fire extinction time at 1000 mL/min foam application rate as depicted in Figure 8c. Unfortunately, the minimum extinction time corresponds to the extinction time measured for the commercial Dowsil502W-Glucopon225DK mixture shown in Figure 4 and indicate by square symbol in Figure 8c.

In addition to varying the trisiloxane head, we also varied the head and tail lengths of the APG surfactant used in siloxne-Glucopon225DK formulation. We varied the APG's head size with the alkyl tail length fixed. Also, we varied the APG's tail length with the glycoside head size fixed. The Glucopon225DK is polydispersed with a distribution of head and tail sizes. Based on BASF Co. literature, it has on average 1.7 units of glycoside head size and 8 to 10 carbon lengths of alkyl tail. Unlike the trisiloxanepolyoxyethylenes discussed above, we did not have to synthesize APGs with the exception of alkyltriglycoside. Fortunately, we found numerous commercial, APGs with varying head and tail sizes, but they were all monodispersed. Nevertheless, formulations were prepared with 0.2% polydispersed-Dowsil502W, 0.3% monodispersed APG, and 0.5% DGBE in water and were used to measure interfacial and foam properties, and heptane-fire extinction times. Figure 9a and b display extinction time versus APG tail length and head size respectively. They show slight minima at 8 to 10 alkyl tail length and at 2 glycoside head units. More importantly, they show that the minimum extinction times are higher than the siloxane-Glucopon225DK formulation's extinction times (shown in Figures 3 and 4), which are indicated by the rectangular boxes in Figures 9a and b. This could be because of two reasons. First, as the tail size is varied with head size fixed or vice a versa, the amphiphilicity of the molecule reduced and affected the interfacial activity. Second, the use of monodispersed APGs might not have allowed them to interact effectively with the polydispersed trisiloxane-oxyethylene (Dowsil502W) and form bilayers at an interface effectively.

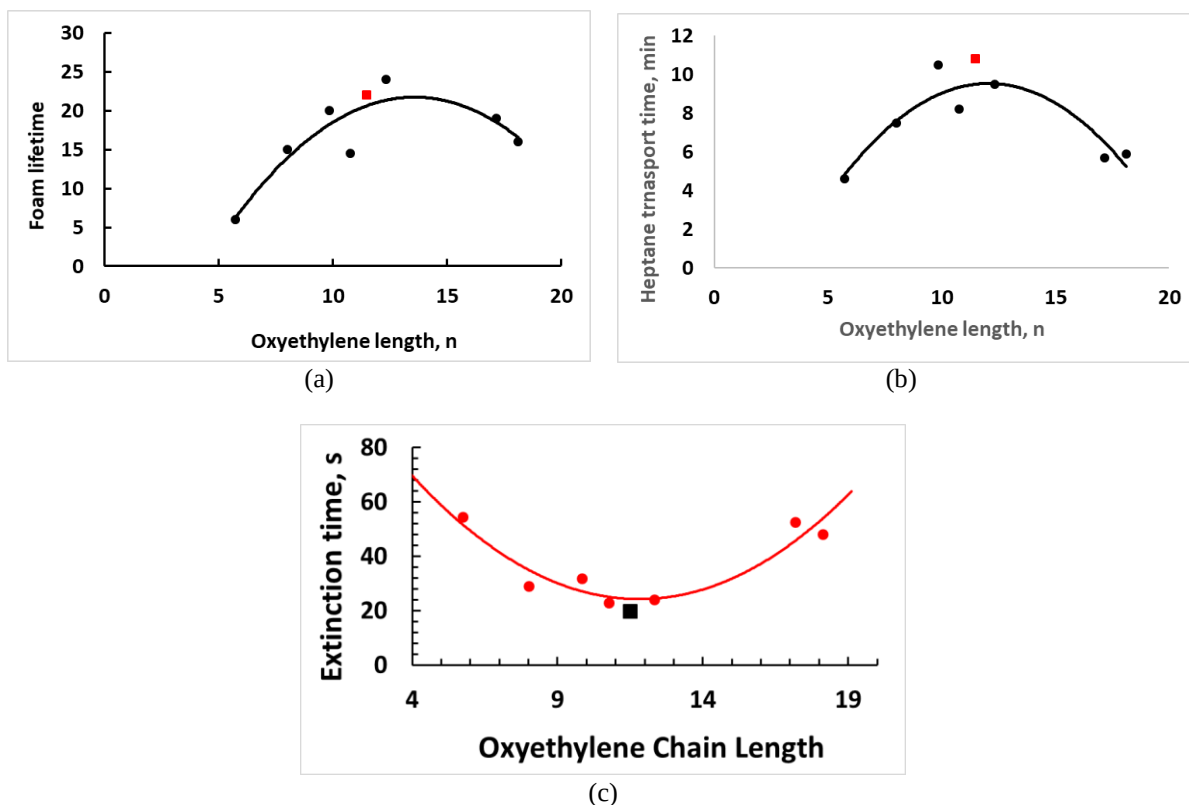


Figure 8. Foam-fuel interaction dynamics and heptane-fire extinction. (a) time for complete degradation of 4-cm foam layer, (b) fuel transport time at which heptane concentration above the foam layer reaches lower flammability limit, and (c) heptane-fire extinction time, versus oxyethylene length, n . Square symbols are the data for Dowsil502W-Glucopon225DK formulation shown in Figures 3 and 4.

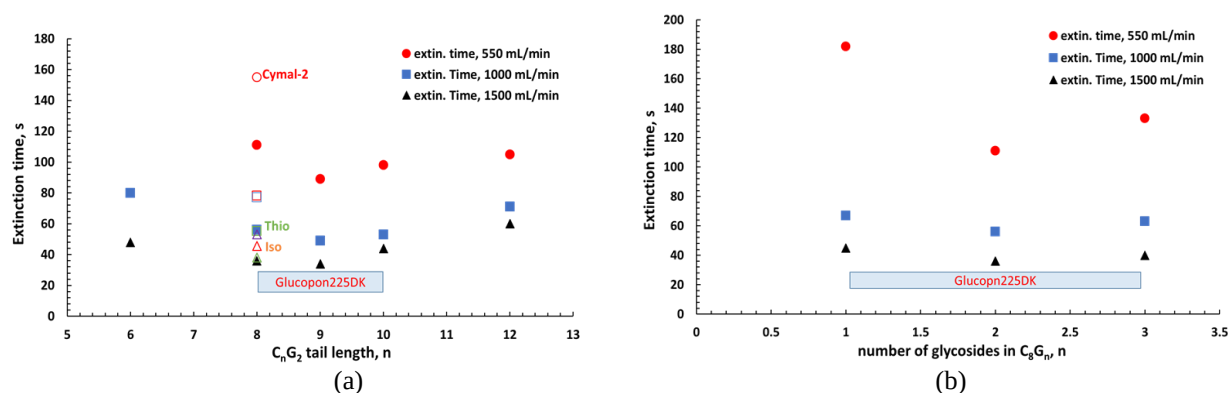


Figure 9. 19-cm diameter heptane-pool fire extinction time versus monodispersed APG's (a) alkyl tail length, and (b) glycoside head units, at different foam application rates.

Environmental impact of the siloxane-Glucopon225DK formulation was evaluated by measuring acute and chronic aquatic toxicities using a number of difference biological species. Both the mixture and individual component values are reported. Also, analytical methods were developed and used to measure the actual exposure concentrations in addition to the nominal values. Table 2 shows the values for the formulation mixture in terms of LC_{50} and EC_{50} in mg/L along with the protocols followed.

Table 2. Toxicity of the mixture to invertebrates, fish, and algae.

Species		Duration	Effect	Mixture: DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK (mg/L)	Method
Invertebrate	<i>C. dubia</i>	48 h (Acute)	LC ₅₀	44.3 (38.7 – 50.7) (nominal) 31.1 (27.2 – 35.5) (measured)	USEPA 2002a
Fish	<i>P. promelas</i>	96 h (Acute)	LC ₅₀	23.8 (21.3 – 26.5) (nominal) 20.1 (18.0 – 22.4) (measured)	USEPA 2002a
Invertebrate	<i>C. dubia</i>	7 d (Chronic)	EC ₂₀	24.6 (20.7 – 29.3) (nominal) 23.2 (19.7 – 27.3) (measured)	USEPA 2002b
Fish	<i>P. promelas</i>	7 d (Chronic)	EC ₂₀	12.6 (11.3 – 14.0) (nominal) 11.9 (10.4 – 13.6) (measured)	USEPA 2002b
Algae	<i>R. subcapitata</i>	72 h (Chronic)	EC ₂₀	92.9 (45.0 – 191.9) (nominal) 83.0 (39.1 – 176.1) (measured)	OECD 2011

Biological endpoints were assessed to determine whether the mixture exhibited additive (no difference in toxicity as a mixture), less-than-additive (reduced toxicity as a mixture), or more-than-additive (increased toxicity as a mixture) effects. The acute studies (toxicity based upon 48-hr or 96-hr survival) demonstrated that the mixture tested had additive or more-than-additive effects. In the chronic tests (72 h or 7 d), the scenario resulted in additive or less-than-additive effects. When comparing each species based upon measured mixture concentrations, *P. promelas* and *C. dubia* were more sensitive to chronic exposures versus acute exposures, while the algae, *R. subcapitata* was the least sensitive to the mixture tested.

5. Implications for Future Research and Benefits

Current work showed that exploiting the chemical mechanisms is the key to developing fluorine-free foams that are equally effective in suppressing gasoline, heptane, and jet fuels and with an efficiency equal to AFFF. Future works should build on a few general principles revealed to date (1) surfactant's chemical structure has a significant effect on foam's ability to suppress fires, (2) when varying surfactant's chemical structure, head's hydrophilicity should be balanced with tail's hydrophobicity to preserve amphiphilicity, which affects interfacial activity and fire suppression, (3) increasing synergism between two types of surfactants adsorbed at an interface is the key to enhancing fire suppression, (4) surfactant head structures that suppress surfactant extraction by fuel can increase fire suppression, (5) surfactant structures that decrease fuel permeation through foams enhance fire suppression, and (6) foams cool pool surface rapidly and reduce fuel vapor pressure leading to enhanced fire suppression for high flash point fuels, whose fire extinction times are close to their pool coverage times.

Future works should focus on revealing the synergistic molecular interactions among different-type surfactants and fuels that control fuel permeation through foams and fire suppression. Further work is needed to improve the fire suppression of siloxane based formulation so that they can suppress gasoline, heptane, and jet fuel fires equally well and reduce siloxane tail's hydrolysis in dilute premix solutions. Future works should examine broader variations of head and tail structures of silicone, hydrocarbon, and boron surfactants to suppress extraction by fuels and to improve fire suppression. Additives that can strengthen hydrogen bonding between the surfactants and foam boosters should also be considered. If successful, siloxane formulations have the potential to be a *drop-in* replacement for AFFF because of their low viscosity and homogeneity of the 3% concentrate, and because of their low acute and chronic aquatic toxicities of the dilute premix solution, unlike many of today's commercial fluorine-free formulations. The new siloxane surfactant formulations and foams have the potential to meet all of the MIL-F-24385F performance standards except for aqueous film formation, which is not necessary.

In addition to fire suppression, burnback performance including thermal degradation of foams should be measured at bench scale. Further improvements to bench scale methods are needed to better correlate with the large scale tests. This should include new bench scale methods for foam generation with the objective of simulating the quality (bubble size distribution and expansion ratio) and properties of foams generated by the MilSpec nozzle.

Fluorine-free Foams with Oleophobic Surfactants and Additives for Effective Pool Fire Suppression

*Dr. Ramagopal Ananth (PI), Dr. Arthur Snow (Emeritus), Ms. Katherine Hinnant,
Dr. Spencer Giles, Mr. John Farley*

*Chemistry Division, U.S. Naval Research Laboratory, Washington, DC,
and*

*Professors Jennifer Field and William Stubblefield
Oregon State University, Corvallis, OR*

Abstract

The objective of our research program is to develop an environmentally-friendly, fluorine-free, firefighting surfactant formulation to replace AFFF by reducing the fuel permeability through foam and foam degradation with increased surfactant oleophobicity. We found that the chemistry of surfactants and oleophobicity play a very important role in controlling pool fires. A reference AFFF formulation containing a fluorocarbon surfactant, a hydrocarbon surfactant (alkylpolyglycoside, APG), and a solvent was shown to extinguish heptane and gasoline pool fires as quickly as a commercial AFFF at bench (19-cm diameter pool) and large (28 ft² pool) scales. By substituting different fluorine-free surfactants for the fluorocarbon and different hydrocarbon surfactants for APG in the RefAFFF, we found that varying the composition significantly affected the fire suppression. The bench scale measurements revealed that synergistic interactions between the siloxane and APG surfactants reduced foam degradation and fuel transport which caused the observed higher fire suppression performance.

In addition to the synergism, surfactant's amphiphilicity and polydispersity can affect fire suppression significantly. We synthesized trisiloxane polyoxyethylene surfactants with different distributions of oxyethylene head sizes with the average values ranging from 0 to 50. We quantified the effects of varying the oxyethylene head size of the trisiloxane surfactant on the degree of synergism, solution and foam properties, foam degradation rate, fuel transport rate, foam spread rate, and heptane-fire suppression. To obtain even larger improvement, we varied the glycoside head size with the tail size fixed, and varied the alkyl tail size with the head size fixed, using monodispersed APGs. We found slight minima in fire extinction time as the head or tail size is varied. Varying head or tail size, one at a time, may have reduced amphiphilicity. Also, the lack of polydispersity of APG could have decreased the degree of synergism.

Biological endpoints were assessed to determine whether the mixture exhibited additive effects. The acute studies (toxicity based upon 48-hr or 96-hr survival) demonstrated that the mixture tested had additive or more-than-additive effects. In the chronic tests (72 h or 7 d), the scenario resulted in additive or less-than-additive effects. When comparing each species based upon measured mixture concentrations, *P. promelas* and *C. dubia* were more sensitive to chronic exposures versus acute exposures, while the algae, *R. subcapitata* was the least sensitive to the mixture tested.

The work revealed a few general principles: (1) surfactant's chemical structure has a significant effect on foam's ability to suppress fires, (2) when varying surfactant's chemical structure, head's hydrophilicity should be balanced with tail's hydrophobicity to preserve amphiphilicity, (3) increasing synergism between two types of surfactants adsorbed at an interface is the key to enhancing fire suppression, (4) surfactant head structures that suppress surfactant extraction by fuel can increase foam stability, and (5) surfactant structures that decrease fuel permeation through foams enhance fire suppression, and (6) foams cool pool surface rapidly leading to enhanced fire suppression for high flash point fuels. Further work is needed to improve the fire suppression of siloxanes, which have the potential to be a drop-in replacements because of low viscosity and homogeneity of the 3% concentrate unlike many of today's commercial fluorine-free formulations, to be effective on different fuel-fires, having acceptable persistence and aquatic toxicity, and to meet MIL-F-24385F performance standards.

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1. Objectives

The objective of our research program is to develop an environmentally-friendly, fluorine-free, firefighting surfactant formulation to replace AFFF by reducing the fuel permeability through foam and foam degradation with increased surfactant oleophobicity as shown in Figure 1. Figure 1 shows that foam acts as a fuel vapor barrier and surfactants adsorbed at bubble surfaces interact with fuel vapors as they permeate through the foam feeding the fire. By increasing the oleophobicity of the fluorine-free surfactants, the fuel vapor permeation could be suppressed quickly to cut-off fuel supply into the fire.

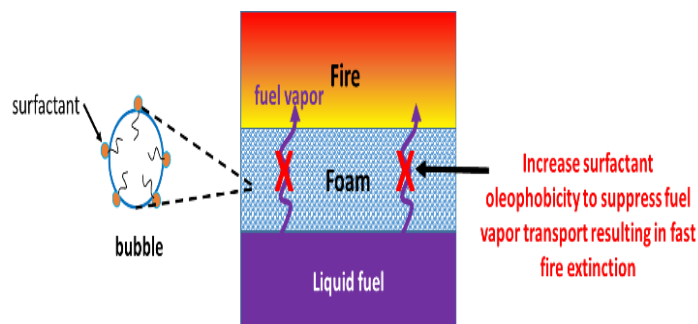


Figure 1. Enhancing fire suppression with surfactants by targeting the foam layer as a fuel vapor barrier rather than the aqueous film formation.

In collaboration with Oregon State University (OSU), we will conduct measurements of aquatic toxicity and biodegradation to assess the environmental impact of the fluorine-free surfactants in comparison to the fluorinated surfactants.

Our overall approach is to build on the research community's understanding and our own research experience on fire suppression mechanisms, laboratory experimental methods, and computational models at the U.S. Naval Research Laboratory (NRL) and environmental impact assessments of Oregon State University. It will benefit the DOD, government and civilian agencies (particularly airports) that use AFFF.

2. Background

Aqueous Film Forming Foams (AFFF) are used worldwide to fight pool fires in military and civilian applications including airports since their invention by the U.S. Naval Research Laboratory (NRL) in the 1960s [1]. They are considered the gold standard for pool fire suppression. The perfluorosurfactants contained in AFFF are the key to the high fire suppression performance, which is critical to prevent weapons “cook-off” [2]. The chemical structure of a perfluorosurfactant is shown in Figure 2. Like any surfactant, it has a hydrophilic head and a hydrophobic tail. But, the tail is perfluorinated. The surfactant gets adsorbed at air water and fuel-water interfaces with the head and tail in water and organic or air phases respectively.

Perfluoro-octanyl based surfactants like the one displayed in Figure 2 were shown to be bio-accumulative, bio-persistent, and toxic [3] due to the extreme stability of the carbon-fluorine bonds in the tail of the chemical structure shown in Figure 2. 3M stopped manufacturing the perfluoro-octanyl surfactants in 2002. The U.S. EPA restricted manufacturing the perfluoro-

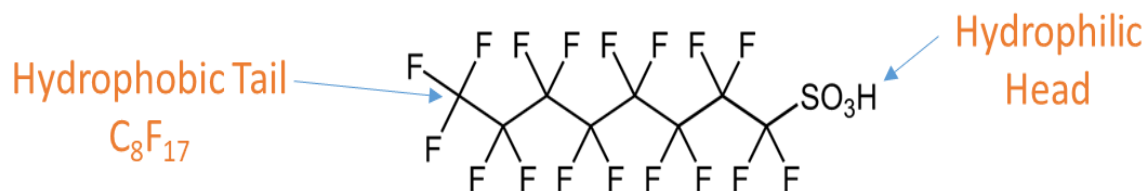


Figure 2. Chemical structure of perfluoro-octanysulfonic acid.

octanyl surfactants in 2003. EPA also conducted a voluntary stewardship program with industry to phase out the perfluoro-octanyl surfactant products by 2015. There have been media reports of contamination at military bases that resulted in litigation against the DOD and industry. Industry developed surfactants with a shorter tail polyfluoroalkyl surfactants to replace the perfluoro-octanyl using a telomere-based process. However, the long-term environmental fate and routes into the environment of the newly formulated fluorocarbon surfactants are poorly understood. Recently, U.S. Congress mandated that a fluorine-free alternative be available by October 1, 2023 and all use of perfluoro and polyfluoroalkyl substances (PFAS) be phased out by October 1 2024 from the DOD as detailed in the National Defense Authorization Act (NDAA) of 2020. Replacing the fluorocarbon surfactant with a fluorine-free surfactant in AFFF will significantly reduce its environmental impact.

Foam industry introduced fluorine-free firefighting foams that completely eliminate the fluorocarbon surfactants and PFAS from the solution and rely only on the hydrocarbon surfactants and other additives. However, existing commercial fluorine-free alternatives to AFFF are unable to meet the stringent gasoline fire extinction time and viscosity requirements listed in U.S. DOD's Mil-F-24385F [4]. The MilSpec includes 28 ft² gasoline pool fire extinction and burnback tests as the gateway test before conducting a larger (50 ft²) fire test. The MilSpec also includes limits on physical properties, such as the viscosity of 3% or 6% concentrates that are within the working limits of the proportioning systems used to generate foams. The U.S. MilSpec was developed based on small (50 ft² gasoline pool), large (1200 ft² gasoline pool), and field testing and has a proven record as a successful test for qualifying AFFFs for DOD firefighting needs over many decades. It is also one of the most stringent tests for firefighting requiring an extinction time of 30 seconds for a 28 ft² pool fire at a low solution application rate of 2 gallons per minute to ensure an adequate safety margin. The extinction time requirement is crucial for preventing weapons "cook-off" because of the presence of weapons on military sites and ships. Therefore, research and development of alternative and novel surfactants to replace the fluorocarbon surfactants in AFFF are crucial for improving the fire suppression performance to meet Mil-F-24385F requirements.

The first step in developing AFFF replacements is to understand the basic mechanisms involved in AFFF fire suppression and the role of surfactants in influencing those mechanisms. AFFF contains a number of components developed over many decades. Tuve et al. [1] developed "light water", which was made by mixing commercial agents (0.25 % L-1083 and 0.25% L-1162 of 3M Co. 1964, and 0.5 % ethylene oxide polymer by weight) with proprietary chemical composition. Tuve et al. [1, 5] demonstrated fire extinction on both bench (20 cm diameter pool) and large-scale (150 ft² pool) gasoline and jet fuel fires. It was a forerunner to a category of fire-suppression products known as AFFF formulations. Norman and Regina [6], R.A. Falk [7, 8] reduced the fluorine content of AFFF by adding hydrocarbon surfactants to "light water" in a series

of large-scale tests in 1977. The AFFF formulation developed by R.A. Falk contained six components with well-defined composition and identities of molecular structures. Thus, “light water” was developed into modern AFFF by the foam industry by adding numerous proprietary components needed for full MIL-F-24385F qualification. They included fluorocarbon and hydrocarbon surfactants, and other components: organic solvents (viscosity control, storage stabilization at subzero or elevated temperatures); polymers (precipitated barrier formation on polar/alcohol fuels); salts (surfactant shielding); chelating agents (polyvalent ions sequestering); buffers; corrosion inhibitors; and biocides [9].

AFFF suppresses fires by forming a physical barrier between the pool and fire, blocking the fuel vapor transport from the pool surface to the combustion process. The fluorocarbon surfactants play a crucial role in blocking the fuel supply to the fire. The firefighting community believes that when AFFF is applied onto a burning fuel pool, excess perfluoro-surfactant solution drains from the foam and forms a thin “aqueous film” on the burning pool surface because the surface tension of the solution is smaller than the hot fuel pool. They presume the film spreads and forms a major barrier to fuel transport, and the foam itself is a means to form the film and protect the film from the fire. However, the evidence for aqueous film formation is limited to fuel pools at ambient conditions and a limited degree to hot fuel pools.

2.1. Aqueous Film as a Fuel Vapor Barrier

The criterion for film formation is based upon the spreading coefficient given by Harkins and Feldman [10] as

$$S = \gamma_f - (\gamma_s + \gamma_i) , \quad (1)$$

where γ_f , γ_s are the surface tensions of the fuel and surfactant solution respectively, γ_i is the interfacial tension between the surfactant solution and fuel, and S is the spreading coefficient. A zero or negative value for the spreading coefficient indicates an inability to form the aqueous film. Investigators at the Naval Research Laboratory [11] demonstrated that fluorosurfactants reduce the surface tension of water far below the surface tension achieved with conventional hydrocarbon surfactants when a solvent was used to increase the solubility of fluorosurfactants in water. The spreading of the aqueous film was demonstrated on JP-4, JP-5, and gasoline fuel pool surfaces at room temperature and the film spreads due to the reduced surface tension, γ_s , in Eq. (1) [1, 5, 10]. Tuve [1, 5] demonstrated that the JP-4, JP-5, and gasoline pools (covered with the aqueous film) did not ignite when a small flame was held over the pool surface. However, Tuve [1] also showed that the aqueous film did not form on an n-heptane pool which has a smaller surface tension, γ_f , than jet fuels and gasoline, which resulted in a negative spreading coefficient for n-heptane [5].

Pabon and Copart [12], and Clark and Kleiner [13] added hydrocarbon surfactants to the fluorocarbon surfactants to decrease both the surface and interfacial tensions (γ_s , γ_i) in Eq. (1), leading to a higher value of the spreading coefficient on a heptane pool. The higher spreading coefficient for the mixture of surfactants was suggested to result in more rapid film formation relative to fluorocarbon and hydrocarbon surfactants individually [12, 13, 14]. Kissa [15] showed that a mixture of fluorocarbon and hydrocarbon surfactants reduced water surface tension more rapidly with time compared to the surfactants individually. Williams [16] measured dynamic surface tension using a bubble tensiometer with bubbles generated at varying frequencies for commercial fluorocarbon (FORAFAC 1157, DuPont Inc. DE) and hydrocarbon (Triton X100, Dow Chemical Co.) surfactants individually and in a 3:1 mixture by volume. Williams showed

that the mixture of fluoro and hydrocarbon surfactants (0.3% FORAFAC 1157, 0.1% Triton X100, 0.5% Butyl Carbitol solvent) had a significantly smaller surface tension (28 mN/m) than the individual surfactant solutions (72 mN/m for 0.3% FORAFAC 1157 and 45 mN/m for 0.1% Triton X100) at a bubble age of 30 ms. The mixture approached the equilibrium surface tension value of the fluorocarbon surfactant solution but at a faster rate. Williams also showed that the spreading coefficient for the mixture was positive (0.8 mN/m) on heptane fuel but negative for the individual surfactants (-1.0 for 0.3% FORAFAC 1157 and -15 for 0.1% Triton X100). The data indicated a lack of film formation on heptane fuel when only FORAFAC was used with the solvent. Williams's data show clearly that hydrocarbon surfactant and fuel type affect aqueous film formation at room temperature. Because commercial AFFFs contain both fluorocarbon and hydrocarbon surfactants, they have a positive spreading coefficient over heptane due to the lower interfacial tension, indicating film formation at room temperature, unlike "light water" which contained fluorocarbon surfactants only. Thus, film formation is considered necessary for rapid fire suppression, so much so that a spreading coefficient of more than 3 mN/m and a "film and seal" test are requirements for military qualification of firefighting foams [4]. To date, a significant emphasis has been placed on film formation and replacement surfactants are screened based on their film forming ability [17, 18]. However, the spreading coefficient is not an indicator of how the foam layer itself may be acting to rapidly suppress a fire. Additionally, past research by Briggs et al. [19] showed that despite a higher spreading coefficient for AFFF over toluene compared to heptane, the toluene flames were more difficult to extinguish with AFFF.

Bernett et al. [20], Moran et al. [21] and Leonard et al. [22] studied the dynamics of aqueous film formation on liquid fuel pools at room temperature by estimating average thickness of the film and measuring the fuel vapor concentration above the film in the absence of a foam and fire. They demonstrated the thinner the film floats longer on a fuel pool by placing the foam solution on an n-octane fuel pool (5 cm diameter) surface. The fuel vapor concentration above the film was measured in a closed chamber by sweeping the vapors with nitrogen flow and analyzing with gas chromatography. The vapor concentration above the film was suppressed by a maximum of 20 times relative to the vapor pressure on bare fuel pool for films greater than 10 μm thick for 10s of minutes. The concentration was suppressed by 1.7 times for a 7.1 μm thick film for several minutes. Above a critical film thickness of 10 μm , the vapor concentration was not significantly suppressed further but appears to increase the length of time the vapors are suppressed. The critical film thickness was found to increase with increased vapor pressure of the fuels from dodecane to heptane. Thicker than 47 μm films led to breaking and sinking of the films to the bottom of the pool immediately. The foam layer can also suppress the fuel vapors because the vast number of bubble lamellae in the foam can be vapor barriers as illustrated in Figure 3. Studies comparing the relative contributions of the foam and "aqueous film" as barriers to fuel transport through AFFF have been lacking.

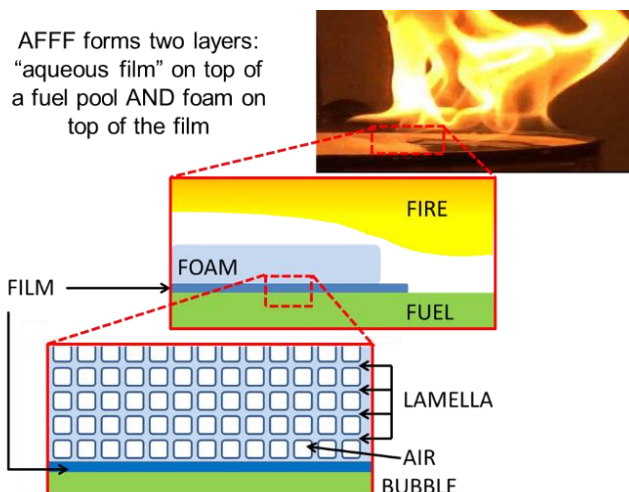


Figure 3. (Top) Fire extinction with foam on liquid heptane, (Middle) “Film” formation with AFFF, (Bottom) many lamellae in foam as fuel diffusion barriers in addition to a “film”.

2.2. Foam as a Fuel Vapor Barrier

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 [23-28]. Schaefer et al. [27, 28], relying on previous designs [23-26], 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” [27].

We designed a flux chamber and an experimental method [29] which was an improvement over previous flux chamber designs in its ability to create a uniform foam layer for studying the transient fuel transport characteristics of the foams rather than the steady state flux because foams degraded with time. Figure 4 compares the percent suppression in the concentration of fuel vapor emerging from a pool covered with only the “aqueous film” as reported by Leonard et al. [22] versus a foam-covered-pool relative to the bare fuel corresponding to 100% on the y-axis (logarithmic scale). The top part of the Figure 4 shows the data collected for the film of different thicknesses [22] and bottom part of the Figure 4 shows our data for the 4-cm thick AFFF foam with the film. It shows that the foam suppresses fuel diffusion by orders of magnitude more than the film despite higher vapor pressure of heptane versus n-octane used by Leonard et al. Figure 4 shows that the vast number of bubble lamellae in a 4-cm thick foam layer are a significant barrier for fuel vapor permeation through the foam layer compared to a single aqueous film covering the pool which could only suppress the fuel vapor pressure by a maximum of 20 times (5%).

We also quantified fuel flux for AFFF over three fuels: n-heptane, methyl-cyclohexane, and iso-octane [29]. AFFF solution was shown not to form a film on iso-octane unlike n-heptane and methyl-cyclohexane. These three fuels have similar vapor pressures, but differ in surface tension and solubility in water. Figure 5 shows the fuel flux through 4 cm thick foam layers of

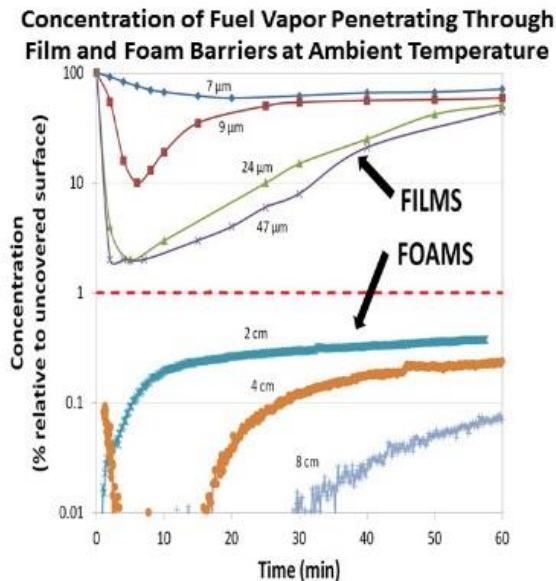


Figure 4. Fuel (% of vapor pressure) above the surface of an “aqueous film”-covered-n-octane fuel (without foam) [21, 22] and above foam-covered-n-heptane fuel, for the indicated film or foam thickness versus time. Even though the n-heptane pool has a higher vapor pressure (5.33 kPa) than the n-octane (1.47 kPa) pool, the foam exhibits orders of magnitude greater suppression compared to film only.

AFFF and RF6 (a commercial fluorine-free foam, Solberg Inc.) placed on n-heptane liquid pool at 20°C. The fuel flux is much smaller than that ($7.5 \text{ e-}8 \text{ mole/cm}^2\text{s}$) reported for an uncovered pool. When the foam layer is applied on top of the pool, the fuel concentration at the foam surface rises slowly over time and the fuel flux into the chamber also increases with time. The slow increase in fuel flux as measured by FTIR is shown in Figure 5 for AFFF and RF6 foams of the same thickness. The slow rise in fuel transport is indicative of the transport resistance of the foam.

Figure 5 shows that AFFF has a lower fuel flux than a commercial fluorine free foam (RF6, Solberg Inc.) by an order of magnitude over 2000 seconds for the same foam layer thickness over the same room temperature n-heptane fuel. The AFFF layer suppresses the fuel flux of n-heptane at the pool surface by a factor of 300 from $7.5 \text{ e-}8$ to $2.5\text{e-}10 \text{ mole/cm}^2\text{s}$ at 1500 s and the suppression is much greater during the initial 10 min. In comparison, the RF6 layer suppresses the n-heptane flux by a factor of 42 from $7.5\text{e-}8$ to $1.8\text{e-}9 \text{ mole/cm}^2\text{s}$ at 1500 s. The fuel vapor breakthrough times are 276 s and 820 s for RF6 and AFFF respectively and are indicated by the “break-through flux” in Figure 5 at a flux of $1.21\text{e-}10 \text{ mole/cm}^2\text{s}$ corresponding to 10 ppm of fuel vapor. The large difference in the measured fuel flux between AFFF and RF6 shown in Figure 5 can be due to differences in the composition of surfactant solution and in properties of the foams.

Figure 6 compares fuel flux through a 4 cm thick AFFF layer over three fuels, n-heptane, iso-octane, and methyl-cyclohexane at 20°C [29]. In Figure 6, AFFF has the smallest fuel flux over iso-octane, slightly greater for n-heptane, and largest for methyl-cyclohexane. The break-through times are greater than 1900 s for iso-octane, 820 s for n-heptane, and less than 80 s for methyl-cyclohexane. At 1500 s, fuel flux is $1\text{e-}11 \text{ mole/cm}^2\text{s}$, $2.5\text{e-}10 \text{ mole/cm}^2\text{s}$, and $2.4\text{e-}9 \text{ mole/cm}^2\text{s}$ for iso-octane, n-heptane, and methyl-cyclohexane respectively.

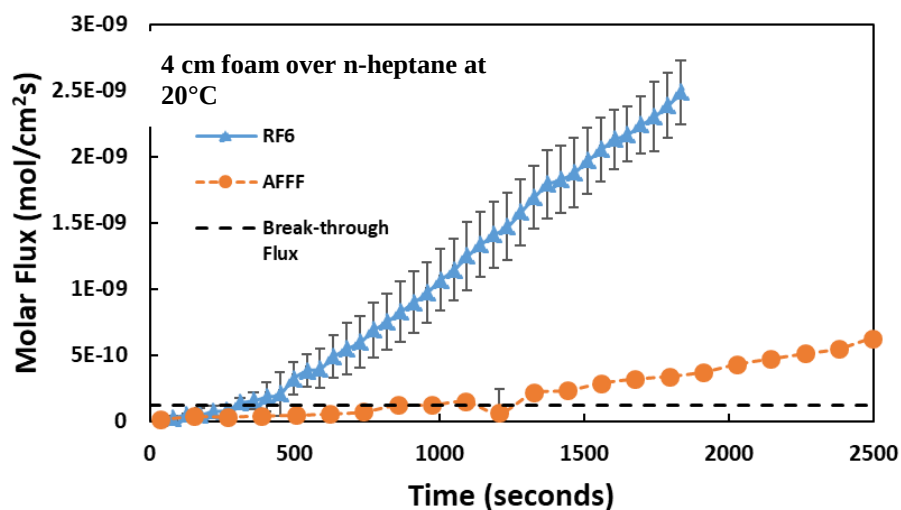


Figure 5. Measured fuel flux with time through 4 cm thick foam layer covering n-heptane pool at 20°C [29].

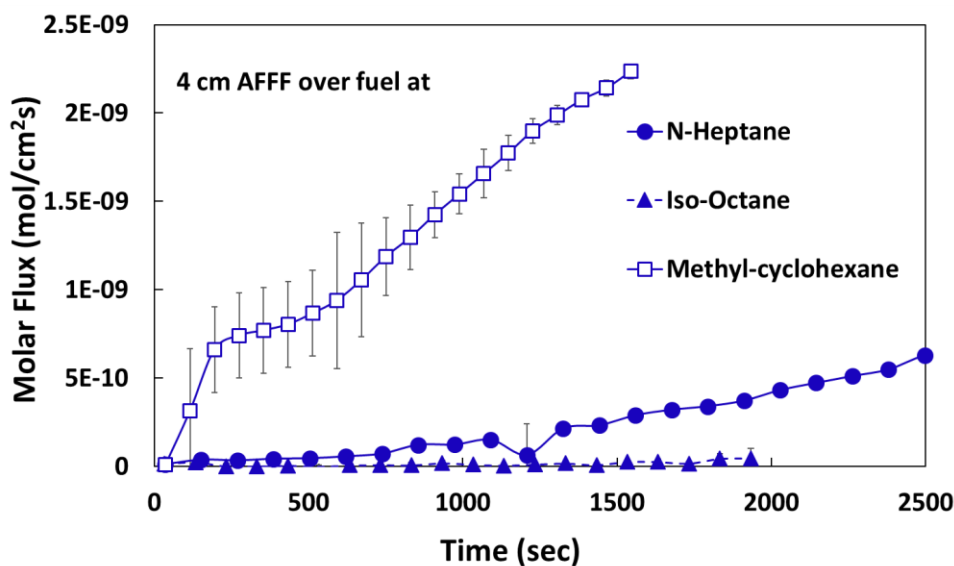


Figure 6. AFFF, 4 cm thick layer covering different fuel pools at 20°C [29].

One of the most interesting observations from the data shown in Figure 6 is that the smallest molar flux through AFFF measured for the fuel iso-octane, which is the most unyielding fuel for AFFF solution to form an “aqueous film” among the three fuels because iso-octane has the lowest surface tension of the three fuels. Moran et al. [21] showed that AFFF solution (6% FC195, 3M Co.) had either very low (0.2 dynes/cm) or negative (-1.3 dynes/cm) spreading coefficient (see Table 3 of [21]) leading to marginal or no “aqueous film” formation on an iso-octane pool. This means the aqueous solution that drains from AFFF foam cannot form a film over an iso-octane pool surface during our experiment. Despite the absence of a film barrier, Figure 6 shows that very small amounts of iso-octane vapor are transported through AFFF foam relative to n-heptane and methyl-cyclohexane, which enables film formation. In comparison to the iso-octane pool, AFFF

solution was found to form an “aqueous film” easily on a methyl-cyclohexane pool. Despite the film formation, methyl-cyclohexane pool exhibits the highest steady-state fuel flux and transient fuel flux as shown in Figure 6. Figure 6 suggests that the aqueous film may be less effective than the foam layer as a barrier to fuel vapor transport. The transient fuel transport measurements suggested a mechanism for the surfactant’s role in fuel transport through aqueous foams as shown in Figure 7 [29].

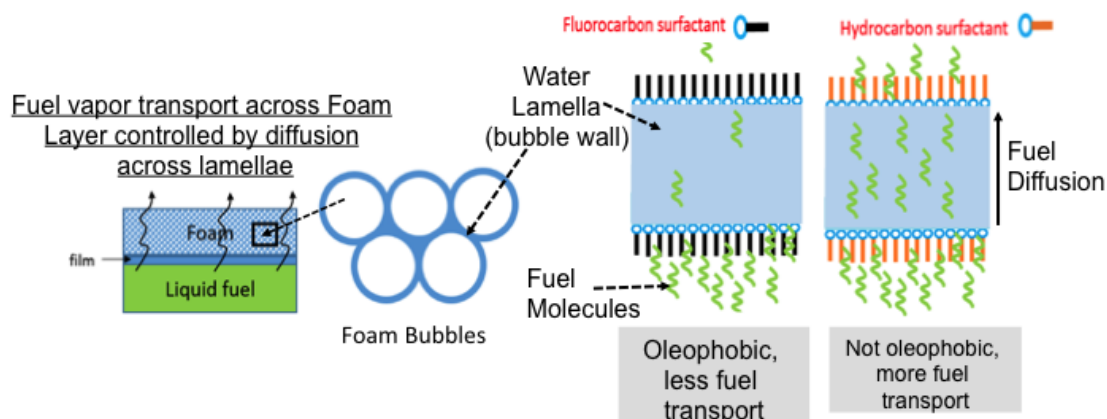


Figure 7. Fuel transport within the bubble structure and the lamellae, and the role of fluorocarbon and hydrocarbon surfactants in the transport across a lamella [29].

A 4 cm foam layer contains a myriad of aqueous lamellae and air, forming a significant barrier to fuel transport relative to a few micrometers thin, single “aqueous film”. Fuel transport through the foam layer can occur as the fuel travels through the gas phase contained in the foam bubbles, through the liquid lamella (liquid layer between two adjacent bubbles or bubble wall) surrounding the bubbles, and through the plateau borders (liquid columns formed at the junction of three adjacent bubbles) as shown in Figure 7. The vaporized fuel first dissolves into the liquid lamella. Transport through liquids is much slower than transport through gases due to differences in diffusion coefficients between gases and liquids by four orders of magnitude. Therefore, the dissolved fuel vaporizes from the lamella into a gaseous bubble in the foam. The fuel vapor then re-dissolves into another liquid lamella further up the foam layer and continues this transport until the vapor has reached the foam layer surface as depicted in Figure 7. The foam solution composition may affect fuel transport since AFFF has both fluorocarbon and hydrocarbon surfactants and commercial fluorine-free foam (RF6, Solberg Inc.) has only hydrocarbon surfactants. All surfactants adsorb at the lamella interface (bubble surface) as shown by the individual lamella diagrams in Figure 7, which only shows fluorocarbon surfactant versus hydrocarbon surfactant absorption at the lamella interface for emphasis. Fluorocarbon surfactants in AFFF are unique in having both hydrophobic and oleophobic repulsions. The surfactant repels a hydrocarbon fuel like n-heptane and suppress fuel dissolution into the liquid lamella as depicted by the lamella diagram in Figure 7. The fluorocarbon surfactant may impede the transport through the foam layer. RF6 contains hydrocarbon surfactants which are also hydrophobic, but the hydrocarbon tails do not repel the hydrocarbon fuel and are not as oleophobic as fluorocarbon surfactants. Fuel vapors can easily dissolve into the liquid lamella and move unimpeded by the hydrocarbon surfactant of RF6 through the foam layer resulting in faster transport in RF6 foam compared to AFFF as shown in Figure 7.

In addition to repulsion towards fuel, foam stability and lamella thickness are also important to reduce fuel flux through the lamellae. Surfactants can affect the thinning dynamics of lamellae and thereby affect foam degradation directly. We discovered that fuel vapors can accelerate the degradation of foam by rupturing bubble lamellae promoting bubble coalescence [30]. Experiments were conducted to quantify foam degradation when placed on top of a hot liquid fuel surface. We quantified foam degradation by measuring the foam layer thickness over time. We did not consider changes in the “quality” of the foam as indicated by its translucency or density. Liquid drainage from the foam can change the foam’s density. When the foam was exposed to fuel, we observed the formation of a large bubble near the foam-fuel interface similar to that reported by Osei-Bonsu et al. [31, 32]. In our experiments, foam is exposed to the fuel at the fuel-foam interface and the large bubble grows to cover the entire fuel surface in the container forming a “gap”. A single large bubble or “gap” separates the entire foam layer from the fuel surface in the container. We measured both the size of the “gap” and the total foam layer thickness inclusive of the “gap” volume for the circumstances in which a gap formed. Furthermore, in some cases, the foams expand and become translucent; we reported the increase in foam layer thickness as foam expansion rather than degradation.

Figure 8 shows time-lapse images from AFFF and RF6 placed on a hot *n*-heptane at 50°C. About 30-40 mL of foam initially at room temperature is placed over 60 mL of hot (preheated) liquid fuel or water in a 150 mL glass beaker (5.5 cm diameter and 8 cm height). The liquid temperature was maintained to be constant during the experiment by placing the lower part of the beaker (up to the 60 mL mark) in a heated water bath equipped with a thermostat which was set at the desired temperature during the experiment. A clamp used for handling can be seen at the top of the beaker in Figure 8. As time continues, the foam thickness changes. Figure 8 shows that AFFF lasts significantly longer than the commercial fluorine-free foam (Solberg Inc. RF6) as indicated by the average foam height in the beaker. When hot fuel is replaced by hot water, no change in foam height was observed for both the foams in the same period of 4.5 minutes.

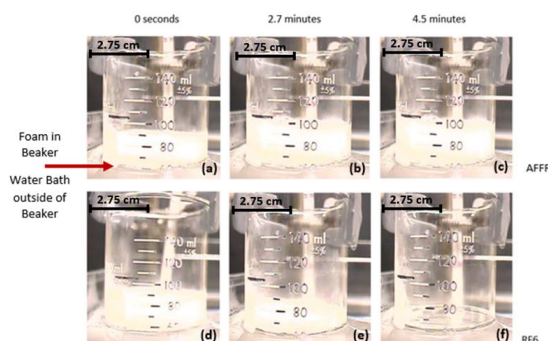


Figure 8. Images taken during experiments with AFFF (a-c) and RF6 (d-f) foam floating on liquid *n*-heptane at an elevated temperature (50°C). Red line indicates the level of the water bath outside of the beaker in (a) to (f). Fuel is inside the beaker at the same height as the water level outside of the beaker. Initial foam layer thickness was 1.8-2 cm above the fuel layer [30].

Figure 9 and 10 are time-lapse images of the interface between the foams over *n*-heptane (Fig. 9(a-d) and Fig. 10(a-c)) and water (Fig. 9(e-g) and Fig. 10(d-f)) at 50°C for AFFF and RF6 foam respectively. At higher temperatures, the vapor pressure of the fuels increase and a greater amount of fuel vapor escapes from the liquid fuel surface. At higher temperatures, the rate of bubble growth occurs much more rapidly than at room temperature.

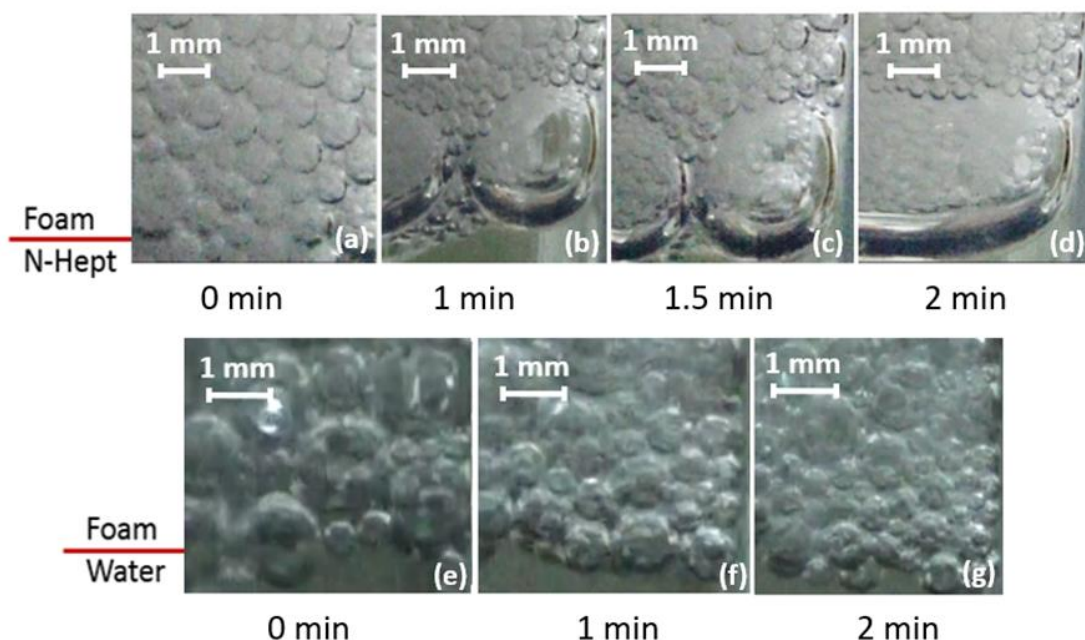


Figure 9. Interfacial images of AFFF foam over *n*-heptane (a-d) and water (e-g) at 50°C; interface position between the liquid and foam is shown by a red line on the left of the images [30].

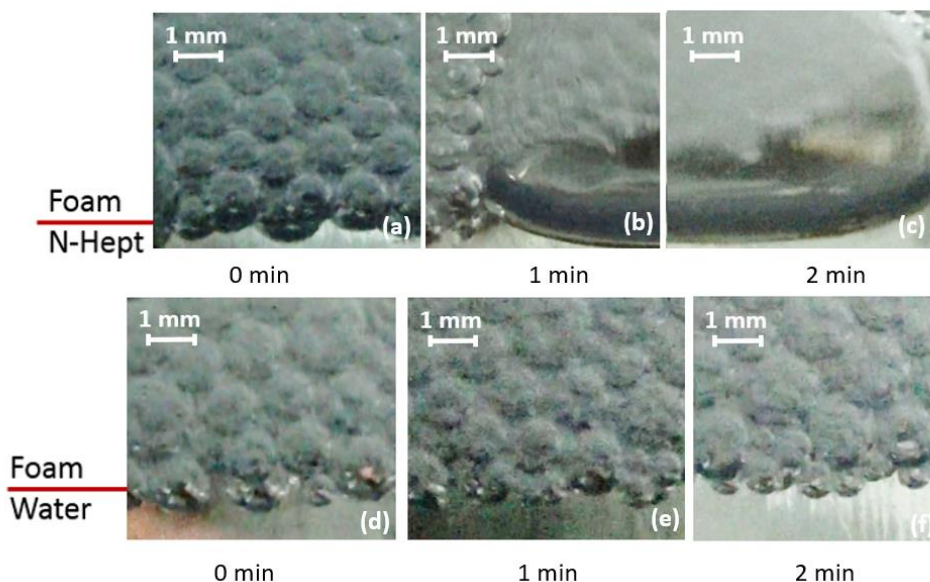


Figure 10. Interfacial images of RF6 foam over *n*-heptane (a-c) and water (d-f) at 50°C; interface position between the liquid and foam is shown by a red line on the left of the images [30].

Focusing closely on bubbles adjacent to the foam-fuel interface, videos showed that all bubbles at the interface, large and small, grew but at different rates. Slightly away from the interface the bubbles remained unaffected during the same time period. The videos showed that at some point during the growth, the lamella separating adjacent bubbles ruptured and bubbles coalesced. This process was more rapid in RF6 foam compared to AFFF foam. This is how degradation is initiated at the interface. This cannot be seen in Figures 9(b) and 10(b) because the

growth and coalescence had already taken place adjacent to the interface and other smaller bubbles away from the interface migrated to the interface. Even as the temperature increased, Figures 9 and 10 show that there is no drastic change in bubble diameter when the foams are placed over hot water. In the images of foam placed over hot water, the bubbles at the interface appear to be getting smaller. Because the rapid bubble growth observed for foams placed over *n*-heptane was not observed with hot water, the video observations of bubble growth and the increased rate of foam degradation must be induced by *n*-heptane.

When an aqueous foam is applied on to a burning pool, the hot (at its boiling point) pool surface can be cooled instantly by direct contact with the foam, which is near room temperature. The foam layer absorbs heat from the pool. The decrease in surface temperature can lead to a significant decrease in fuel vapor pressure, which depends exponentially on the temperature. To measure this cooling, we performed experiments using a 19-cm diameter heptane pool with thermocouples distributed at different depths from the pool surface and at different radial positions. The pool was ignited and burned for 60 seconds before the fire was extinguished by placing a metal plate on top [33]. Within 15 seconds after the fire extinction, a foam layer of 2 cm thickness was placed on to the hot pool using a springform pan with removable bottom. The filling of the springform cylindrical container was strategically timed such that it was completed just before the end of the 60 seconds preburn. The measured temperature at the center of the pool and at different depths into the pool versus time are shown in Figure 11. The first figure shows that the measured pool temperature at 1 mm below the surface drops from 85 °C to 60 °C within a few seconds after the foam is applied at time=0, and continues to decrease relatively slowly.

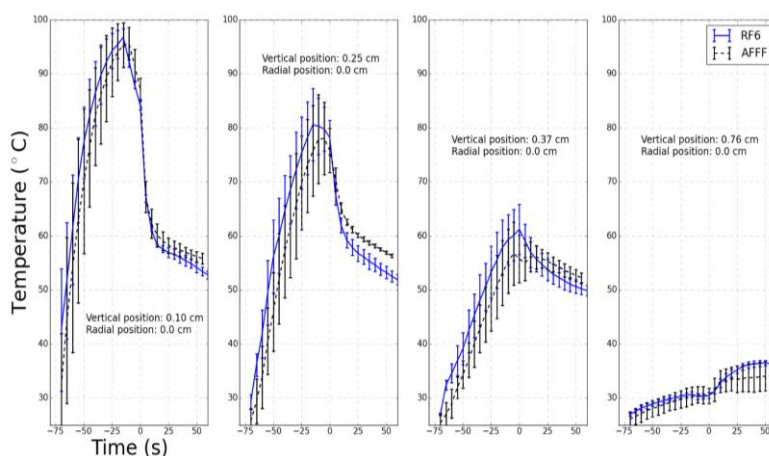


Figure 11. Comparison of measured pool temperatures versus time for different foams: RF6 and AFFF. Temperature measurements with thermocouples placed at different depths in the fuel at the radial center of the pool. Foam is applied at time=0 following a 60 seconds preburn and fire extinction by placing a metal plate on the burning pool [33].

2.3. Bench Scale Evaluation of Fire Extinction

We developed a 19-cm diameter bench-scale pool fire suppression apparatus to measure time to cover the pool surface by foam and fire extinction time for a heptane pool [34]. It includes a sparging method for foam generation, where air is bubbled through a porous disk immersed at a fixed height in surfactant solution. The foam was applied to the center of a burning pool at a constant volumetric flow rate after a 60 second preburn. Both coverage and extinction times were

measured as functions of foam flow rate as shown in Figure 12. Figure 12 shows extinction time decreases as the foam flow rate is increases for commercial AFFF and a fluorine-free foam RF6 (Solberg Inc.) for a heptane fire collected in our laboratory. MilSpec application rates of 2 gallons per minute of liquid flow corresponds to $2.9 \text{ kg/m}^2/\text{min}$ in Figure 12. It corresponds to 660 mL/min foam flow rate and 82 mL/min liquid flow rate (assuming 8 mL foam contains 1 mL solution, expansion ratio of 8) for the 19-cm bench scale apparatus. For comparison, Figure 12 also shows the data reported for a recently developed siloxane foam collected by Professor Dirk Blunk, University of Cologne, Cologne, Germany for a jet fuel fire. The fluorine-free foams perform poorly with fire extinction times greater than 35 seconds at the highest foam flow rate of 2400 mL/min relative to the 8 to 10 seconds for the fluorinated AFFF because of the differences in foam degradation and fuel transport rates rather than the aqueous film formation discussed above.

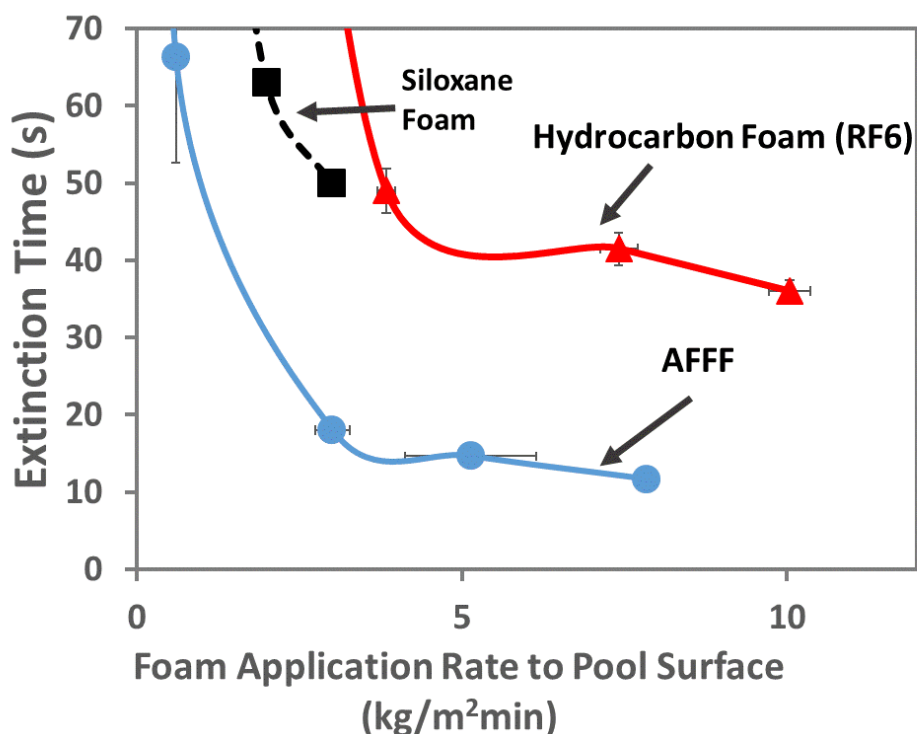


Figure 12. 19-cm diameter heptane pool fire extinction at different foam application rates at the center of the pool with fluorinated and fluorine-free foams [34].

2.4. Drop-in Fluorine-free Replacements

Drop-in replacements for AFFF can be developed with alternate fluorine-free surfactants. The above discussed findings open a new parametric space (lamella thickness, lamella rupture in the presence of fuel, fuel diffusion rate through lamella, lamella number density in foam) that provide multiple avenues to develop new fluorine-free surfactant formulations for a *drop-in* replacement for AFFF. Novel surfactants can influence the foam dynamics in a focused and new ways to bring about needed improvements in fire extinction for heptane and gasoline fuels. The commercial fluorine-free foam, RF6, was developed using alkyl polyglycoside surfactants with a viscous additive (xanthan gum) to reduce liquid drainage from the foam to improve foam stability. We found that the RF6 flame extinction time was much longer compared to AFFF because of higher fuel flux and foam degradation rate. Despite reduced liquid drainage using the thickeners,

degradation of RF6 was high. The high degradation can significantly enhance fuel diffusion and slow the foam spread on the pool surface especially at low foam application rates. Also, the lamellae in the AFFF foam appear to be more fuel resistant than the lamellae inside RF6 foam as indicated by the measured fuel transport and degradation rates. These offer clues to a more fundamental approaches to vary surfactant structure by synthesis and influence foam-fuel interactions depicted in Figure 7 to decrease the fire extinction time.

Although we quantify differences in foam mechanisms between fluorinated and fluorine-free foams, the role of surfactants in fire extinction remains unclear. How do fluorosurfactants and hydrocarbon surfactants in AFFF influence foam dynamics, aqueous film formation, and fire suppression? We aim to define how surfactant structure and properties effect firefighting foam performance.

3. Approach

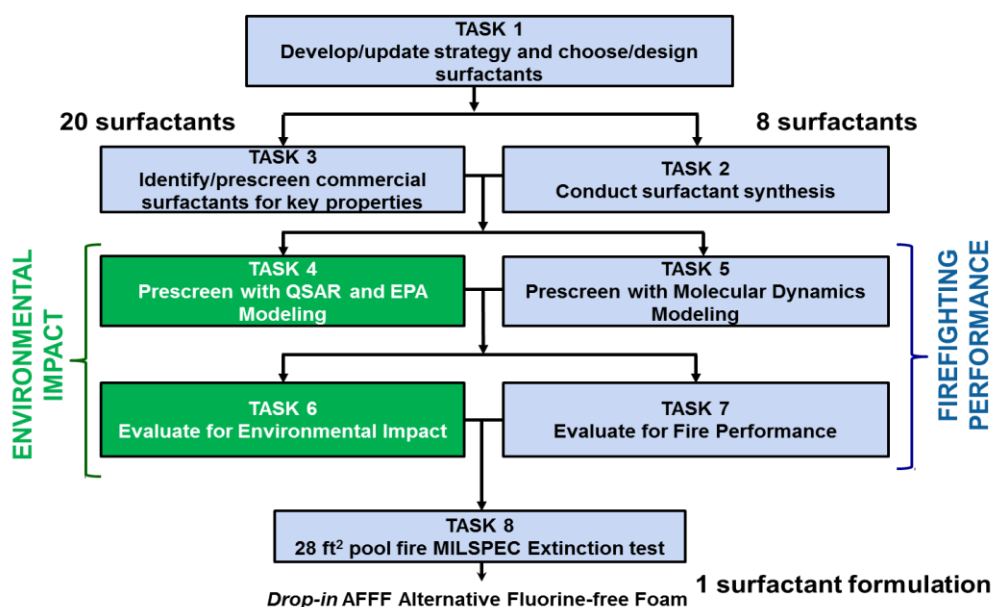


Figure 13. Technical approach and tasks.

Figure 13 shows an overview of the technical approach we used to arrive at the final choice of surfactant for the fluorine-free alternative foam. This overview is followed by a detailed description of individual steps in the approach shown in Figure 13. In the first year, we used the insights and chemical intuition gained in our previous research described in the background (Section 2.3.1) to choose surfactant molecules based on a hydrophobic and oleophobic balance, as indicated by the first box at the top of Figure 13. We used a combination of literature evaluations and predictive models (such as EPA’s EPIWIN models) to estimate the environmental fate of the molecules and to choose the surfactants to eliminate “show-stoppers”. We used dual lines of commercial sources and chemical synthesis to obtain candidate surfactants. We began with more than 20 commercial surfactants and 8 surfactants for chemical synthesis. We pursued parallel efforts to quantify firefighting performance and assess environmental/health impact as shown on the right and left sides of Figure 13 respectively over the entire program. In the first tier of prescreening, we utilized molecular dynamics simulations, and measurements of surfactant

solution properties to down-select surfactants. The second tier of prescreening in the first and second years of the program included measurement of short-term biodegradability and single lamella measurements along with modeling to down-select surfactants. In the latter half of the first year, we began the surfactant evaluation process. The first tier of evaluation was based on the measurements of the short-term acute toxicity using algae, invertebrates, and fish and on the measurements of foam dynamics including fuel transport through the foam, foam degradation, and foam spread. The second tier of evaluation beginning in the second year included the measurements of chronic toxicity using algae, invertebrates, and fish, and biodegradability, along with measurements of fire extinction dynamics. The two-tier evaluation lead to final surfactant formulations in the last year of the program. The formulations' compositions were optimized at bench-scale prior to large scale MILSPEC testing. We used NRL's custom-made foam formulation that passed both MILSPEC fire extinction and burn-back tests, and fuels (n-heptane, methyl-cyclohexane, and when safe, gasoline) to quantify the development of fluorine-free alternative surfactants.

Use of computer models was made throughout the first three years of the program for different purposes. These models were developed and validated in a separate NRL's new start program. The models were used in this proposed SERDP program to determine initial choice of surfactants, to prescreen surfactants, and to add/eliminate/modify the candidate surfactant list. This SERDP proposal also provided additional validation data for the models. The surfactant list was modified and narrowed based on newly gained knowledge from modeling and experimental data in terms of understanding the reasons for failure or success of a surfactant formulation. Therefore, there were feedback loops from the bottom boxes in Figure 13 to the top boxes in Figure 13 to modify the initial choice of surfactants and synthesis of surfactants, and during prescreening and evaluation experiments at bench-scale.

4. Materials and Methods

Our first step is to develop a simple, well-defined, three component (two surfactants and a solvent) custom AFFF formulation with known molecular structures, and show its gasoline fire suppression matches that of a commercial AFFF. This is crucial because the compositions of commercial AFFFs are proprietary and subject to continuous changes. Known as the Reference AFFF, the fluorocarbon surfactant can be replaced with an alternative and the alternative's properties and performance can be evaluated against the fluorocarbon surfactant. This enabled us to empirically formulate cause-effect relationships which are used as the basis for changes due to the molecular structure of the alternative surfactants for improved performance.

A broad spectrum of commercially available siloxane and hydrocarbon surfactants are evaluated using bench scale methods as alternatives that are not necessarily designed for firefighting. Using bench scale methods, the surfactants are ranked and promising candidates are identified for large scale fire extinction testing.

Novel surfactants are designed based on chemical intuition for increased oleophobicity and by performing molecular dynamics (MD) simulations to predict monolayer structures for surfactants at heptane-water and water-air interfaces. The novel surfactants are synthesized by chemical reactions at 10 grams scale using routes that are well established for hydrocarbon surfactants but are established only to a very limited degree for the siloxane surfactants.

Characterizations of the synthesized chemical structures are performed using NMR and LC/MS methods.

A number of bench-scale experiments are used. A single lamella is formed with the surfactant solution and its dynamics of rupture was studied; lamella is a representation of a bubble wall. Solution and foam properties, foam degradation, fuel transport through a foam layer, foam spread, and fire extinction are measured at bench scale to evaluate the surfactants. The surfactants are evaluated for heptane, jet fuel (JP-5), and gasoline fire suppression. Bench scale experiments have two purposes; (1) to screen and rank fluorine-free surfactants and the top-ranked surfactants are then subjected to large scale testing, (2) to guide the design of new surfactant molecular structures by varying the experimental parameters under well controlled conditions to establish cause-and-effect relationships. Because, the bench scale tests use tens of grams of surfactant to vary a parameter (e.g., vary foam application rates by a factor of 20, three fuels, many surfactant compositions) rather than 100s of grams needed for a single large scale test, they are the most appropriate tool to understand the effects of surfactants on foam dynamics and fire suppression unlike the large scale tests. The bench scale experiments are the only convenient choice for synthesized surfactants that are available only in small quantities. The bench-scale experiments also allow for more detailed measurements unlike the large scale tests. But, the bench scale experiments are not a replacement for the large scale tests. Therefore, we also conducted large scale, 28 ft² heptane and gasoline pool fire extinction and burnback tests at varied foam application rates to a very limited degree (2, 3, 4 gpm of solution flow).

We have been collaborating with Dow Silicones Co., Midland, MI on synthesizing and developing novel siloxane structures for firefighting. This started as a request for free samples and contacting one of their chemist for a recommendation on their products. This led to their commercial silicone DOWSIL 502W surfactant, which we identified as promising for fire suppression. After the performance evaluations, discussions began and we received another set of samples of their products. This is a new application for them and they had to be convinced by their market research before jumping into this area for research and development. Their present commercial silicone DOWSIL 502W surfactant which we identified as promising for fire suppression was designed as an intermediate in polyurethane foam synthesis. To make them effective for fire suppression, they are synthesizing new variations of silicone molecular structure to suppress surfactant extraction by gasoline, and down selecting samples by using NRL developed bench-scale methods. We have been evaluating the Dow samples by quantifying foam degradation, fuel transport, foam spread, and fire extinction at bench-scale.

4.1. Choose/Design Surfactants (Task 1)

Surfactant design is guided by physicochemical interactions between the surfactant molecules and the fuel as shown in Figure 14. Fuel molecules such as alkanes interact through weak induced dipoles with other similar molecules based on the principle of “likes dissolve likes”. The strategy is to design surfactants such that they interact by strongly induced dipoles and permanent dipoles so that they have less attraction to alkanes by creating surfactants that are different from the alkanes.

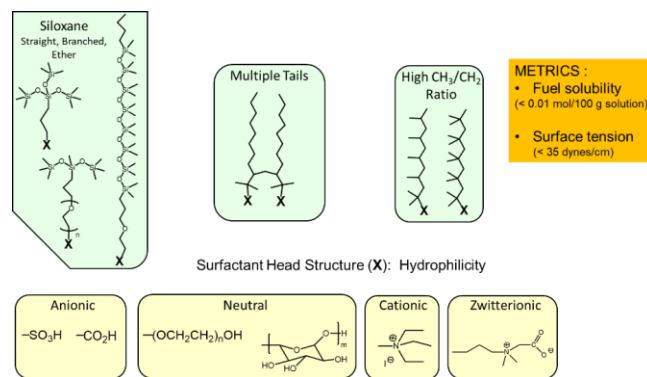


Figure 14. Candidate surfactants to suppress fuel transport through foam.

Perfluorosurfactant tails are unique because they are both oleophobic and hydrophobic because fluorine is least polarizable. To mimic this feature of a fluorosurfactant, we attempt to reduce the molecular interactions between surfactants and fuels. Figure 14 shows chemical structures of tails on top and head at the bottom of the figure. Siloxane tails have Si-O bonds with permanent dipoles in linear and branched configurations. Another feature is to take advantage of differences in the degree of polarizabilities. Methyl groups are 25% more polarizable than methylene groups. The dipole moment of dimethyl siloxane is in between that of water and heptane so that it does not like either of them. The branched siloxane packs more methyl groups in a smaller area than the linear siloxane and increases the difference with heptane fuel. It also includes oxyethylene groups to further incorporate dipoles into the tail. The hydrocarbon surfactants shown in Figure 14 use steric crowding of multiple tails that prevent the double tailed hydrocarbon surfactant from interacting with an alkane. Similarly, we vary CH₂/CH₃ ratio of the pendant groups of a hydrocarbon surfactant tail to vary polarizability and reduce interactions with alkanes. As the tail's oleophobicity is varied, its hydrophobicity varies as well. Ideally the hydrophilicity of head and hydrophobicity of the tail should be in balance to provide optimum amphiphilicity needed for a surfactant to create foam. The head groups at the bottom allow us to vary amphiphilicity of the surfactants so that it is optimally placed at air-water and heptane-water interfaces. The surfactant structure in Figure 14 are only a starting point, the data obtained from them will guide the design of the next set of molecules.

4.2. Identify/Prescreen Commercial Surfactants (Task 3)

Many commercial surfactants are available and are categorized as hydrocarbon, siloxane, non-ionic, anionic, cationic, and zwitterionic. The first level properties are surface tension and critical micelle concentration (CMC) that are important for foam generation, a prerequisite for fire suppression. We prioritized surfactants with surface tension below 35 mN/m and CMC values less than 0.1 weight%. These are used individually and as part of Reference AFFF formulation replacing the fluorocarbon surfactant.

4.3. Modeling Interface Structure with Molecular Dynamics (MD) (Task 5)

We leveraged molecular dynamics models developed in in-house funded program (6.2 NRL/ONR). The details of the model are described in NRL memorandum report [35,36]. In that program, simulations are performed to study the effect of structure of surfactants on the surfactant monolayer properties at the air/water and heptane/water interfaces. The model for well-established hydrocarbon surfactant molecules is validated by experimental data [35].

The MD simulations [35,36] are performed on air-water and heptane-water interface systems with and without a surfactant, some of which are shown in Figure 15. A specified constant number of molecules, volume, and temperature (NVT^1) ensemble was applied for the air-involved systems, such as air/water and air/surfactant-monolayer/water interfaces (Figure 15b). Simulations with NVT ensemble predict positions and velocities of atoms, and pressure with time which are used to calculate surface tension and then Gibbs elasticity. A specified constant number of atoms, pressure, and temperature (NPT^2) ensemble was applied for the systems not involving air, such as

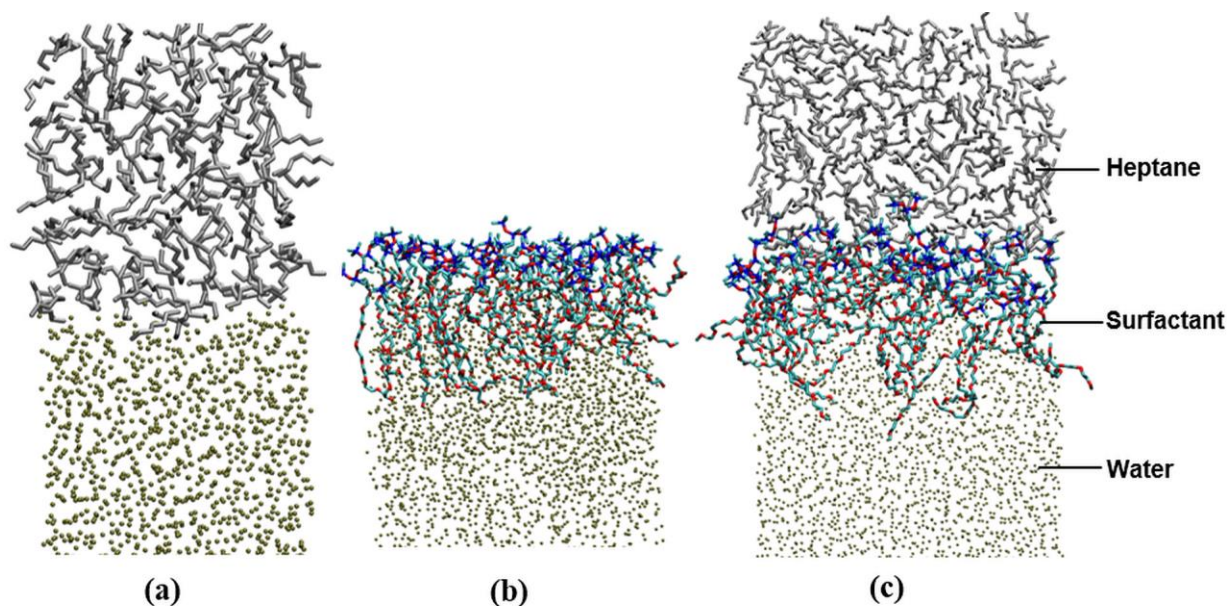


Figure 15. (a) The heptane/water, (b) siloxane surfactant-monolayer/water, and (c) heptane/siloxane surfactant-monolayer/water systems at the end of the MD simulations. Water is shown as tan spheres, heptane as silver lines. Siloxane surfactant L77, C, O, Si atoms are shown in cyan, red, and blue, respectively. Only the top half in the z direction of the simulation setup are shown, the bottom half is a mirror image of top [35].

water, heptane, heptane/water and heptane/surfactant-monolayer/water interfaces (Figure 15a and 15c). Simulations with NPT ensemble predict positions and velocities of atoms and volume with time which are used to calculate the densities of the pure water and heptane liquid, and also the interfacial properties related to surfactant packing such as area per molecule, component density, and interfacial thicknesses.

4.4. Synthesis of Homologous Nonionic Siloxane Surfactants (Task 2)

The initial choice of surfactants for synthesis are continuously informed and refined by using computational models, experimental data on performance, and synthetic accessibility throughout the program. We synthesize selected silicone surfactant structures (Si-O chain) that increase the quantity and density of methyl groups attached to Si. These compounds are not commercially available, but reagents and adaptable literature procedures from other siloxane

¹ NVT : constant number of atoms, volume, and temperature

² NPT : constant number of atoms, pressure, and temperature

molecules are available. For the head group and the connecting linkage between the hydrophilic head group and the silicone tail structure, the reagents are readily available and routinely used in the literature to accommodate using a short trimethylene (-CH₂CH₂CH₂-) chain as a connecting linkage. Figure 16 shows an example synthesis steps to attach commercially available tail and head to make a surfactant. For small molecules with oxyethylene unit of 1 or 2, distillation can be performed to purify the surfactant product. But for longer molecules, it becomes difficult to purify surfactants by solvent extraction methods because surfactants tend to dissolve in almost every solvent to some degree. So, we focus on finding reaction routes with high yield which often means one or two step synthesis as indicated in Figure 16. We follow the extent of reaction by intermittently analyzing small samples using ¹H NMR. It is important to ensure the trisiloxane tail is intact at the end of each step. Reaction is conducted initially at an mg scale and then at a 10 g scale. The products are structurally characterized using ¹H NMR, ¹³C NMR, and ²⁹Si-NMR as well as transmission IR, and LC/MS methods.

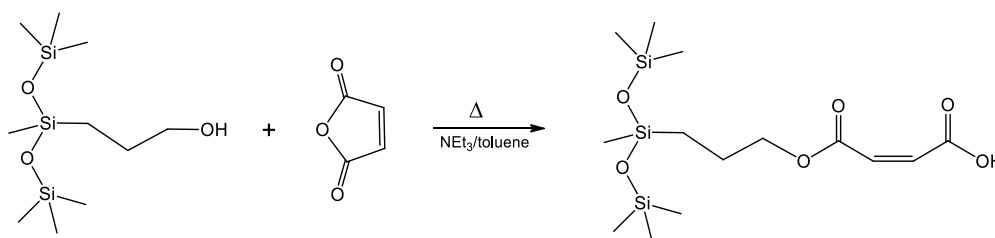


Figure 16. Synthesis routes involving one or two steps for forming a novel siloxane surfactant from commercially available reagents as an example.

4.5. Bench Scale Evaluations

We performed several bench scale measurements to evaluate both commercial and synthesized surfactant properties and performance.

4.5.1. Materials Used (Task 7)

The components of the RefAFFF formulation are: Glucopon[®] 215 CS UP (an alkyl polyglycoside concentrate contributed by BASF Corporation, Ludwigshafen, Germany and referred to as “Gluc215” [37]; Capstone[™] 1157 (fluorotelomer sulfonamide alkylbetaine concentrate contributed by Chemours Inc., Wilmington, DE and referred to as “Cap”) [37]; Butyl Carbitol[™] (Dow Chemical Co., Midland, MI purchased as diethyleneglycol butylether, “DGBE”, from Sigma Aldrich, St. Louis, MO) [37]. The component chemical structures are depicted in Figure 17.

The Siloxane-Gluc215 formulation was prepared by replacing Cap in RefAFFF with Dow Corning[®] 502W Additive 502W Additive, which is a silicone polyether copolymer, a 100% by weight concentrate contributed by Dow Corning Co., Midland, MI density 0.97 g cm⁻³ [38]. The Siloxane-Gluc225 and Siloxane-Gluc600 formulations were prepared by replacing the BASF Glucopon[®] 215 CS UP with Glucopon[®] 225DK (an alkyl polyglycoside, a 68-72% by weight concentrate in water, contributed by BASF Corporation and referred to as “Gluc225” in this report, density 1.13 g cm⁻³ [39]) and with Glucopon[®] 600 CS UP [39] (50 to 53 % by weight concentrate) in the Siloxane-Gluc215 formulation respectively. The resulting solutions were used for generating foams for fire suppression as well as for foam and solution properties’ measurements.

U.S. MilSpec compliant commercial AFFF formulations are typically sold as 3% or 6% concentrates, such that the final formulation used for generating the foam should contain 3% or 6% of the concentrates in water respectively. We received 3% concentrates provided by Buckeye Fire Equipment Company, Kings Mountain, NC (BFC-3MS, Lot# 120050, 2003) [40] and by Dafo Fomtec AB, Tyreso, Sweden (FOMTEC AFFF 3% M USA, Batch # US-16-07-07, August 4, 2016) [41] and used them as received for the analytical characterization described by Hinnant et al [37]. The Buckeye and Fomtec concentrates were diluted with water at 3% by volume for generating the foams for fire suppression.

The chemical structures of the siloxane surfactant contained in 502W [37], Capstone™ 1157 [37], Glucopon 215 CS UP [39], Glucopon 225 DK [38], Glucopon 600 CS UP [39], and DGBE [37] are depicted in Figure 17. The exact chemical structures of these commercial surfactants are proprietary, but the general features and chemical family are given in published and vendor supplied literature [37, 38]. The details of the chemical structures of Capstone, Glucopon 215 CS UP, and DGBE were confirmed by analytical characterization described in the supporting material provided in the reference [37].

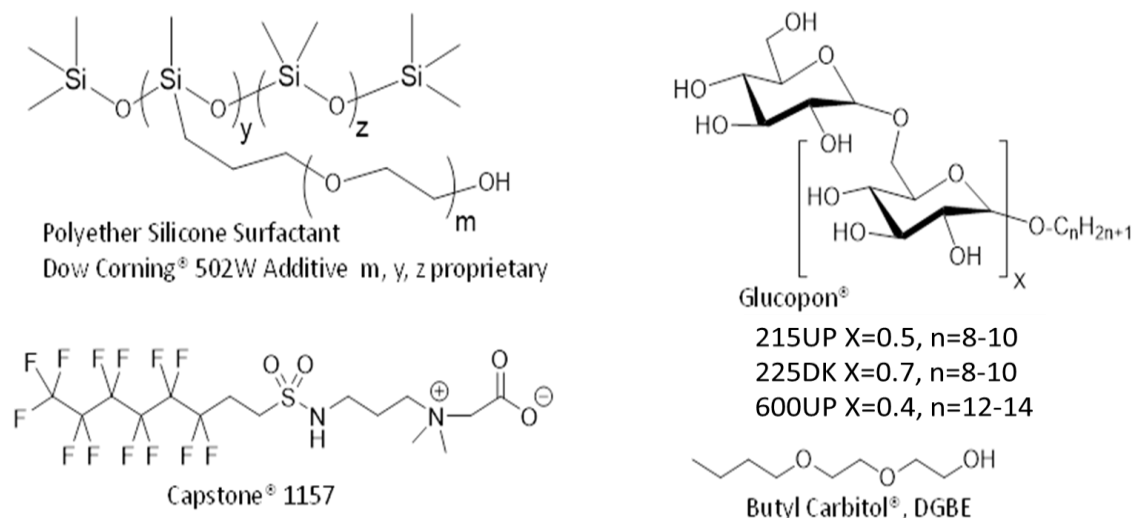


Figure 17. Structures of surfactant components in Siloxane-Glucopon [37-39] and RefAFFF [37] formulations.

The siloxane surfactant in 502W has general structure of siloxane-polyoxyethylene at 100% concentration as shown in Figure 17 [38]. The siloxane surfactant has a hydroxyl functional group (R-OH) and a distribution of polyoxyethylene (OCH₂CH₂) chain lengths represented by the parameters m and y respectively. The distributions and the average values of m , y , and z are proprietary according to Dow Corning Co.'s literature [38]. Glucopon® 600 CS UP, Glucopon® 215 CS UP, and Glucopon® 225 DK are alkyl polyglycoside surfactant products of BASF in concentrate form. All three Glucopons have a distribution in both the number of glycoside structural units and in the number of methylene units in the alkyl tail structure as represented in Figure 17, but differ only in the average number of glycoside units of the head group according to BASF literature [39]. Glucopon® 600 CS UP, Glucopon® 215 CS UP, and Glucopon® 225 DK have $x=0.4$, 0.5 , and 0.7 respectively and have $n=8$ to 10 except Glucopon® 600 CS UP, which has

n=12 to 14. Increased glycoside head size increases the number of OH functional groups on the hydrophilic head. The hydrocarbon surfactant's structures shown in Figure 17 are poly-D-glucopyranose with octyl and decyl alkyl chains [39]. Butyl Carbitol™ is a Dow product available in a relatively pure form of diethylene glycol butyl ether (DGBE) with a molecular weight of 162.2 g mole⁻¹ [37]. DGBE has a relatively long history as a component in AFFF formulations [6-9] being a good solvent for fluorocarbon surfactants, hydrocarbon surfactants and water. Capstone™ 1157, also known by its earlier tradename Forafac® 1157 [9], is a Chemours/DuPont product. The fluorosurfactant's structure shown in Figure 17 is tridecafluorooctyl sulfonamide alkylbetaine. Comparative analytical data of the Capstone™ 1157, Buckeye 3% and the Ref AFFF formulations are displayed in the supporting material provided in Reference [37].

4.5.2. Measuring Solution Properties (Task 7)

Dynamic surface tension [42] is measured using a bubble pressure tensiometer (Model BP2, KRUSS, Hamburg, Germany) as a function of the bubble's age (frequency⁻¹, 10 ms to 10000 ms). The tensiometer generates bubbles at a capillary tube lip (0.22 mm diameter) continuously at a specified frequency by pushing nitrogen through the capillary immersed in a surfactant solution. Surfactant diffuses from the solution to the bubble surface, where it gets absorbed and suppresses the surface tension. Pressure inside the bubble increases and reaches a maximum when the bubble diameter is equal to the capillary tube diameter before the bubble detaches from the capillary. Surface tension is calculated from the measured maximum pressure using Young's equation. Critical micelle concentrations (CMC) and static surface tensions for the Siloxane-Gluc600, Siloxane-Gluc215 and Siloxane-Gluc225 were measured using a ring (radius 9.58 mm, wire radius 0.185 mm) tensiometer at 20°C (Du Nouy Model Sigma 701, Biolin Scientific Inc., Gothenburg, Sweden). Surface tension was measured at different concentrations of the total surfactant. CMC values were determined from the log plot of surface tension against weight % of the sum of 502W and Gluc surfactant concentrates supplied by the manufacturers. Interfacial tensions were measured with the ring tensiometer between heptane and the siloxane formulations at 20°C. The viscosity was measured at 20°C using a Cannon™-Fenske viscometer (Fisher Model 50 13616B, capillary size #50).

4.5.3. Measuring Single Lamella Stability (Task 7)

We leveraged the single lamella apparatus developed under in-house program (6.2 NRL/ONR). The details are described in NRL memorandum report [43]. In that program, an experiment was designed to study individual solution lamella, measuring the thickness of a thin lamella, suspended on a horizontal ring, using interferometry with a Filmetrics® LS-DT2 light source and software. The setup has since been altered and a sketch and an image of the new setup is seen in Figure 18. A glass cross was designed to suspend a lamella at one end, with UV-light directed vertically down onto the lamella from the top, and an IR light source directed horizontally above the film. The glass cross was an improvement over the old system using a suspended ring. We found that unless a wire ring was level and flat, film lifetimes would only be a few seconds long due to instabilities of the ring. A mechanical stage was used to raise a 30 mL beaker containing the surfactant solution, submerging the open end of the cross. The stage was then used to remove the beaker, leaving a film suspended on the glass. Film thickness data collection began when the ring was submerged and stopped when the film ruptured. Data at each time was fit using the refractive index, an appropriate wavelength range, an initial thickness estimate, and confidence interval (part of the interferometer internal software). The confidence interval was generally set to

95% to ensure the initial parameters could be used over multiple time steps as the lamella thinned. The initial thickness was taken as the first data point that showed interference patterns, within 1 second of film generation. Thicknesses with time plots were also collected to compare differences between the surfactant solutions. Lamella thickness tests were repeated 3-4 times to improve precision. Lifetime measurements were recorded from the time when the film completely separated from the liquid in the beaker until film rupture. Lamella lifetimes were taken using a stopwatch.

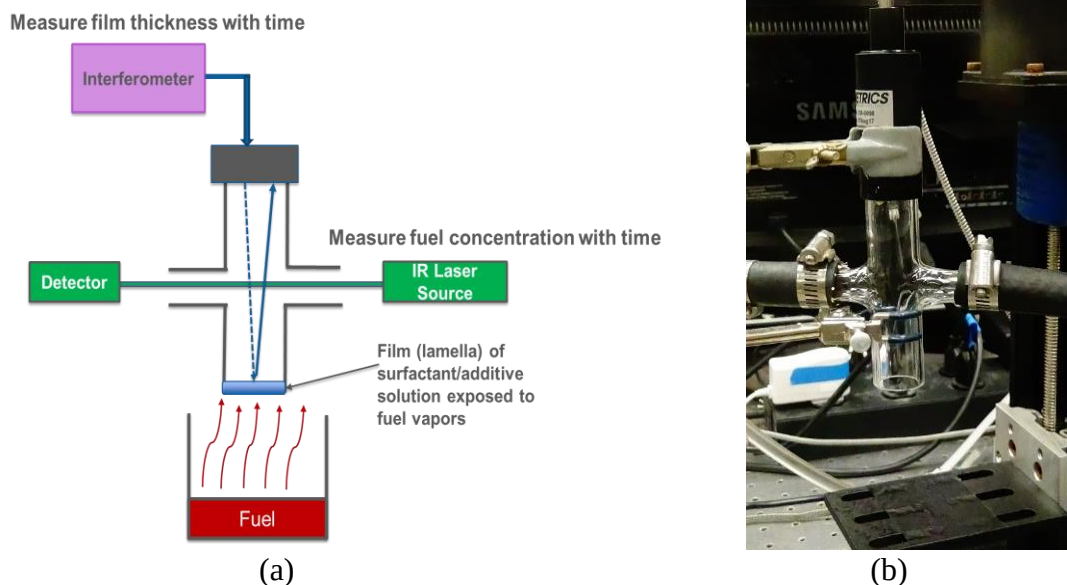


Figure 18. (a) Diagram of single lamella apparatus for measuring thinning dynamics with an interferometer and fuel vapor diffusion through the lamella with IR, (b) An image of the apparatus.

4.5.4. Generation of Foams (Task 7)

Foam generation method was developed under in-house program (6.2 NRL/ONR) and are leveraged in this research. Foams are generated from the Siloxane-Glucopon formulations using a sparging method for bench-scale evaluations as detailed by Hinnant et al. [37]. Air flows through a circular sparger disc (2 cm dia., 25-50 μm pore size) placed 3 cm deep in the surfactant solution at a constant rate to generate bubbles as shown in Figure 19. The foam is dispensed through an outlet tube of the generator at a constant foam flow rate. The tabulated foam properties are measured as foam is dispensed at a constant foam flow rate of 1000 mL min^{-1} . A single cup, as shown in Figure 19, is used for generating small volumes of foam needed to characterize the foams by measuring degradation and fuel transport. But for fire extinction experiments where the foam flow rate is varied, a liquid leveling system is used to maintain constant liquid depth above the sparger.

The candidate formulations are also used to generate foams at large-scale by pushing the foam solution from a pressurized tank (689.5 kPa or 100 psi) through an air aspirated nozzle at constant solution flow rate of 7.57 L min^{-1} (2 gallons per minute) as described in MIL-F-24385F [4]. A larger diameter inlet tube is placed in the nozzle to increase the liquid flow rate to 11.36 L min^{-1} (3 gpm) as needed.

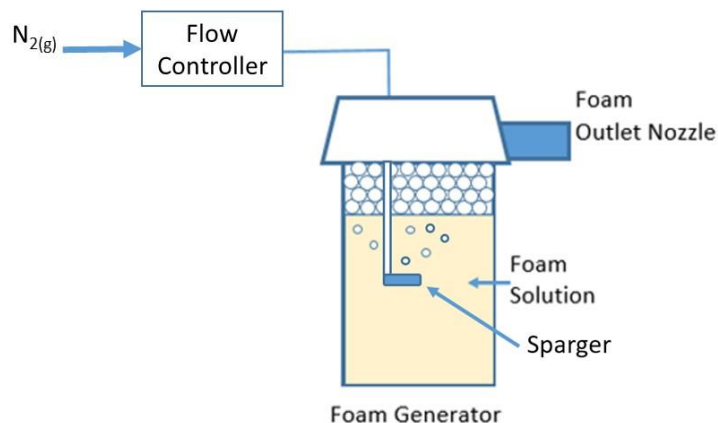


Figure 19. Foam generation by using a porous disc sparger.

The foam characterization method is developed using Dynamic Foam Analyzer in the current program. The foams are characterized by measurements of initial bubble size, initial expansion ratio, and liquid drainage rate versus time at bench scale and large scale. Expansion ratio is the volume of foam per unit volume of liquid contained in the foam. Expansion ratio is measured by generating a fixed volume of foam into a graduated cylinder and measuring the foam's mass, which is converted to liquid volume using the density of water. Foams are generated with air externally using the extinction apparatus at a constant foam flow rate between 950 to 1000 mL min⁻¹ and fed directly to fill the glass container of a Dynamic Foam Analyzer (DFA100, KRUSS GmbH, Matthews, NC) shown in Figure 20 for the bench-scale measurements. The DFA container (40 mm diameter, 25 cm height cylinder) has part of its walls (inner and outer) shaped flat. The flat surface is in contact with the bubbles of the foam. A prism attached to the flat surface reflects light forming a mirror image of the foam-surface bubbles at a video camera's focal plane. The camera is placed 13 cm from the top of the foam column. Starting within one minute of the foam generation, the video images are continuously analyzed by the computer software (ADVANCE) to provide plots of bubble size distributions, average bubble size, and the position of foam-solution (drained solution) interface with time. In additions to the bubble size distributions, the plots provide bubble coarsening and liquid drainage rates from the 25 cm height foam column.

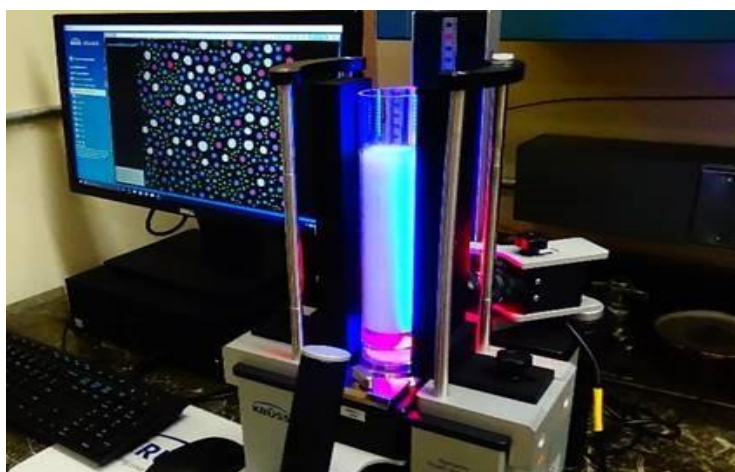


Figure 20. Dynamic Foam Analyzer (DFA) for characterizing foams.

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Foam generated at large-scale is measured differently than foam collected for characterization at bench-scale. As prescribed in MilSpec [4], foam is sprayed on to an aluminum plate and the foam is collected into a rectangular container for characterization. The foam fills a rectangular glass container (4.2 cm x 4.2 cm x 30.5 cm) affixed with a millimeter ruler positioned in front of a digital camera (Nikon DSLR) placed at 13 cm height of the 30.5 cm foam column. Images of the foam in the column with the ruler were taken within two minutes of the foam being collected. The diameter of 50 to 100 bubbles for three independent images (150 to 300 total bubbles) were measured using open source software (ImageJ). The liquid drainage rate was measured by collecting a 28 cm height column of foam into a 500 mL graduated glass cylinder (5 cm diameter) and measuring the change in liquid level at the base of the container with respect to time.

4.5.5. Degradation and Fuel Permeation in Foams (Task 7)

We measured foam degradation following a procedure similar to those described elsewhere [30] and shown in Figure 21. Figure 21 depicts foam degradation rate. The foam height is measured as a function of time in a 100 mL glass beaker (5.0 cm diameter) in a water bath (150 mL) controlled by using a heating tape and a thermostat set at 60°C, based on our previous measurements of the foam-pool interface temperature during fire extinction [33]. We then poured 50 mL of preheated heptane liquid into the beaker using a funnel, leaving a head space of 4 cm height to accommodate the foam layer. Foam was generated at a constant foam flow rate between 950 to 1000 mL min⁻¹ using nitrogen gas flow of 900 mL min⁻¹. Foams were generated by the sparging method and fed directly into the beaker. A spatula was used to scrape excess foam from the top of the beaker, forming an even 4 cm foam layer on top of the preheated liquid fuel. We were careful to keep the water bath level just below the foam-fuel interface in the beaker so that the foam is not heated by the water bath directly. A video camera monitored the foam height over time. We determined the thickness of foam by measuring the height of the top surface of the foam layer and the liquid fuel surface seen in the recorded video. In the cases where a gas bubble or “gap” lifted the entire foam layer from the liquid fuel surface, the volume of the gap was excluded from the total foam height. The “gap” is a result of foam bubbles bursting and coalescing to form a single bubble that spans the width of the container when in contact with the liquid fuel [30]. Thus, the gap contains the nitrogen that was inside the foam bubbles along with warm fuel vapor.

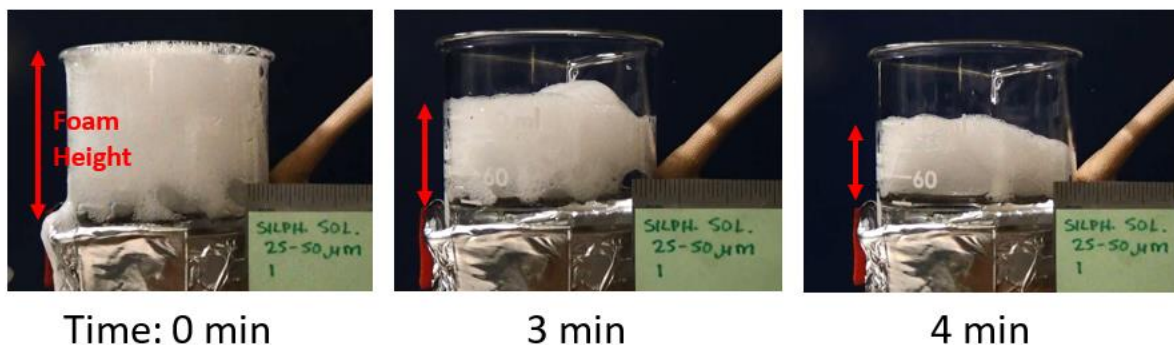


Figure 21. Measuring change in the height of 4 cm thick foam layer placed on a heptane pool maintained at a constant temperature of 60°C versus time [30].

Schaefer et al. [27, 28] used a flux chamber to measure fuel vapor suppression by AFFF and a fluorine-free foam (RF6) in the absence of a fire. They also measured times for ignition of vapors permeating through a foam layer on top of heptane and gasoline fuel pools at room temperature. We designed new flux chambers to capture new phenomena that had not been monitored before in flux chamber designs. The chambers were designed to measure fuel vapor permeation rates at small times through foams covering hot fuel pools [44]. We monitor fuel transport over a heated fuel to emulate aspects of a flame environment. We also monitor changes in foam height with time during the fuel transport experiment to understand how differences in collected flux data may be related to differences in foam lifetime versus fuel vapor diffusion effects within the foam.

Our chamber designs consisted of a two piece flux chamber initially as described in detail in reference [29]. However, challenges with hot fuel led to the need for an updated chamber material. Glass was chosen as an initial material to minimize effects and data was successfully collected over heated fuel in this apparatus [44]. A water bath was used to heat fuel contained in the bottom piece, foam was then generated above the fuel. A top piece was then secured to the bottom which contained a sparger and outlet to sweep fuel vapors above the foam out to an FTIR for gas analysis. This glass flux chamber was roughly 5 cm in diameter and cylindrical. The curved sides of the container and large clamping mechanism (described and shown in reference [44]) made it difficult to monitor changes in foam height with time and a new chamber was designed.

A new fuel transport apparatus was made using a 250 mL thin-walled, transparent, PET (polyethylene terephthalate) rectangular plastic bottle, shown in Figure 22 on the right. The flat shape enables an undistorted photographing of foam thickness during the test. The PET bottle was cut horizontally to create a top and bottom piece. The top piece had a 1/8" pipe fitting hole drilled and tapped into it to feed gases from the fuel transport container into an infrared spectrometer (FTIR). A 3/4" pipe fitting hole was drilled and tapped into the screw cap of the bottle to hold a nitrogen sparger (frit 3 cm diameter, 25-50 μ m pore size). The glass tubing of the nitrogen sparger was held in place with a compression fitting (Cajon) in union with a bored through 3/4" pipe fitting. Two Plexiglas plates were milled out to fit snugly over the cut ends of the PET bottles and sealed to the bottle with plastic adhesive (Weld-On). Guide holes were also drilled on two sides of the plates to hold small screws, ensuring the top and bottom piece were directly on top of each other while closing. To close the top and the bottom piece, a flexible 1/8" neoprene gasket was placed in between the top and bottom layer. Four spring clamps were used to seal the two pieces together in a closed, air-tight configuration.

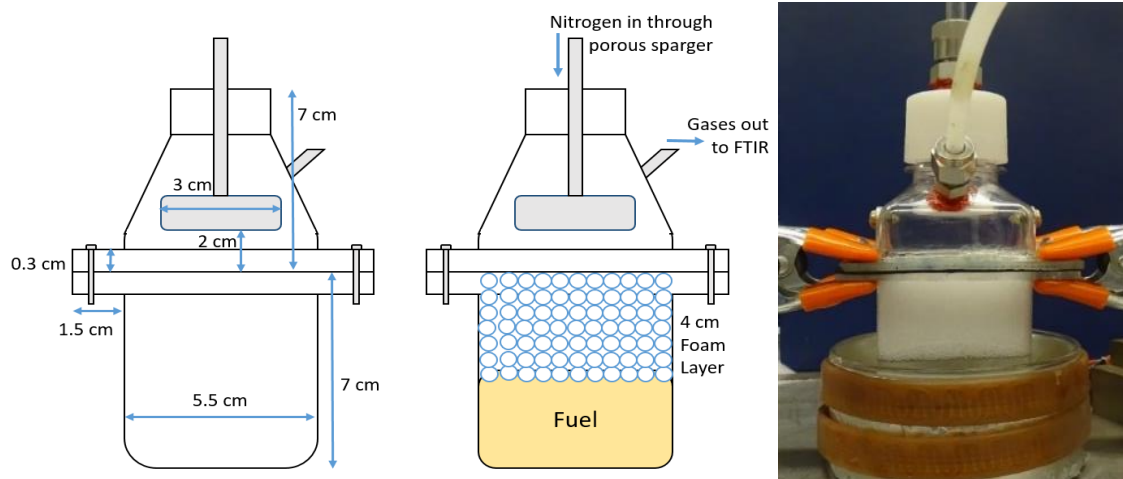


Figure 22. Schematic of a container to measure fuel vapor transport rate through foam laid on a heated fuel pool with nitrogen gas fed through a porous disc to sweep the fuel vapors emanating from the foam surface in a stagnation flow (left), schematic of assembled test (center), image of actual container with a 4 cm (initial thickness) foam layer and the bottom piece placed in a hot water bath to maintain constant pool temperature (right).

Fuel transport was measured by pouring 90 mL of heptane into the bottom piece. The bottom piece was then placed in a water bath, thermostated with heating tape to ensure a fuel temperature of 60°C. The water bath only extended to the height of the fuel layer, actively heating the fuel pool, but not the foam. Foam solution was then poured into a foam generator that generated foam using a 25-50 μm sparger. Foam was generated into the bottom piece above the fuel layer and a timer was started, indicating time 0 for foam lifetime. Foam filled the headspace of the bottom piece and was leveled with a spatula, creating a flat 4 cm layer. The neoprene gasket and top piece were then lowered onto the bottom and sealed with 4 spring clamps on the 4 corners of the container. The sparger in the top piece fed nitrogen into the container at a flow rate of 500 mL/min. The stream was then opened to the FTIR and the time between when foam entered the container and when the FTIR began collecting data was recorded. This value was then added to the initial time of the FTIR data (40-100 seconds). The FTIR had an additional by-pass of nitrogen, 100 mL/min, resulting in a total flow of 600 mL/min into the FTIR. The FTIR measured fuel concentration by collecting vapors in a 10 cm long heated gas cell (50°C), comparing observed signal to a reference standard of n-heptane, 1000 ppm, 50°C, 10 cm path length. The measured concentration of fuel by FTIR was converted to molar flux by multiplying the heptane vapor concentration (volume fraction, # ppm/1000000) with molar flow rate ($4.45 \times 10^{-4} \text{ mole sec}^{-1}$) of total nitrogen flowing (600 mL min^{-1}) through the FTIR and dividing by the pool surface area.

Foam height was measured using a camera oriented perpendicular to a rectangular face of the container. A ruler was placed in the same plane as the rectangular face in order to have a pixel to distance ratio for all images collected. Foam lifetimes in the fuel transport container are not expected to mimic foam degradation measurements collected in a beaker. The closed container creates a moist environment around the foam and provides vertical wall space above the foam. Foam can cling to this space creating a large physical gap between itself and the fuel pool. The gap would not be sustained as long as it is in the absence of the excess wall space or a moistened

environment. We therefore only use the degradation data to better understand fuel transport rates rather than for determine its relationship to fire suppression which is in open space. The measurement of foam height with time while simultaneously collecting fuel transport data will allow for the derivation of intrinsic fuel transport profile for a given fuel-surfactant system. This will ultimately separate effects of surfactant structure that may be related to foam stability or fuel transport, allowing surfactant structural optimization for either mechanism of foam fire suppression.

4.5.6. Bench Scale Fire Extinction Apparatus (Task 7)

An extinction apparatus was developed fully as part of in-house program (6.2 NRL/ONR) and is leveraged in the current program. Detailed description of the apparatus is given in [44] and briefly described here. A 19 cm diameter, 11 cm deep Borosilicate glass container with an outlet at the bottom was used to contain a fuel pool. A heptane fuel layer (1 cm thick) was formed on top of a water layer (9 cm deep) with a 1 cm lip above the fuel layer to accommodate the foam. Foam was generated and applied onto the center of the pool at a constant foam flow rate. The constant foam flow rate was achieved by maintaining constant air flow and by the liquid leveling system that continuously transfers additional solution from the leveling vessel to the foam generation vessel. The liquid level was maintained at 3 cm above the sparger disc. Extinction experiments consisted of a pre-burn of the heptane pool for 60 seconds followed by the foam application at a constant flow rate until fire extinguishment. In cases, when no extinction event was observed at low foam flow rates, foam flow was turned off after 180 seconds to prevent overflow of the foam. As the foam drained liquid into the fuel, fuel overflow from the extinction vessel was prevented by lowering the tygon tube connected to the bottom of the extinction vessel to a specified height as shown in Figure 23.

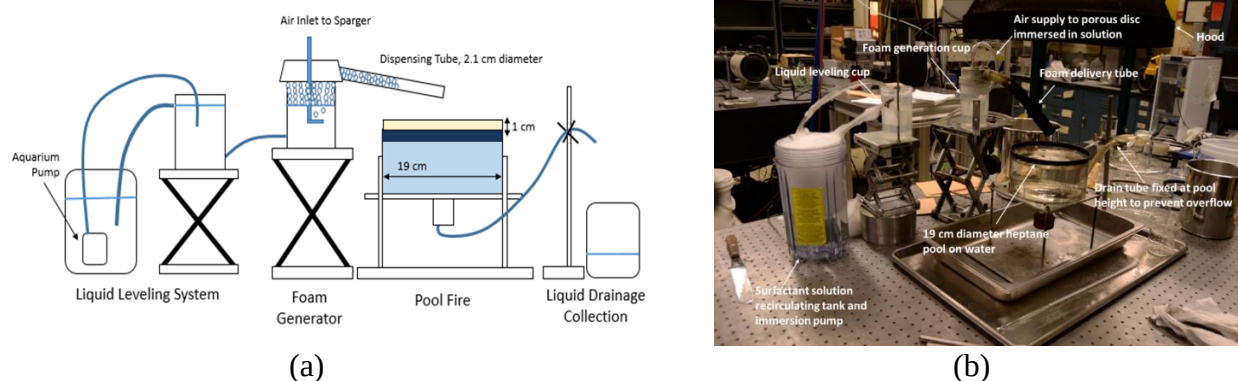


Figure 23. (a) Diagram of a bench-scale extinction apparatus; 1 cm heptane layer placed on top of water layer and 1 cm lip to accommodate the foam layer [37], (b) Picture showing foam generation, leveling system, and pool fire [44].

Foams were deposited at a fixed position on the pool at a constant rate. At the beginning of the project, the glass delivery tube was placed at the center of the pool and the foam was deposited until the fire was extinguished. It worked fine except at very low foam application rates. At the low foam flow rates, the glass tube got very hot and foam disintegrated to mostly solution emerging from the glass tube. Therefore, we changed the protocol to depositing the foam at the edge (about 1" inside from the lip of the container). These extinctions are labeled as EDGE in the extinction time versus foam application rate plots.

4.6. 28 ft² MilSpec Fire Extinction Test (Task 8)

Six foot diameter pool fire tests outlined in MIL-F-24385F [4] are performed as shown Figure 24. Both gasoline and heptane are used at different solution application rates. Only tests related to fire extinction performance are performed. An active firefighter is involved in spraying the foam on to the pool surface unlike in the bench-scale tests. Fire extinction tests are performed on the candidate formulations following tests with AFFF for comparison using fresh water at full strength [4]. The extinction time is measured from the time of initiating deposition of the foam onto the 2.6 m² (28 ft²) heptane pool fire, which has been burning 10 sec (pre-burn) before starting the foam application, until the time of extinguishment. The burnback test involves a reignition of the extinguished pool fire after 90 sec of total foam application (includes time to extinguish fire). The foam covered pool is reignited by lowering a 30.5 cm diameter pan of burning heptane-fuel into the center of the pool and recording the time for fire re-involving 25% of the pool surface. The film and seal test is conducted by covering the cyclohexane fuel surface in a small container with foam, then inserting a wire screen to scoop out the residual foam, waiting 60 sec then placing a small butane lighter flame approximately 1.27 cm (½ inch) above the surface to ignite the fuel vapors permeating through the water-surfactant film on the fuel surface. If the cyclohexane fuel does not ignite, it receives a pass [4].



Figure 24. 28 ft² pool fire extinction test.

4.7. QSAR and EPA Modeling Methods (Task 4)

Oregon State University researchers have been working with scientists from the Naval Research Laboratory (NRL) to develop effective, environmentally safe alternatives to the currently available “fluorine containing” aqueous film-forming foam (AFFF) used in fire-fighting. The objective of the project is to develop “new” surfactants whose foams can potentially meet the performance requirements defined in sections 3.4, 4.7.13.1, and 4.7.13.2 of MIL-F-24385F and

have acceptable persistence and aquatic toxicity in order to replace current environmentally hazardous AFFF.

The objective of this task was for the new candidate surfactants, developed by NRL scientists, to be evaluated based on their potential aquatic toxicity and environmental fate properties using extant computer models, such as those physicochemical models contained in the USEPA's EPI (Estimation Programs Interface) Suite software. The EPI Suite is a screening-level tool developed by EPA and Syracuse Research Corp. It is comprised of a suite of physicochemical property and environmental fate estimation programs including: KOWWIN, AOPWIN, HENRYWIN, MPBPWIN, BIOWIN, BioHCwin, KOCWIN, WSKOWWIN, WATERNT, BCFBAF, HYDROWIN, KOAWIN and AEROWIN, and the fate models WVOLWIN, STPWIN and LEV3EPI. These EPI Suite programs were used to estimate physicochemical parameters such as octanol-water partition coefficients, Henry's Law constants, aerobic and anaerobic biodegradation, etc.. ECOSAR (Ecological Structure Activity Relationships (ECOSAR) Predictive Model) was used to estimate toxicity. It is a computerized model that estimates a chemical's acute (short-term) and chronic (long-term) toxicity to aquatic organisms, such as fish, aquatic invertebrates, and aquatic plants.

All of these models are recognized to provide "rough" estimates of properties and, as stated in the EPA's program guidance, values from EPI Suite and ECOSAR should not be used in lieu of acceptable empirically-derived values when available. A word of caution; in the case of the cationic and anionic surfactants, there are specific concerns given the lack of underpinning data to support the estimation models; therefore, in addition to running the EPI Suite models, efforts were made to identify and review any available information in the peer-reviewed literature relevant to the candidate materials.

European Chemical Agency (ECHA) was developed to implement regulations on chemicals for the European Union. The ECHA website holds information on chemicals registered under REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) which includes information about chemical safety, proper handling, and environmental concerns. All of the data stored here is freely available to the public. The information comes from manufacturers and importers of the chemicals. Some of the chemicals proposed in the grant did not have information in the ECHA database. Many do not have to be registered until May of 2018, leaving information unavailable. Some information is derived from experimentation, some comes from similar structures. The reliability of information derived from similar structures is questionable and should be considered as an estimation.

EPI (Estimation Programs Interface) Suite, as described earlier, is a computer model designed by the EPA to estimate physical and chemical properties of substances. Chemicals can be looked up by name, or the chemical structures can be directly put into the model for analysis. This model uses the estimations to predict environmental fate and transport of chemicals. Some properties EPI Suite can estimate include partitioning coefficients, water solubility, bioaccumulation and bioconcentration potential, biodegradability, and environmental fate. Because this is a computer model, it should only be used as a screening level tool. The algorithms used to develop the modules in EPI Suite were based on specific chemicals, making the program very accurate for chemicals with similar structures (nonionic organic chemicals). Other types of chemicals may not be modeled with high accuracy using the program. Some classes which may

not be accurately modeled by the program include charged chemicals, polymers, organometallics, and nanoparticles. The model does not accurately predict values for charged chemicals, so is not applicable for ionic hydrocarbons or the charged siloxane surfactants. Predictions of biodegradability should be treated with caution given that there is relatively little data in the literature to support or confirm such predictions.

4.8. Methods for Evaluating Impact on Environmental (Task 6)

The conduct of the study of acute and chronic Toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK, and their mixture to the cladoceran, *Ceriodaphnia dubia*, the fathead minnow, *Pimephales promelas*, and the green algae, *Raphidocelis subcapitata* was reviewed for compliance with OSU AquaTox Standard Operating Procedures (SOPs). Analysis and documentation for the study were carried out in the spirit of U.S. EPA and OECD Good Laboratory Practice (GLP) standards.

The testing reported herein was conducted to evaluate the potential acute and chronic toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK, and a mixture designed to represent an end-use product, to the cladoceran, *Ceriodaphnia dubia*, fathead minnow, *Pimephales promelas*, and the green algae, *Raphidocelis subcapitata*. Accompanying the toxicity tests were measurements of DOWSIL™ 502W Additive and Butyl Carbitol of exposure concentrations, while exposures for Glucopon® 225 DK are reported as nominal concentrations due to the lack of an analytical method.

The toxicity tests were conducted, where applicable, the test methodologies followed U.S. Environmental Protection Agency (USEPA) and Organization of Economic Co-operation and Development (OECD) guidance as described throughout this report. Analysis and documentation for the study were carried out in a manner consistent with U.S. EPA and OECD Good Laboratory Practice (GLP) standards. The toxicity tests were performed at the Oregon State University Aquatic Toxicology Laboratory (OSU AquaTox, Corvallis, OR, USA) and the analytical verification was performed at the OSU Field Laboratory (Corvallis, OR, USA). All data related to this study will be maintained in the OSU AquaTox archives for 10 years.

All culturing and testing with the fathead minnow is regulated and approved by the Oregon State University Institutional Animal Care and Use Committee (IACUC) under an approved animal care and use protocol (ACUP).

4.8.1. Toxicity Test Method and Test Substances

Acute toxicity tests were performed according to USEPA standard methodology [45,46]. Chronic and short-term chronic toxicity tests were performed according to USEPA [47] and OECD [48]). The test substance, DOWSIL™ 502W Additive (Dow Silicones Corporation), Lot # H05216U170 (with a reported purity in the SDS of >72 - < 92%), was shipped from the U.S. Naval Research Laboratory (NVRL) under chain-of-custody and received by the OSU Field Lab. Following receipt at the OSU Field Lab, the test substance was stored sealed in its original container at room temperature. For the series of toxicity testing, a 50 mL subsample was taken from the parent bottle and stored in a 50 mL polypropylene tube under room temperature conditions. The test substance, Diethylene Glycol Butyl Ether (Butyl Carbitol), (CAS #112-24-5) was sampled (NVRL/KMH 8/7/19) and shipped from the NVRL under chain-of-custody and

received by the OSU Field Lab. Following receipt at the OSU Field Lab, the test substance was stored sealed in its original container at room temperature. For the series of toxicity testing, a 50 mL subsample was taken from the parent bottle and stored in a 50 mL polypropylene tube under room temperature conditions. The test substance, Glucopon® 225 DK (BASF Material 50224120), was sampled (NVRL/KMH 8/7/19) and shipped from the NVRL under chain-of-custody and received by the OSU Field Lab. Following receipt at the OSU Field Lab, the test substance was stored sealed in its original container at room temperature. For the series of toxicity testing, a 50 mL subsample was taken from the parent bottle and stored in a 50 mL polypropylene tube under room temperature conditions.

4.8.2. *Test System and Specie Sources*

Cladoceran, *Ceriodaphnia dubia*

Both the acute and chronic *C. dubia* tests were initiated with <24 hr old neonates from in-house cultures. Original cultures of *C. dubia* were obtained from Aquatic BioSystems (Fort Collins, CO, USA) and in-house cultures have been successfully maintained at OSU AquaTox for 10+ years. Parental organisms were isolated onto brood boards in order to obtain <24 hr old neonates for testing.

Fathead minnow, *Pimephales promelas*

Original broodstock cultures of *P. promelas* were obtained from Aquatic BioSystems (Fort Collins, CO, USA) and in-house cultures have been successfully maintained at OSU AquaTox for 10+ years. Adult broodstock are held in 80-liter tanks under continuous flow-through conditions receiving UV-sterilized, oxygenated well water at a rate of 1 L/minute (approximately 64 volume additions per day) to maintain a water temperature of 25±2°C and optimal water quality. Fish are held under a 16 hr:8 hr light:dark photoperiod under fluorescent lights. Broodstock are fed a combination of defrosted frozen adult brine shrimp (Brine Shrimp Direct, Ogden, UT, USA) and a crum mash (fish meal, fish oil, vitamin/mineral extruded starter feed; Bio-Oregon, Longview, WA, USA). Broodstock are fed ad libitum during twice daily feedings. Health and reproduction are monitored daily. Reproduction in the broodstock tanks is monitored daily by maintaining suitable male to female ratios and monitoring breeding (as described in USEPA fathead minnow culture guidelines [USEPA 1987]). Eggs are enumerated on the breeding tiles and removed from the broodstock tanks daily. Breeding tiles are then held in moderately hard reconstituted water until hatching.

At test initiation of the short-term chronic tests, fish were less than 24 hrs old, while fish for acute testing were 6 days old. All culturing and testing with the fathead minnow is regulated and approved by the Oregon State University Institutional Animal Care and Use Committee (IACUC) under an approved animal care and use protocol (ACUP).

Green algae, *Raphidocelis subcapitata*

R. subcapitata was cultured at OSU AquaTox using standard OECD (2011) algal medium with EDTA. The cultures were originally obtained from Aquatic Biosystems (Fort Collins, CO, USA) and have been cultured at OSU AquaTox. At test initiation, the cultures were 5 days old and in log-phase growth.

4.8.3. *Organism Culture/Acclimation*

Cladoceran, *Ceriodaphnia dubia*

C. dubia are cultured at OSU AquaTox in moderately-hard reconstituted water (hardness of 100 mg/L as CaCO₃, alkalinity of 80 mg/L as CaCO₃, and pH of 7.8 – 8.0). Organism survival and reproduction were optimal (exceeding performance endpoints as per USEPA 2002) prior to use in testing.

Fathead minnow, *Pimephales promelas*

Fertilized eggs were treated in a dilute fungal guard solution (ParaGuard; Seachem, Madison, GA, USA) for 48 hours to remove biofilm growth during the holding period. After the fungal guard solution treatment, embryos were transferred (on their breeding tiles) to moderately hard reconstituted lab water with a hardness, alkalinity, and pH of 100 mg/L as CaCO₃, 70 mg/L as CaCO₃, and 8.0, respectively. The embryos were hatched in moderately hard water. Larval fish were less than 24 hrs old for the short-term chronic toxicity tests. For the acute tests, larval fish were held in moderately hard reconstituted water with daily feeding and water renewals for a period of 6 days. Acclimation of the embryos and the fish occurred under the same temperature and light conditions as those of the broodstock and those employed during the test.

During the holding period of the larval fish for acute testing, fish were fed concentrated suspensions of brine shrimp (*Artemia salina*) nauplii (Brine Shrimp Direct, Ogden, UT, USA) twice daily. Brine shrimp were hatched by introducing resting cysts into 30 ppt saltwater and vigorously aerating until hatch, followed by rinsing in freshwater. Brine shrimp were <24 hrs old upon feeding. Fish were fed an ad libitum amount of food without excessive food remaining between water renewals. Uneaten food and waste were siphoned from the culture tank on a daily basis during water renewal. During the acclimation period, mortality was less than 1% and showed no signs of disease, stress, or poor condition.

Green algae, *Raphidocelis subcapitata*

R. subcapitata are cultured at OSU AquaTox in standard OECD (2011) algae media with EDTA. The culture media under ambient conditions has a hardness of 32 mg/L as CaCO₃, an approximate pH of 7.5, and a DOC of < 0.5 mg/L. The algae were cultured at 25 ± 2 °C under continuous fluorescent lighting (at 400 ± 60 ft. candles) and were hand-shaken twice daily. Axenic cultures were initiated three months prior to the onset of testing.

4.8.4. Control/Dilution of Waters

Cladoceran, *Ceriodaphnia dubia* and Fathead minnow, *Pimephales promelas*

The control water used in the *C. dubia* and *P. promelas* toxicity tests was a moderately hard reconstituted laboratory water prepared by adding the reagent grade salts (CaSO₄·2H₂O, MgSO₄, KCl, NaHCO₃) to deionized water (DI; 17.6-18.0 Ω) to achieve the desired nominal values shown in Table 1. Reconstituted water was prepared as detailed in standard USEPA methods (USEPA 2002). The control water was prepared with a molar calcium:magnesium (Ca:Mg) ratio of 0.70. For the *C. dubia* tests, control water was amended with trace amounts of vitamin B12 (3 µg/L) and Se (2.5 µg/L Se, as Na₂SeO₄), as per USEPA [46,47] and ASTM [49] methodology for *C. dubia* culture and testing.

Algae media was prepared as per OECD (2011) methodology (with EDTA) (Table 2). Each nutrient stock solution was sterilized by filtration using a vacuum filtration apparatus with a 0.20 µm filter (nylon membrane, Whatman, Maidstone, England). The hardness and alkalinity were

measured at test initiation in the control/dilution water. The control/dilution was warmed to test temperature ($25 \pm 2^{\circ}\text{C}$) and aerated overnight prior to use in the toxicity tests.

Table 1. Nominal water quality parameters of laboratory control water.

Parameter	Unit	Nominal Value
Calcium	mg/L	16.5
Magnesium	mg/L	14.3
Sodium	mg/L	36.8
Potassium	mg/L	3.14
Chloride	mg/L	2.86
Sulfate	mg/L	96.0
Dissolved Organic Carbon	mg/L	< 0.50

Table 2. OECD Algae Media recipe.

Algae Nutrient Stocks	Stock Concentration (gram/L)	Final Concentration in media (mg/L)
Stock #1 : macro nutrients		
NH ₄ Cl	1.5	15
MgCl ₂ x 6H ₂ O	1.2	12
CaCl ₂ x 2H ₂ O	1.8	18
MgSO ₄ x 7H ₂ O	1.5	15
KH ₂ PO ₄	0.16	1.6
Stock #2 : iron		
FeCl ₃ x 6H ₂ O	0.064	0.064
Na ₂ EDTA x 2H ₂ O	0.1	0.1
Stock #3 : trace elements		
H ₃ BO ₃	0.185	0.185
MnCl ₂ x 4H ₂ O	0.415	0.415
ZnCl ₂	0.003	0.003
CoCl ₂ x 6H ₂ O	0.0015	0.0015
CuCl ₂ x 2H ₂ O	0.00001	0.00001
Na ₂ MoO ₄ x 2H ₂ O	0.007	0.007
Stock #4 : bicarbonate		
NaHCO ₃	50.0	50

4.8.5. Selection of Exposure Concentrations and Route

In order to obtain a sufficient exposure response in the definitive tests, range-finding experiments were performed prior to the selection of definitive exposures. For the single compound tests with DOWSIL™ 502W Additive, stock solutions of 5,000 and 10,000 mg/L were prepared by addition (by volume with micropipette) of the 100% test substance to moderately hard reconstituted freshwater. These concentrated stock solutions were then used for preparation of nominal exposure concentrations. Stock solutions were prepared fresh immediately prior to

preparing solutions for testing. For the single compound tests with Butyl Carbitol, the 100% test substance was not diluted to make a stock solution and was used to directly spike (by volume with micropipette) the control to make a series of dilutions. For the single compound tests with Glucopon® 225 DK, concentrated stock solutions of 22,600 and 45,200 mg/L were prepared by weighing the compound on an analytical balance and adding moderately hard reconstituted freshwater to the weighing vessel. These concentrated stock solutions were then used to for preparation of nominal exposure concentrations. Stock solutions were prepared fresh immediately prior to preparing solutions for testing. Stock solutions were gently mixed by inverting slowly approximately 50 times to ensure homogenization. This was necessary to avoid stratification of the test substance in water prior to preparing exposure solutions.

Preparation of the stock and exposure solutions were conducted using plastic polypropylene bottles with screw-top lids. Plastic was necessary instead of glass due to the high amount of sorption onto glass surfaces by the surfactants present. This limited the possibility of cross contamination, and the closed lid plastic containers were a more efficient vessel for thorough mixing. To prepare each exposure solution, either the stock solution (DOWSIL™ 502W Additive or Glucopon® 225 DK) or the 100% compound (Butyl Carbitol) were added directly to a new empty plastic bottle via micropipette to obtain a target nominal concentration. Next, the calculated volumes of control/dilution water were gently added. Each bottle was then capped and inverted slowly 50 times. Following mixing, aliquots were gently poured into test chambers and vials for analytical chemistry measurements. This method of mixing and suspension was necessary to obtain uniformity and consistency between chambers.

For preparation of the mixture of the three compounds, a recipe prescribed by NRL was used. The recipe consisted of: 2000 mg/L DOWSIL™ 502W Additive, 3000 mg/L Butyl Carbitol, and 5000 mg/L Glucopon® 225 DK, in water (laboratory water). Each compound was added by weight directly into a single weigh boat, zeroing the weigh boat between each addition of compound. Laboratory water was then gently added and the compounds were mixed together with a plastic pipette until fully homogenized. The mixture was prepared fresh for each day of use. The mixture was then handled in the same technique as was used with the single compounds.

Cladoceran, *Ceriodaphnia dubia*

Each test with the single compounds and mixture included five exposure concentrations and a laboratory water control. Four replicate chambers were used for acute testing and ten replicate chambers were used for chronic testing for each treatment and control.

Fathead minnow, *Pimephales promelas*

Each test with the single compounds and mixture included five exposure concentrations and a laboratory water control. Four replicate chambers were prepared for each treatment and control for both acute and chronic testing.

Green algae, *Raphidocelis subcapitata*

The green algae test with the mixture (only) included five exposure concentrations and an algae media control. Three replicate chambers were prepared for each concentration and six

replicate chambers were prepared for the control. An extra replicate was added to each concentration (without algae) to allow for background absorbance measurements through the test.

4.8.6. Test Conditions

Table 3. A summary of test conditions.

Test organism	<i>C. dubia</i>	<i>C. dubia</i>	<i>P. promelas</i>	<i>P. promelas</i>	<i>R. subcapitata</i>
Test type:	Acute	Chronic	Acute	Chronic	Chronic
Standard Method:	USEPA 2002a	USEPA 2002b	USEPA 2002a	USEPA 2002b	OECD 2011
Renewal type:	Static	Static-Renewal	Static-Renewal	Static-Renewal	Static
Test duration:	48 hrs	7 days	96 hrs	7 days	72 hrs
Temperature (°C):	25 ± 1 °C	25 ± 1 °C	25 ± 1 °C	25 ± 1 °C	25 ± 1 °C
Light quality:	Cool-white fluorescent	Cool-white fluorescent	Cool-white fluorescent	Cool-white fluorescent	Fluorescent lighting
Light intensity:	Ambient 100 ft-c	Ambient 100 ft-c	Ambient 100 ft-c	Ambient 100 ft-c	400 - 460 ft-c
Photoperiod:	16h light: 8 h dark	16h light: 8 h dark	16h light: 8 h dark	16h light: 8 h dark	Continuous
Test chamber type:	Plastic (Polystyrene)	Plastic (Polystyrene)	Plastic (Polypropylene)	Plastic (Polypropylene)	Plastic (Polystyrene) loosely capped soufflé cups to prevent contamination and allow CO ₂ exchange.
Test chamber size:	30 mL	30 mL	250 mL	250 mL	250 mL
Test solution volume:	25 mL	25 mL	200 mL	20 mL	100 mL
Renewal of test solutions:	None	Daily, 100%	48 hrs, 80%	Daily, 80%	None
Age of test organisms at initiation:	< 24 hrs	< 24 hrs	6 days	< 24 hrs	5 days
Initial number of organisms/chamber:	5	1	10	10	10,000 cells/mL
Number of replicates:	4	10	4	4	6 (control), 3 (treatment)
Feeding regime:	YTC and Algae while holding 2 hrs prior to the test	Daily (0.15 mL YTC; 0.15 mL algae (3 x 10 ⁷ cells/mL))	<i>Artemia nauplii</i> during holding prior to the test; add 0.2 mL <i>Artemia nauplii</i> concentrate 2 h prior to solution renewal at 48 h	<i>Artemia nauplii</i> fed 2x daily (a.m. / p.m.) between renewal	N/A
Test chamber aeration:	None	None	None	None	Gentle shaking 3x daily to avoid generation of foam

Cladoceran, Ceriodaphnia dubia

To initiate the acute tests, neonates (< 24 hours old) from the in-house cultures were combined into a beaker of control water and fed an algae concentrate (*Raphidocelis subcapitata*, cell density 3.0 x 10⁷ cells/mL) and yeast/trout chow/cereal leaf (YTC; 1850 mg/L total solids) suspension (1:1) for a period of 2 hours prior to test initiation. At test initiation, neonates were randomly seeded into each test chamber until five organisms were within each chamber/replicate. To initiate the chronic tests, neonates (< 24 hours old) from a single adult from the culture were distributed into one row (one neonate for one replicate of each treatment; for a total of 10 replicates per treatment) of randomly ordered test chambers. This process was repeated using a new brood

of neonates from a single adult for each row of the entire randomization pattern to initiate testing. On a daily basis, only the original organism was transferred to a freshly prepared test chamber (with test solution and food) and neonates were counted daily. In the chronic test, each test chamber was fed 0.3 mL of an algae concentrate (*Raphidocelis subcapitata* (formerly known as *Pseudokirchneriella subcapitata*), cell density 3.0×10^7 cells/mL) and yeast/trout chow/cereal leaf (YTC; 1850 mg/L total solids) suspension (1:1). Each test chamber was fed at test initiation (prior to introduction of the test organism) and once daily prior to water renewal.

Fathead minnow, *Pimephales promelas*

For both the acute and chronic tests, at test initiation, ten fish were impartially distributed into each test chamber/replicate. Each concentration had four replicates for a total of 40 fish per concentration. Each test chamber was randomly assigned to a location within a temperature controlled environmental chamber. For the acute tests, larval fish were fed at least 2 hrs prior to test initiation with no subsequent feeding at test initiation. After 48-hours, each test chamber was fed 0.20 mL per chamber of a concentrated suspension of brine shrimp (*Artemia salina*) nauplii (Brine Shrimp Direct, Ogden, UT, USA). Brine shrimp were hatched by introducing resting cysts into 30 ppt saltwater and vigorously aerating until hatch, followed by rinsing in freshwater. Brine shrimp were <24 hrs old upon feeding. The concentrated suspension was prepared so that the small aliquot provided an ad libitum amount of food without excessive food remaining between water renewals. All chambers containing live fish were fed an equal amount. Following two hours of feeding, a water renewal was performed on each chamber by siphoning out approximately 80% of test solution and replacing it with freshly prepared waters. For the short-term chronic tests, larval fish were fed 0.15 mL per chamber of the concentrated suspension of brine shrimp (*Artemia salina*) nauplii twice a day. A minimum of three hours of feeding were allowed until the daily water renewal was performed by siphoning out approximately 80% of test solution and replacing it with freshly prepared waters. Feeding was suspended 24 hrs prior to test termination.

Green algae, *Raphidocelis subcapitata*

Algal inoculum was harvested from cultures that were in log-phase growth (5 days old). Approximately 50 mL of the stock culture was centrifuged for approximately 30 minutes. The resulting clear supernatant was decanted and the algae were resuspended using test dilution water. This centrifugation, decantation, resuspension process was repeated two additional times. The cell density of the resulting algae suspension was determined using a hemacytometer. The algae suspension was then diluted with the test dilution water to achieve a target inoculum density of approximately 1.0×10^6 cells/mL. The test was initiated by delivering the appropriate volume of algal inoculum to each test chamber containing 100 mL of test solution to achieve a nominal cell density of 10,000 cells/mL per chamber.

4.8.7. Test Monitoring

Water Quality

Hardness, alkalinity, pH, and conductivity were measured in the control water of each test at initiation. Temperature, pH, and conductivity were measured in each exposure at test initiation, daily (of both old and new water during renewal, if applicable), and at test termination. Dissolved oxygen (DO) was only measured in the control waters throughout the tests due to the inability to clean the DO probe after use. Temperature was measured with a standard laboratory thermometer. Test solution pH, conductivity, and DO were measured using a HACH (Loveland, CO, USA)

HQ40d meter with separate calibrated probes for each analyte. Water hardness and alkalinity were measured by colorimetric titration (Standard Methods 2340B/C and 2320B APHA 2012)[50].

Biological Monitoring

Cladoceran, *Ceriodaphnia dubia*

Observations of live and dead organisms were conducted on a daily basis. Dead organisms were removed from the test chambers. In the chronic test, only original live adult organisms were moved to fresh solution daily and the number of young was counted daily.

Fathead minnow, *Pimephales promelas*

Observations of live and dead organisms were conducted daily from initiation to termination. Mortality was defined by no visible movement (by body or gill) following gentle flushing of water past the gill or touching the caudal penducle with no movement. After recording in the raw data packet, dead fish were removed immediately.

At test termination, the fish in each test chamber were counted, examined for grossly-observable abnormalities, and sacrificed via immersion in an overdose of MS-222. For the short-term chronic test with the growth endpoint, the fish from each replicate were then placed into a pre-weighed pan and dried at 105°C for over 12 hours and then re-weighed to the nearest 0.01 mg to obtain a dry weight.

Green algae, *Raphidocelis subcapitata*

At test initiation, cell density was counted in three specially prepared inoculation blanks by a hemacytometer using a Neubauer counting chamber and compound light microscope to verify initial cell density. Measurements of cell density occurred daily using a HACH DR2800 absorbance spectrophotometer. Calibration curves correlating cell density (manual counts with a Neubauer counting chamber) with absorbance were created at test initiation. Curves were developed for two wavelengths (684λ and 750λ) (based upon the range of cell densities observed from test initiation to termination), but only the 684λ was used for final measurements. Absorbance was measured using a 1" 10-mL glass sample cell. Using these calibration curves, daily absorbance measurements were translated into cell density (cells/mL). During the conduct of the test (every 24 hours), small aliquots were removed from each test replicate for absorbance measurements. The volume removed for daily measurements was not replaced. On a daily basis, four randomly selected samples were counted manually by hemocytometer using a Neubauer counting chamber as quality control checks to verify cell density in relation to absorbance. Quality control checks were performed daily to verify the correlation between absorbance measurements and cell density. Algae growth was monitored on a daily basis utilizing absorbance to quantify cell density. Two biological growth endpoints were assessed: cell yield and average specific growth rate. Cell yield was calculated based upon the final cell density minus the initial density (10,000 cells/mL). Average specific growth rate was calculated as the logarithmic increase in cell density of each test chamber per day. For each treatment and group, the mean value was calculated for the entire duration of the test (3 days).

4.8.8. Analytical Sampling

Analytical samples from each treatment were collected for analysis of measured concentrations of DOWSIL™ 502W Additive and Butyl Carbitol at multiple time points (i.e., test

initiation, water-renewal of both old and new solutions, and test termination) throughout the tests. Approximately 8-10 mL of sample was poured into a 15 mL polypropylene conical tube. Samples were preserved by freezing at -20 °C prior to analysis. Samples for Glucocon® 225 DK analysis were not sampled due to the lack of an analytical verification method. Analytical samples from each treatment were collected for analysis of measured concentrations of DOWSIL™ 502W Additive and Butyl Carbitol at multiple time points (i.e., test initiation, water-renewal of both old and new solutions, and test termination) throughout the tests. Approximately 8-10 mL of sample was poured into a 15 mL polypropylene conical tube. Samples were preserved by freezing at -20 °C prior to analysis. Samples for Glucocon® 225 DK analysis were not sampled due to the lack of an analytical verification method. Samples were analyzed at the OSU Field Laboratory (Corvallis, OR, USA) for DOWSIL™ 502W Additive and Butyl Carbitol exposure concentrations.

DowSil 502W Additive

All samples were prepared with the same 50:50 water:methanol composition as the calibration standards. All samples were diluted 2:1 by adding; any further dilutions were performed by adding 50:50 water:MeOH. Regardless of dilution, internal standards were added after the dilution. Samples were placed in polypropylene autosampler vials. Preparation of the standard solutions started with a large aliquot of neat Dow 502W, previously determined to be at a concentration of 1,000,000 mg/L. Serial dilutions were made with MeOH and stored at 0 °C. DOW 502 standards were prepared in 50% H₂O (moderately hard reconstituted lab fresh water) and 50% MeOH. The ¹³C₆ p-N-nonylphenol diethoxylate (Cambridge Isotope) was used as an internal standard during analysis due to its similar structure and elution time as the DOW 502W trisiloxane. A single dilution of the internal standard was performed by diluting 200 mL its original concentration (100 mg/L) in 10 mL of methanol to create a 2 mg/L internal standard.

Analysis of 502W was performed via HPLC-MS/MS. An Agilent 1100 liquid chromatograph fitted with a Phenomenex Polymer X RP-1 3 µm guard (3 x 4mm) and analytical column (50 x 4 mm) were heated to 40 °C, while samples sitting in the autosampler were held at 6 °C. A 100 µL sample loop is used for all injections for a 10 µL injection volume. The mobile phase is made up of (A) 20 mM ammonium formate and 0.01 % formic acid in water and (B) 20 mM ammonium formate and 0.01 % formic acid in 50/50 methanol and acetonitrile. Before the sample is injected, the needle is dipped in 50/50 isopropanol and acetonitrile ten times to reduce carryover. The initial conditions for separations are 50 %B at a flow rate of 1 mL/min. The percent B ramps up to 100% in 1.25 min and was held at 100 %B until 9 min, with an increase in flow rate to 1.5 mL/min from 4.1 to 9 min to reduce carryover where sample sticks to the analytical needle and potentially transfer to the next vial. Initial conditions are brought back at 9.1 min, for a total run time of 11 min. A Waters Quattro Premier XE triple quadrupole mass spectrometer was operated in positive electrospray mode with a source temperature of 150 °C and a desolvation temperature of 200 °C, 950 mL/hr gas flow, and a cone flow of 75 mL/hr. Each of the 502W species analyzed was monitored for two daughter transitions, one for quantitation and one for qualification. For the internal standard, three transitions were monitored and averaged (Table 4).

Calibration curves consisted of 10 DOW 502W concentrations that ranged from 0.01 mg/L to 10 mg/L and all were spiked with 50 mL internal standard. Calibration curves were fitted with a second order quadratic function after weighting by 1/x and gave $r^2 > 0.990$. Standards were required to be within +/- 30 of their true value concentrations. To ensure the absence of carryover,

a blank spike only with internal standard was ran immediately following the highest point of

Table 4. Transitions used for DOW 502W analysis.

Analyte	Precursor Ion	Product Ion (Quant)	Product Ion (Qual)
EO9 Quan	694.4	102.8	
EO10 Quan	738.4	102.8	147
EO11 Quan	782.6	102.8	147
EO12 Quan	826.4	102.8	147
EO12 Qual	826.4	147	147
EO13 Quan	870.6	102.8	147
EO13 Qual	870.6	147	147
EO14 Quan	914.7	102.8	147
EO14 Qual	914.7	147	147
Internal Standard	332.4	126.9, 141, 253.4	NA

The calibration curve and was required not contain analytes above the limit of quantitation (LOQ), which corresponded to the lowest calibration level. Prior to sample analysis, the instrument is calibrated with a ten-point calibration curve as described above. Samples are then bracketed by quality control standards with a maximum of ten samples analyzed between each set of quality control samples. Quality control sets of samples consisted of one solvent blank (spiked with internal standard) to ensure system cleanliness and the two lowest calibration points to confirm accuracy at and near the LOQ and a midpoint. The standards were required to be within +/- 30% of their true value. Internal area counts were also monitored to ensure instrument and were required to be +/-50% of the internal standard area counts in calibration standards.

Butyl Carbitol

Samples were diluted 5 to 50× in methyl tert-butyl ether (MTBE) and spiked with butyl carbitol acetate as the internal standard (100 ppm for samples containing only butyl carbitol and 1 ppm for samples containing mixture) prior to analysis. Butyl carbitol and butyl carbitol stock solutions were prepared from a large aliquot of neat butyl carbitol and butyl carbitol acetate (Sigma-Aldrich, St. Louis, MO) in lab deionized water, respectively, both of which were previously determined to be at a concentration of 1,000,000 ppm. Serial dilutions were prepared with lab deionized water and stored at 0 °C. Butyl carbitol and butyl carbitol acetate standards were diluted in laboratory deionized water and MTBE to create the calibration curve. Butyl carbitol acetate was used as an internal standard due to its similar structure of butyl carbitol. Butyl carbitol analysis was performed using an Agilent 6890 gas chromatography (GC), with an Agilent DB5-MS (30 m × 0.25 mm I.D. × 0.25 µm film thickness) capillary column, coupled with a 5973N mass spectrometry (MS) operated in electron impact (EI) mode. The GC oven temperature was

held at 50 °C for 3 min., then ramped to 100 °C at 45 °C min⁻¹, and further ramped to 270 °C at 15 °C min⁻¹, followed by a 1.5 min. hold. The GC inlet and auxiliary temperatures were set at 280 and 225 °C, respectively. Helium was used as the carrier gas (1 mL min⁻¹, constant flow). MS temperatures were set at 230 and 150 °C for the source and quadrupole, respectively. The analysis was performed in selective ion monitoring (SIM) mode (Table 5).

Table 5. SIM ions used for butyl carbitol analysis.

Analyte	Quantifier ion	Qualifier ion 1	Qualifier ion 2
Butyl carbitol	45.1	57.1	87.1
Butyl carbitol acetate	87.1	43.1	57.1

Calibration curves containing six different butyl carbitol concentrations with butyl carbitol acetate as the internal standards were prepared in MTBE in the range of 2.5 to 100 ppm for samples containing only butyl carbitol and in the range of 0.05 to 5 ppm for samples containing mixture. Calibration curves were fitted with linear regression function and gave $r^2 \geq 0.995$. Prior to sample analysis, the instrument was calibrated with the same six-point calibration curve as described above. Limit of quantitation (LOQ) was determined to be 0.05 ppm based on the lowest concentration of the calibration curves. Method blank, containing deionized water and prepared the same way as the samples, was also analyzed together with the samples. A concentration standard (50 ppm for samples containing only butyl carbitol or 1 ppm for samples containing mixture) was injected every eight samples (calibration curve check) and the concentrations had to be within +/- 30 % of their true value to ensure the calibration curve was still valid. Solvent blank was also injected after every calibration curve check to ensure there was no carryover in the system. Samples were diluted 5 to 50× in methanol and spiked with butyl carbitol acetate as the internal standard (100 ppm for samples containing only butyl carbitol and 1 ppm for samples containing mixture) prior to analysis. Butyl carbitol analysis was performed using an Agilent 6890 gas chromatography (GC), with an Agilent DB5-MS (30 m × 0.25 mm I.D. × 0.25 µm film thickness) capillary column, coupled with a 5973N mass spectrometry (MS) operated in electron impact (EI) mode. The GC oven temperature was held at 50 °C for 3 min., then ramped to 100 °C at 45 °C min⁻¹, and further ramped to 270 °C at 15 °C min⁻¹, followed by a 1.5 min. hold. The GC inlet and auxiliary temperatures were set at 280 and 225 °C, respectively. Helium was used as the carrier gas (1 mL min⁻¹, constant flow). MS temperatures were set at 230 and 150 °C for the source and quadrupole, respectively. The analysis was performed in selective ion monitoring (SIM) mode. Calibration curves were prepared in methanol in the range of 2.5 to 100 ppm for samples containing only butyl carbitol and in the range of 0.05 to 5 ppm for samples containing mixture. Limit of quantitation (LOQ) was determined to be 0.05 ppm based on the lowest concentration of the calibration curves. Method blank, containing deionized water, was also analyzed together with the samples. A concentration standard (50 ppm for samples containing only butyl carbitol or 1 ppm for samples containing mixture) was injected every eight samples to ensure the calibration curve was still valid.

4.8.9. Statistical Analysis

Statistical analysis was performed for each test using average measured concentrations of DOWSIL™ 502W and Butyl Carbitol, while nominal concentrations of Glucopon® 225 DK were used (due to the lack of an analytical method to quantify concentrations). Differences in survival, growth, and/or reproduction (dependent upon species) were evaluated using a statistical computer package (Comprehensive Environmental Toxicity Information System ,CETIS, version 1.8.4.7, Tidepool Scientific Software, version 1.30, McKinleyville, CA, USA) [51] following the USEPA statistical decision tree (USEPA 2002). As the data met the assumptions of normality and homogeneity, the no-observable effect concentration (NOEC) and the lowest observable effect concentration (LOEC) were estimated using an analysis of variance to compare ($p = 0.05$) organism performance in the experimental treatments with that observed in the control.

In the acute *C. dubia* and *P. promelas* tests, survival was the measured endpoint. In the chronic *C. dubia* tests, both survival and reproduction (as total number of neonates per original female) were evaluated. In the short-term chronic *P. promelas* tests, both survival and growth (as mean dry biomass: total dry weight at test termination divided by original number of organisms) were evaluated. In the chronic *R. subcapitata* test, growth (as both cell yield and average specific growth rate) was evaluated. Comparisons between treatments and the laboratory water control were made using a Steel Many-One Rank Sum test or Fisher Exact/Bonferroni-Holm Test according to the USEPA statistical decision tree (USEPA 2002a, 2002b).

For the determination of median-lethal effect concentrations (LC_x) and sublethal effect concentrations (EC_x), two statistical programs were used. The statistical program, Toxicity Relationship Analysis Program, TRAP (version 1.30a, Duluth, MN, USA) [52], was used for the determination of effect concentrations to reduce reproduction or growth by 10%, 20% and 50% relative to control performance (EC₁₀/EC₂₀/EC₅₀). In cases where TRAP identified non-monotonic dose responses, the CETIS package was used in order to plot the responses and analyze using linear interpolation. EC_x statistical analyses of reproduction or growth (or survival in cases where a suitable dose response was observed) were conducted using a weighted regression analysis (mean biological measurement weighted by standard deviation). Exposure concentrations were log-transformed before determination of the EC_x values. Endpoints were estimated using threshold sigmoid regression analysis or linear interpolation.

5. Results and Discussion

5.1. A Well-Defined Reference AFFF

Commercial AFFF solutions contain numerous proprietary components preventing us from isolating the effect of a surfactant on fire extinction from other components in the solution. We need a simple, well-characterized, and known chemical structures to constitute a Reference AFFF formulation to establish baseline properties and performance. We demonstrated that a simple four-component Ref AFFF formulation matches the small and the large-scale fire extinction performance of a commercial AFFF [37]. This Ref AFFF formulation is prepared by mixing 0.2 % Glucopon 215 CS UP (poly-D-glucopyranose with octyl and decyl alkyl chains), 0.3% Capstone 1125 (tridecafluorooctyl sulfonamide alkylbetaine), 0.5% DGBE (diethyleneglycol monobutyl ether) by volume in distilled water. All chemicals are used as supplied. Based on the analytical characterizations of the individual components and the molecular structures of the surfactants contained in the concentrates are shown in Figure 17. The composition of Ref AFFF corresponds

to 3.7 mMole/L of the hydrocarbon surfactant, 1.6 mMole/L of the fluorosurfactant, and 29.3 mMole/L of the solvent in distilled water. We examined two other candidate formulations where Triton X-100 (4-{1,1,3,3-Tetramethylbutyl}-phenyl-polyethylene glycol) was used as the hydrocarbon surfactant at two different ratios. A bench-scale fire extinction apparatus using n-heptane as the fuel enabled us to rank the candidate AFFF formulations, which were qualitatively consistent with the ranking exhibited in the large-scale (Milspec 28 ft² gasoline pool fire) test despite the differences in foam generation methods and fuels used. Use of a bench-scale foam generation method more similar to the large-scale may improve quantitative comparison of fire extinction at different scales. Both bench and large scale fire extinction tests showed that replacing Triton X-100 with Glucopon 215 CSUP as the hydrocarbon surfactant in the candidate AFFF formulations resulted in the reduction of fire extinction time. The Ref AFFF passed a subset of Milspec criteria relevant to fire extinction.

The Ref AFFF formulation may be used for basic research in the study of foam properties and mechanisms important to fire suppression. Also, the development of simple analytical and small scale inexpensive extinction performance apparatus can be used to more effectively screen candidate formulations prior to large scale testing. As to the very difficult challenge of replacing fluorocarbon surfactants in AFFF formulations by fluorine-free surfactants, a simple substitution of a fluorine-free surfactant for the Capstone in the Ref AFFF formulation may not rapidly solve this problem. Progress will require more scientific insight as interactions and synergies between candidate surfactants and other formulation components may play a major role in determining foam formation and properties. However, the Ref AFFF formulation can serve as reference point of known composition with MilSpec extinction qualification.

5.1.1. Designing RefAFFF Composition

Table 6 shows the compositions of three candidate formulations used for making the foams. For a proper comparison of the three candidate formulations, we prepared candidate formulations at concentrations significantly higher (two to five times) than their respective CMC values, which are measured. Based on the above analysis of the individual components, we calculated the actual surfactants' mole ratios and molar concentrations as shown in Table 7, which correspond to the volumetric compositions of the candidate AFFF formulations shown in Table 6. Table 7 defines the Ref AFFF's composition in column four; commercial AFFF's surfactants' contents are proprietary preventing calculation of molar ratios for proper substitution of the fluorosurfactant with alternate surfactant.

Table 6. Candidate AFFF Formulations¹ containing Capstone concentrate (27.5 weight % surfactant), Glucopon concentrate (63.6 weight % surfactant), TritonX-100, and DGBE. The values shown under each column are volume percentages of the individual components (used as supplied by manufacturers) in distilled water [37].

3:1 Cap/Trit	3:2 Cap/Trit	3:2 Cap/Gluc (Ref AFFF)
0.15 % Capstone	0.3% Capstone	0.3% Capstone
0.05% TritonX100	0.2% TritonX100	0.2% Glucopon
1.0% DGBE	0.5% DGBE	0.5% DGBE

¹The formulation compositions shown are used for generating foams and for measuring foam and solution properties.

Table 7. Surfactant mole ratios and molar concentrations for the compositions of candidate AFFF formulations shown in Table 6 [37].

Surfactant or solvent	3:1 Cap/Trit	3:2 Cap/Trit	3:2 Cap/Gluc (Ref AFFF)
fluorocarbon/hydrocarbon surfactants (mole ratio)	1:1	1:2	1:2
tridecafluorooctyl sulfonamide alkylbetaine (mMole/L)	0.8	1.6	1.6
4-(1,1,3,3-Tetramethylbutyl)-phenyl-polyethylene glycol (mMole/L)	0.8	3.3	0
poly-D-glucopyranose (mMole/L)	0	0	3.7
diethylene glycol monobutyl ether (mMole/L)	58.7	29.3	29.3

5.1.2. Evaluation of RefAFFF at Bench Scale

Fire extinction time measurements using the benchtop pool fire extinction apparatus was described in the previous section to compare commercial AFFF and fluorine-free foams. Here, we present fire suppression data for the candidate surfactant formulations and a commercial AFFF, Buckeye. Figure 25 presents time-lapse images of this fire suppression over a 19-cm diameter n-heptane pool fire using a foam application rate of 1500 mL/min for 3:2 Cap/Trit and 3:2 Cap/Gluc formulations and Buckeye. At 0 seconds, the foam is introduced to the pool fire surface after the pool has been burning for 60 seconds. After 12 seconds, Figures 25c, 25k, and 25g show that the 3:2 Cap/Gluc formulation extinguished the fire similar to Buckeye, while the 3:2 Cap/Trit formulation could not completely extinguish the fire even at the highest foam flow rate (1500 ml/min) studied. We noticed fire above the Cap/Trit foam even in the regions of the pool covered with the foam as shown in Figure 25(g). The fire above the foam covered surface of the pool is indicative of fuel leakage through the foam. The fire was extinguished in 25 s using 3:2 Cap/Trit formulation at 1500 ml/min foam flow rate.

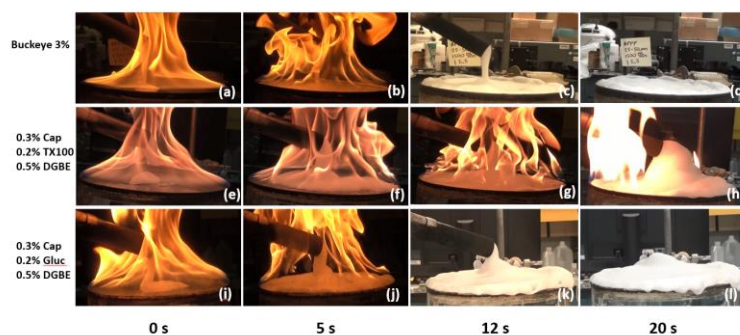


Figure 25. Time-lapse images of Buckeye (a-d), 3:2 Cap/Trit (e-h), and 3:2 Cap/Gluc (i-l) foams extinguishing an n-heptane pool fire at a foam application rate of 1500 mL/min at the center of the pool. Images are taken at times 0, 5, 12, and 20 s during extinction [37].

Figure 26 compares fire extinction times for the candidate surfactant formulations and Buckeye foams at low and high foam flow rates. Figure 26a and 26b show that the extinction times of 3:2 Cap/Gluc formulation are closest to those for the commercial AFFF, Buckeye. But, the two formulations of Cap/Trit have significantly higher fire extinction times. Only one foam flow rate was tested for the 3:1 Cap/Trit formulation. Figure 26 shows that replacing the hydrocarbon surfactant Triton -100 with Glucopon has reduced the extinction times.

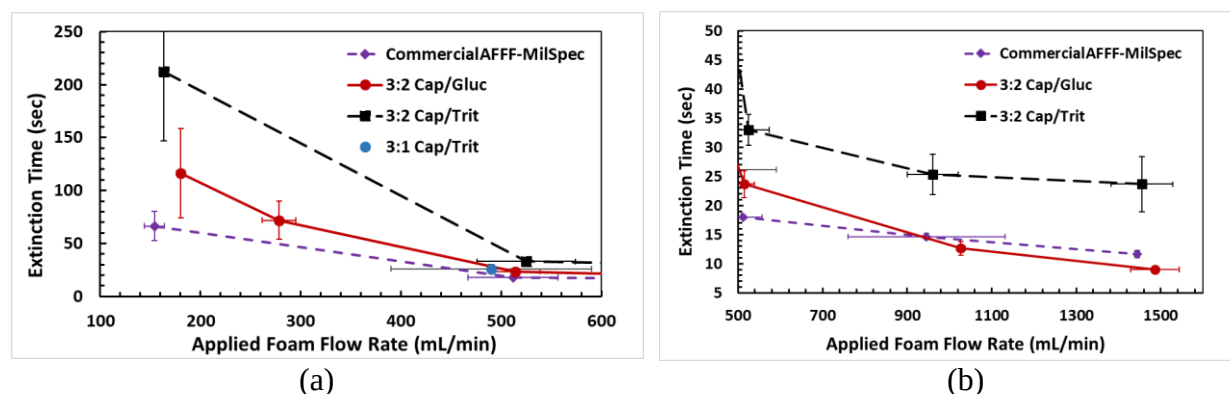


Figure 26. Bench-scale fire extinction of n-heptane pool fire showing extinction time of candidate surfactant formulations relative to the commercial formulation (Buckeye) (a) at low foam application rates, (b) at high foam application rates [37], at the center of the pool.

5.1.3. Evaluation of RefAFFF at Large Scale

To further develop the Ref AFFF we progressed from the 0.4 ft² bench-scale apparatus with a sparged foam delivery system to the 28 ft² MilSpec standard pool fire [4]. We focused on a subset of five required metrics in the MilSpec standard MIL-F-24385 to evaluate the candidate AFFF and a commercial AFFF (Fomtec) formulations wherein we measured five parameters and compared with passing metrics. The parameters measured were (1) 28 ft² gasoline pool fire extinction time, (2) burnback time, (3) film and seal, (4) expansion ratio, and (5) 25% drainage time, and are described in MilSpec standard MIL-F-24385. Results are presented in Table 8.

Both the 3:2 Cap/Gluc and the Fomtec formulations passed all five criteria. Both 3:1 Cap/Trit and 3:2 Cap/Trit failed fire extinction and burn back tests. The results are a little

surprising in that the commercial AFFF formulations contain 10 to 12 components, but a four component 3:2 Cap/Gluc formulation successfully extinguished a pool fire in under 30 seconds; some of the components in the commercial AFFF are needed to meet all aspects of the MilSpec while the Ref AFFF is designed to meet mainly the fire extinction metrics. This work gives insight into the role of hydrocarbon surfactants in fire suppression in that extinction performance appears to be directly related to the surfactant type.

Table 8. Comparison of candidate AFFF formulations with a commercial AFFF (Fomtec) and MilSpec criteria [37].

MilSpec Test	Criteria	3:1 Cap/Trit	3:2 Cap/Trit	3:2 Cap/Gluc	Fomtec
Extinction (s)	< 30	54	37	26	23
Burnback (s)	>360	295	358	562	496
Film and Seal	PASS	PASS	FAIL	PASS	PASS
Expansion Ratio	5-10	7.35	7.41	7.46	7.6
25% Liquid Drainage (s)	>150	238	295	317	281

Based on measured fire extinction times, Table 8 shows a ranking of the candidate surfactant formulations that is similar to that found using the bench-scale extinction apparatus, when the full range (150 ml/min to 1500 ml/min) of foam flow rates are considered. The bench-scale apparatus is a qualitative tool able to identify the superior performing surfactant consistent with the large scale test. However, it is unclear as to the ability of the bench-scale test to show quantitative agreement with the large scale test at a fixed foam application rate per unit area of the pool because of significant differences in foam generation and foam properties.

Table 9 lists arithmetic average bubble sizes, which show that the air-aspirated foams have 2 to 2.5 times smaller average bubble sizes than the sparged foams for all of the surfactant formulations examined. The initial bubble size distributions at large-scale are likely even smaller than shown in Table 9 because of significant coarsening that could have occurred during the 5 minutes after their generation. Due to issues collecting foam and filming at large-scale, data collection could not begin until 5 minutes into foam lifetime. Among different formulations examined, Table 9 shows that the arithmetic average bubble sizes differ by less than 35% for the sparged and 19% for the air-aspirated nozzle foams, respectively. Table 9 suggests that the differences in surfactant formulations examined in this report have a smaller effect on the bubble size relative to the generation methods. It is also possible that the hydrocarbon surfactant effect on bubble size is small compared to the effect of the fluorosurfactant, whose replacement with a fluorine-free surfactant is the ultimate research goal. Both commercial foams Buckeye and Fomtec were MilSpec qualified and the differences in average bubble sizes are expected to be small.

Table 9. Measured foam properties for the three candidate and commercial AFFFs at bench and large-scales respectively [37].

Scale	Property	3:1 Cap/Trit	3:2 Cap/Trit	3:2 Cap/Gluc	Commercial AFFF ¹
Bench scale	Expansion ratio	10.63 ± 0.44	14.67 ± 2.47	8.19 ± 0.82	6.68 ± 0.92
	Bubble Diameter (mm)	0.35 ± 0.08	0.47 ± 0.03	0.36 ± 0.02	0.37 ± 0.03
	25% liquid Drainage (s)	108 ± 3	55 ± 2	53 ± 2	68 ± 1
Large Scale	Expansion ratio	7.35	7.41	7.46	7.6
	Bubble Diameter (mm)	0.17	0.19	0.16	0.18
	25% liquid drainage	238	295	317	281

¹Commercial AFFF was Buckeye for bench-scale measurements and Fomtec was used in large-scale measurements. Both Buckeye and Fomtec were MilSpec qualified; MilSpec testing of Buckeye gave expansion ratio of 9.4, 360 s for 25% liquid drainage, 30 s extinction time for 28 ft² gasoline pool fire, 500 s for 25% burnback time, and pass for film and seal test.

5.2. Role of Surfactants in AFFF

In this report, we evaluated fire suppression performance of a fluorocarbon surfactant and two hydrocarbon surfactants, both individually and as mixtures to quantify the role of a surfactant in fire suppression [53]. The fire suppression performance was also evaluated on a large-scale gasoline fire (28 ft² US MilSpec), which showed trends consistent with the bench-scale evaluations. To understand how a surfactant affects fire extinction, we examined the surfactant's effect on three different contributing mechanisms; (1) aqueous film formation by measuring the spreading coefficients, (2) fuel-foam layer interactions by measuring foam spread rates, fuel transport rate through a foam layer, and foam layer degradation rate by fuel, and (3) foam structure by measuring bubble diameters, bubble coarsening, and liquid drainage from the foam in the absence of a fuel [45]. The three contributions are quantified independently in the absence of a fire; it is very difficult to quantify them during the fire extinction measurements. Based on these independent measurements, we found that trends in fire extinction performance among different

surfactants can be explained by trends in fuel-foam layer interactions as measured by foam spread rates, fuel transport rates, and foam degradation rates [53]. The measurements for the six formulations show that surfactants that reduce foam degradation and fuel transport through a foam layer covering a hot pool can lead to more rapid extinction of heptane pool fires. A fluorocarbon surfactant is especially effective in suppressing foam degradation and fuel transport rates through a foam by quickly covering the pool, extinguishing the fire rapidly by blocking the fuel supply to the fire. Furthermore, for the surfactants and conditions employed in this work, trends in fire extinction performance among different surfactants did not directly follow trends in aqueous film formation or foam properties [53]. The molecular mechanisms by which a surfactant affects fuel-foam interactions remain unclear and their understanding is needed to design effective fluorine-free replacement surfactants.

5.2.1. Effect of Surfactants on Fire Extinction

Table 10 shows the five compositions of surfactant solutions contained RefAFFF and their mixtures. The component surfactant solutions were made with 0.5 weight % total surfactant concentrate supplied by the manufacturer, 0.5 weight % DGBE, and the remainder distilled water. The surfactants evaluated individually and as mixtures had critical micelle concentrations well below the 0.5 weight % concentrations in the surfactant solutions. Five formulations were made to compare the fire extinction performance of fluorocarbon, hydrocarbon, and mixtures of the two surfactants. The five-surfactant formulations along with a commercial AFFF, Buckeye 3%, were characterized through foam and solution properties [53].

Table 10. Surfactant formulations; Cap+Gluc215 formulation is also referred to as RefAFFF [53].

Cap+TX100	Cap+Gluc215	Cap	Gluc215	TX100
0.3% Capstone	0.3% Capstone	0.5% Capstone	0.5% Gluc 215UP	0.5% Triton X100
0.2% Triton X100	0.2% Gluc 215UP	0.5% DGBE	0.5% DGBE	0.5% DGBE
0.5% DGBE	0.5% DGBE	distilled water	distilled water	distilled water
distilled water	distilled water			

5.2.2. Components versus Mixture (RefAFFF) - Bench Scale

Figure 27 compares interesting fire suppression behavior between the Cap solution, the RefAFFF, and the Gluc215 solution. At foam application rates less than 500 mL/min, Figure 27(a) shows that the Cap foam suppresses the fire faster than a mixture of Cap with Gluc215 or TX100. This does not correlate with aqueous film formation being the key player; Capstone alone does not form an “aqueous film” on heptane [5, 12, 14] unlike Cap+Gluc215. For example, at 250 mL/min foam flow rate, Cap foam extinguishes the fire in 40 seconds compared to the 70 to 100 seconds for the surfactant formulations that include TX100 or Gluc215. A similar inconsistency is found in the large-scale results on gasoline discussed later. Furthermore, at a fixed foam flow rate, Figure 27(a) shows that the extinction time increases in the order Cap, Buckeye, Cap+Gluc215 or Cap+TX100, TX100, and Gluc215. There is a significant variation (e.g., up to 75 s at 100 mL/min foam flow rate) in extinction time as indicated by a cluster of three points at low foam flow rates, and the error decreases with increasing foam flow.

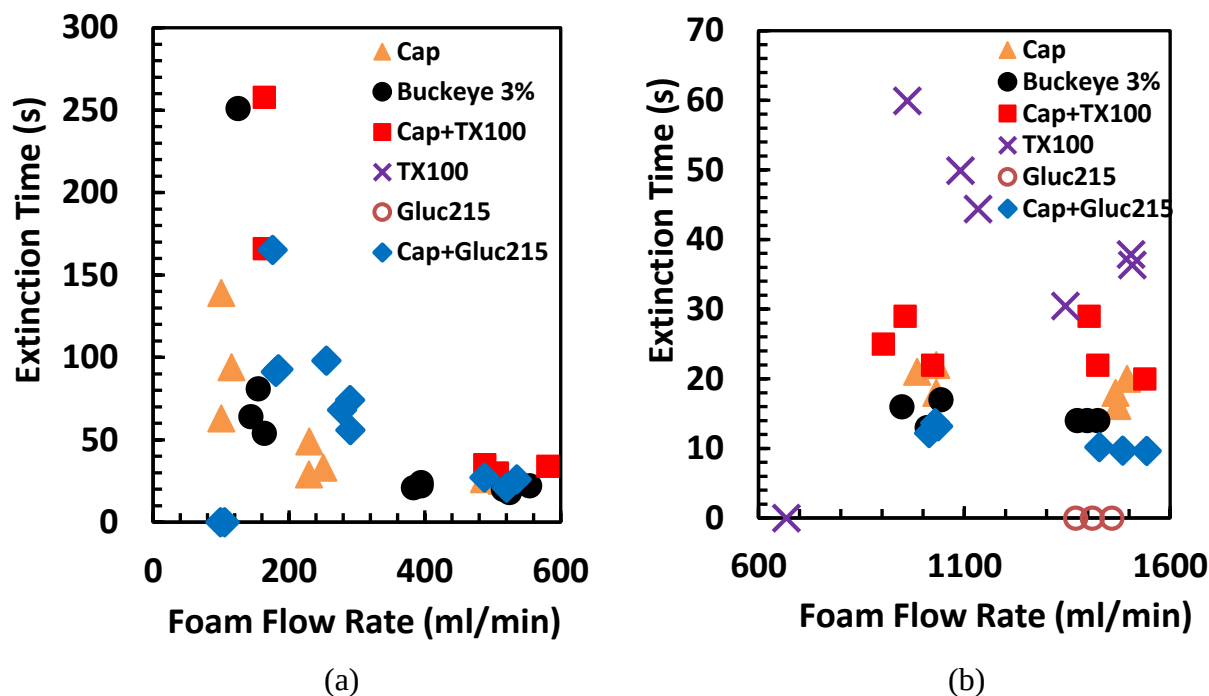


Figure 27. Bench-scale heptane-pool fire extinction results for foam formulations shown in Table 10 and a commercial AFFF at (a) low foam application rates, and (b) high foam application rates, at the center of the pool. Points along the x-axis indicate a foam flow rate at which extinction did not occur in 5 minutes. Even though three extinction time data points were collected at each airflow rate, they are presented as individual points in the figure because of the variability in the measured foam flow rates [53].

Above 500 mL/min foam application rates, the fire extinction times for Cap+Gluc215 are slightly smaller by 5 to 10 s than those for the Cap only solution as shown in Figure 27(b); the error in extinction time was 5 s at 1400 mL/min. The surfactant mixture containing TX100 took longer to extinguish the fire than the fluorosurfactant alone at all foam application rates shown in Figure 27. At a fixed foam flow rate, the fire extinction time increases in the order Cap+Gluc215, Buckeye, Cap, Cap+TX100, TX100, and Gluc215. The data in Figure 27 show that the effect of hydrocarbon surfactant on extinction performance depends on the foam application rate. The extinction times in Figure 27 vary nonlinearly with the foam flow rates, and are sensitive to small variations in foam flow rate especially below 500 mL/min. Small variations (< 100 mL/min) in foam flow rate occur despite accurately fixing the air flow rate (to the sparger generating the foams, 1% error) across three repeated measurements. Therefore, we decided to display three repeated experiments at a fixed air flow as individual points in Figure 27 rather than averaging.

One may expect the fire extinction times for the surfactant mixture containing Gluc215 and Cap to be in between the extinction times for the individual surfactants following the law of averages. But, there is a slight synergistic effect between Cap and Gluc215 on fire extinction. Figure 27(b) shows that the mixture (Cap+Gluc215) foam has slightly more rapid extinction than Cap and very rapid extinction relative to Gluc215 for foam application rates greater than 500 mL/min. Also, one may expect a mixture of Cap and TX100 to exhibit more rapid fire extinction than the Cap+Gluc215 solution. This would be because TX100 can extinguish the fire at some

foam flow rates whereas Gluc215 cannot as shown by the open circle along the x-axis in Fig. 27(b). Figure 27 shows the opposite behavior because of slight synergism between Cap and Gluc215 and no apparent synergism with TX100. Although slight synergism between Cap and Gluc215 can be seen at high flow rates, at foam application rates below 500 mL/min the Cap solution extinguishes faster than the Cap+Gluc215 solution. This is because Cap foam is very wet and the foam spreads faster as will be discussed in more detail later in the report.

5.2.3. Components versus Mixture - Large Scale

Fire extinction time of a 28 ft² gasoline pool fire, burnback time, aqueous film formation by film and seal test, expansion ratio, and 25% liquid drainage time are recorded in Table 11 [53]. The first row lists the necessary criteria for a foam to pass MIL-F-24385F and the other rows list the measurements made for different formulations. The film and seal test was measured with cyclohexane. Only one test per surfactant formulation was performed in view of the limited resources and materials required for the large-scale.

Table 11. Large-scale pool fire data collected over a 28 ft² gasoline pool fire, with foams generated from some of the surfactant formulations listed in Table 6 using an aspirated nozzle at 2 gpm solution flow rate as detailed by MIL-F-24385F.

Foam	28 ft² Ext Time (s)	Burnback Time (s)	Film and Seal	Expansion Ratio	25% Liquid Drainage Time (s)
<i>MilSpec Criteria</i>	< 30	> 360	No flame	5-10	> 150
Cap+TX100	37	358	Flame	7.41	295
Cap+Gluc215	26	562	No flame	7.46	317
Cap	24	505	No flame	7.80	695
Buckeye 3% (2003)	30	500	No flame	9.40	360

Large-scale extinction results given in Table 11 show similar fire extinction times for the fluorocarbon surfactant (Cap, 24 s) without and with a glycoside hydrocarbon surfactant (Cap+Gluc215, 26 s), and the commercial AFFF (Buckeye 3%, 30 s). The fluorosurfactant (Cap) solution also shows a burnback time similar to the commercial AFFF, and the longest drainage time of the four formulations. This limited test series shows that the fluorosurfactant solution, without a hydrocarbon surfactant, rapidly suppresses a gasoline pool fire, passing the MilSpec requirements shown in row 1 of Table 11 and is consistent with the tests performed by Tuve et al. [1, 5]. This is inconsistent with spreading coefficient values; the Cap solution has a smaller spreading coefficient than Cap+Gluc215 by 2.3 mN/m on cyclohexane (0.9 mN/m smaller for gasoline, as will be shown later in the paper). The measurements also show that the fire extinction time increases and burnback time decreases when the hydrocarbon surfactant is switched from Gluc215 to TX100. The effect of the identity of the hydrocarbon surfactant on fire extinction is significant. Clearly, a surfactant's effect on fire extinction is critical and the fluorocarbon surfactant is so effective that a simple mixture with a solvent can meet one of the most stringent MilSpec fire performance for a 28 ft² gasoline pool.

5.2.4. Components versus Mixture – Foam/Fuel Interaction Dynamics

To explain the fire extinction results, foam degradation by heptane and fuel permeation through a foam layer (4 cm thick) covering a hot (60°C) fuel pool were measured in the absence of a fire [53]. Foam degradation is defined as the decrease in foam layer thickness. Change in foam layer thickness due to degradation versus time is plotted in Figure 28. The foam lifetimes at 100% degradation increase in the order Cap+Gluc215, Cap, Buckeye, Cap+TX100, Gluc215 or TX100. Foam degradation data show long foam lifetimes for fluorinated foams, including the commercial AFFF, Buckeye 3%, but rapid foam degradation for foams without fluorocarbon surfactants (Gluc215 and TX100). The hydrocarbon only foams degrade in under 3 minutes. The Cap solution, the Cap+TX100 solution, and Buckeye 3% degrade in a similar time around 35-45 minutes, whereas the Cap+Gluc215 solution degrades in 60 minutes over a heated heptane pool. The rapid foam degradation of hydrocarbon-only solutions provides insight into their limited use as fire suppressing foams unlike the fluorocarbon surfactant containing foams.

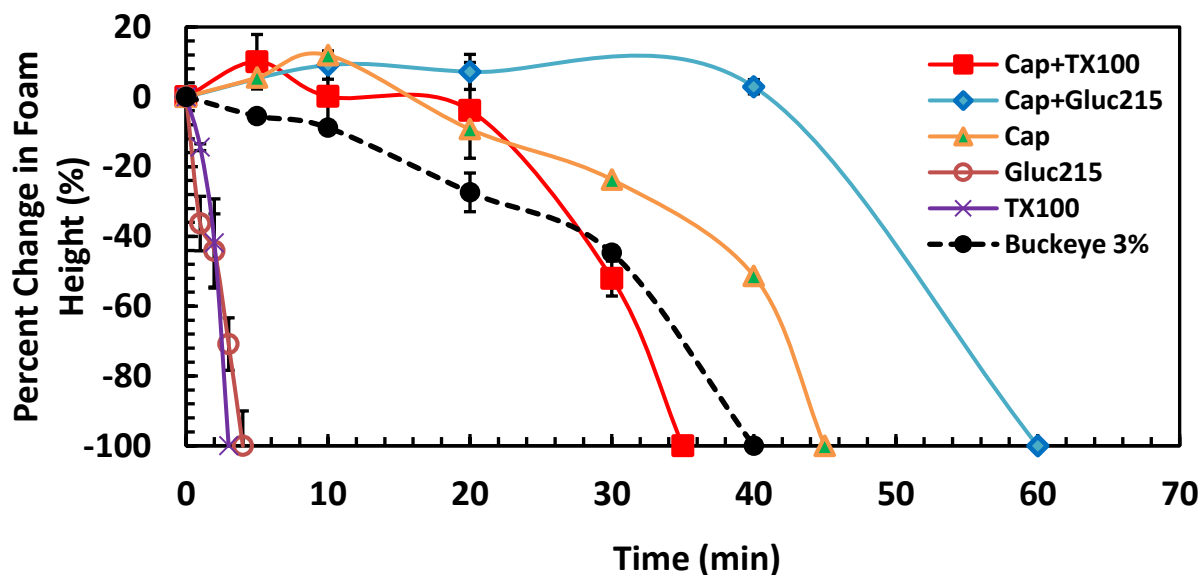


Figure 28. Percent change in foam layer thickness versus time over 60°C heptane for five foam formulations listed in Table 10 and a commercial AFFF, Buckeye 3%. The error bars represent one standard deviation from the averaged value of three trials for each foam [53].

Fuel vapor flux through foams were also quantified for the six foams as shown in Figure 29. The fuel fluxes increase in the order of Cap+Gluc215, Cap or Buckeye, Cap+TX100, Gluc215, and TX100 at ten minutes time. The measured fuel flux for the Cap foam was found to be comparable to that of a commercial AFFF. Synergism between Capstone and Glucocon 215 UP is seen in fuel transport in Figure 29; the Cap+Gluc215 foam had about half the fuel flux of the Cap foam and more than 10 times smaller flux than the fuel flux of the Gluc215 foam after 6.7 min. This synergism is not seen between Capstone and Triton X100, similar to the lack of synergism in foam degradation between the two individual surfactants. The measured fuel flux for the Cap+TX100 foam is in between the fuel flux for the TX100 and Cap foams. The addition of Triton X100 to Cap increases the fuel flux by a factor of 2 but has only a small effect on foam degradation. Even though synergism between fluorocarbon surfactants and hydrocarbon surfactants has been

shown in spreading and wetting [28], to our knowledge, Figure 29 is the first report of synergistic enhancement in fuel transport.

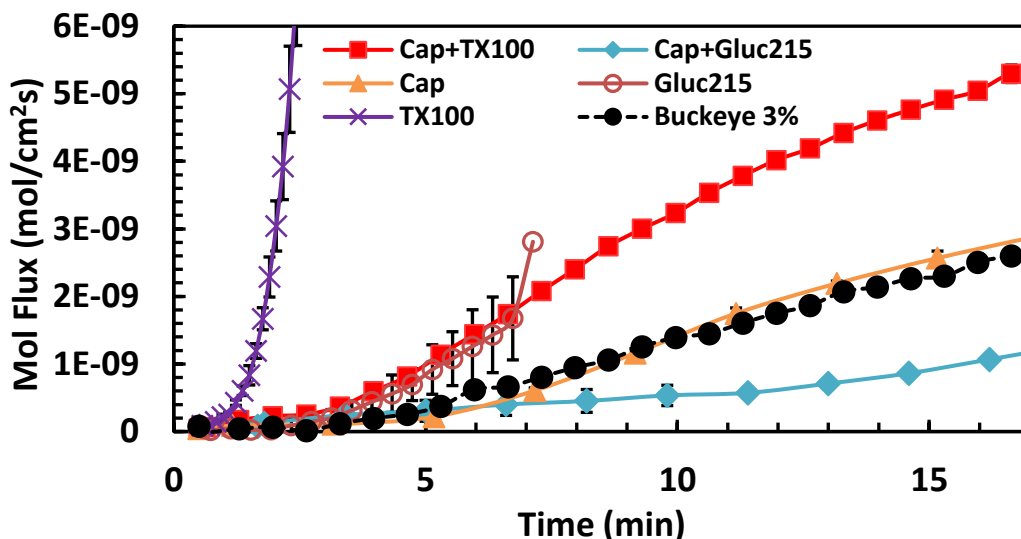
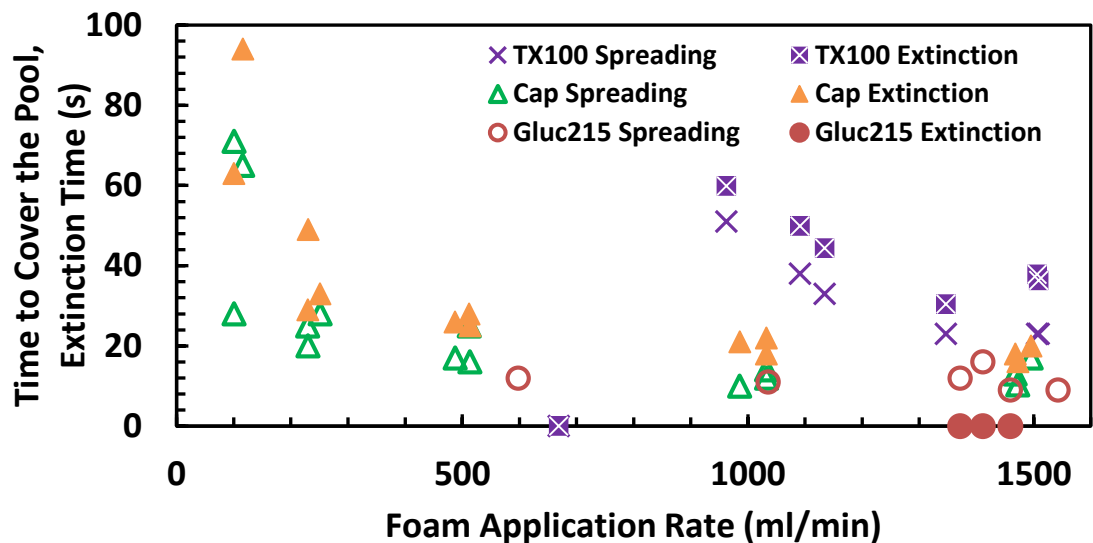


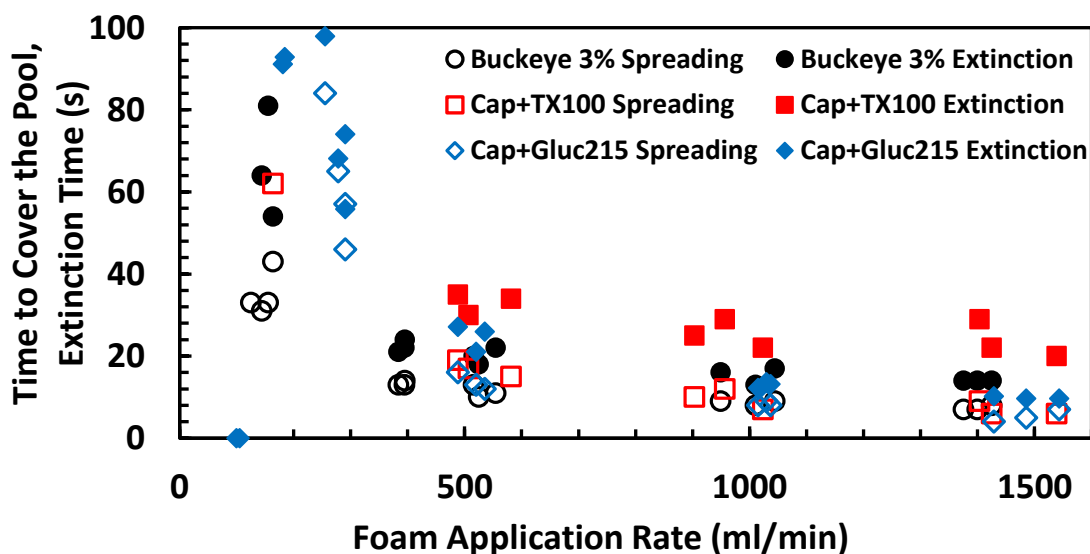
Figure 29. Fuel flux over time through a foam layer (4 cm initial thickness) covering a heptane pool at 60°C for the five formulations shown in Table 10 and Buckeye 3%. The error bars represent one standard deviation from the averaged value of three trials for each foam[53].

During an extinction experiment, foam is applied at the center of a burning heptane pool at a constant rate. For some surfactant formulations, typically a thin layer of foam spreads initially and covers the entire pool, coverage time is noted based on visual observation. However, the pool continues to burn after complete coverage. As the foam application continues, the foam layer builds up and thickens (visually) near the center where the fire is extinguished. But, the edges of the pool continue to burn until a thicker foam layer builds and extinguishes the edge flames, and the extinction time is noted. Figure 30 plots pool coverage and extinction times versus foam flow rates for the individual surfactant solutions in Figure 30(a) and for the mixtures as well as Buckeye 3% solutions in Figure 30(b).

Figures 30(a) and (b) demonstrate that the foam spreading time (not aqueous film spread time) decreases as the foam application rate increases. At low foam flow rates, Cap foam spreads faster on the pool compared to Cap+Gluc215 and the other four formulations; Cap spreads in 25-70 s compared to other formulations, which could not cover the pool surface at 100 mL/min foam flow rate in Figure 30. The reasons are due to unique foam properties of Cap at very low foam flow rates that are used in the sparging method. For Cap only formulation, we found that the expansion ratio decreases from 8 to 4 as the foam flow rate is decreased. For most surfactant formulations, the expansion ratio typically increases from 7 to 12 as the foam flow rate is decreased because foam accumulated in the foam generation cup drains liquid for a longer time before exiting on to the burning pool. We also found that the expansion ratio of Cap+TX100 foam remains high (13) as the foam flow rate decreased.



(a)



(b)

Figure 30. Time for full coverage of a 19 cm heptane pool surface and extinction times for foams generated from the (a) individual surfactants and (b) the surfactant mixture solutions at various foam flow rates applied at the center of the pool. Three extinction-time and coverage-time data points were collected at each airflow rate and are presented as individual points in the figure due to variability in the measured foam flow rates. Data points shown along x-axis indicate foam flow rates where no extinction occurred; the figures show all pool coverage data but not all of the corresponding foam flow rates where extinction did not occur [53].

Trends in fire extinction among the surfactant formulations can be related to the trends in foam degradation, fuel transport, and foam spread rates. A surfactant can affect foam degradation by fuel and fuel vapor transport through foam, which can affect the foam spread rate and fire extinction time depending on the foam application rates. Figure 31(a) shows fuel transport times as functions of foam lifetimes for different surfactant formulations. The fuel transport times are

defined as times to reach the lower flammability limit of 1.1 volume % at the foam surface and is obtained from Figure 29 as time to reach a corresponding fuel flux of 5.4×10^{-9} mol/cm²s. The fuel concentration of 1.1 volume % is 28 times smaller than the vapor pressure (28 volume %) of heptane at 60°C. An increase in foam lifetime increases the fuel transport time or decreases the fuel flux through a foam covering a pool. As the foam degradation is decreased, foam can better maintain the barrier to fuel vapor transport through the foam layer, and surfactants that decrease foam degradation decrease fuel vapor transport rate or increase the fuel transport time. Figure 31(b) shows the foam flow rates needed to achieve a 30 s fire extinction time as function of fuel transport times for different surfactant formulations; the foam flow-rate values are obtained from Figure 27 that shows extinction time as a function of foam flow rate. The smaller the foam flow rate at 30 s extinction, the better fire extinction performance as the foam can rapidly suppress the fire with minimal amount of foam. As the fuel transport time is increased, fuel transport rate through the foam layer is decreased. As the rate at which fuel feeds the fire is decreased, the fire is extinguished faster and the foam flow rate needed to achieve 30 s extinction decreases. Figure 31(b) shows that the surfactants that decrease fuel transport rates decrease fire extinction time.

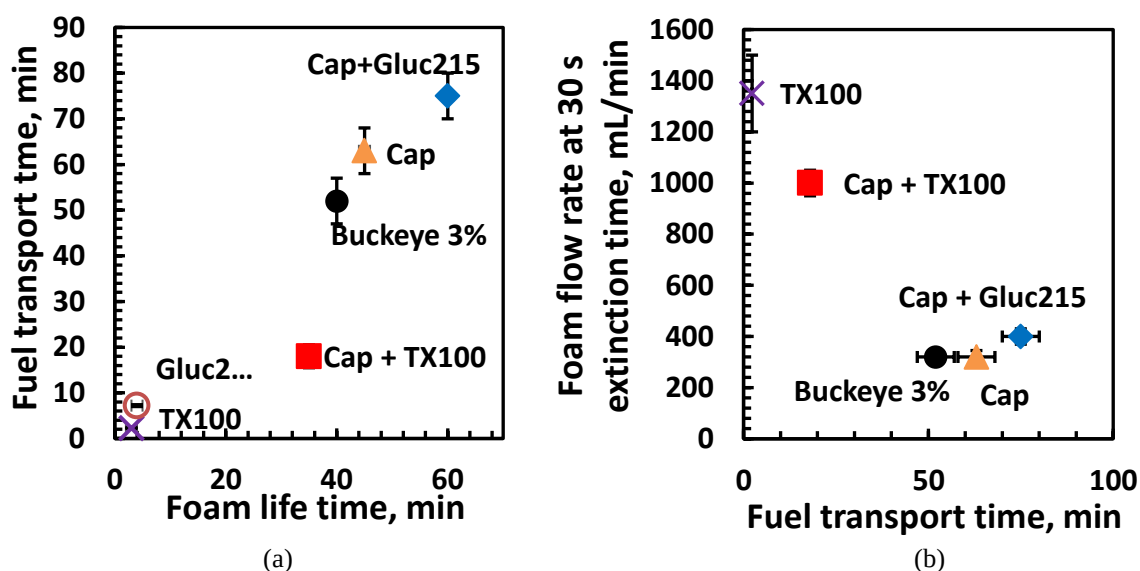


Figure 31. (a) Foam transport time for heptane vapor concentration to reach the lower flammability limit 1.1 volume % (or flux 5.4×10^{-9} mole/cm²s) on a foam surface versus foam lifetime, (b) foam application rate needed to achieve 30 s heptane-fire extinction time versus fuel transport time. Fuel transport times are longer than foam life times because foams lasted longer in the closed chamber used in the transport measurements than in the open beaker used for foam life time measurements [53].

When foam application rate is much larger than foam degradation rate, foams spread quickly to cover the pool, and the trends in fire extinction time are qualitatively consistent with the trends in fuel transport. The extinction times increase as the fuel transport rates increase in the order Cap+Gluc215, Buckeye, Cap, Cap+TX100 at foam application rates greater than 500 mL/min in Figures 27 and 29. Synergistic effects between Cap and Gluc215 lead to half the fuel flux for the mixture Cap+Gluc215 compared to Cap and resulted in small synergistic effects in fire extinction times for the mixture. When the foam application rate is comparable to or smaller than

the foam degradation rate, foam spread is affected by foam degradation. The trends in pool coverage times are largely consistent with measured foam lifetimes, and the coverage times increase in the order Cap or Buckeye, Cap+TX100, Cap+Gluc215, TX100, and Gluc215 at a foam flow rate of 300 mL/min in Figures 28 and 30. At very low foam flow rates (100 mL/min), Cap foam has low expansion ratio (4.5) and spreads faster than Cap+Gluc215 mixture as shown in Figure 30, despite the slightly longer (by 30%) foam lifetime of the mixture. Fire extinction times follow the same trends as in pool coverage times in Figure 30. They can be influenced by both foam degradation and fuel transport, which vary significantly among the surfactant formulations.

In general, foam degradation rates, fuel transport rates, foam spread rates, and fire extinction times for surfactant mixtures, Cap+TX100, Cap+Gluc215, are closer to the values measured for the fluorocarbon surfactant, Cap, than to the individual hydrocarbon surfactants (TX100, Gluc215). The two hydrocarbon foams degrade so rapidly by heptane, that their pool coverage times are influenced greatly by foam degradation even at high foam application rates (1500 mL/min). The fire extinction times for TX100 are not completely consistent with its similar foam lifetime and higher fuel transport rate than those for Gluc215. This could be due to the influence of slow spreading dynamics of TX100. At 1400 mL/min foam flow rate, we noticed that the TX100 foam forms a thick layer that spreads slowly exposing a smaller area of the foam to the fuel pool, which could result in reduced degradation by the fuel, unlike Gluc215 foam, which spreads as a relatively thin layer covering the entire pool area relatively quickly. For a quantitative relationship, one must investigate the dynamics of foam application, foam spread, fuel transport, foam degradation, and fire suppression. Also, heat transfer from fire to the foam can increase foam degradation and fuel transport rates during the fire extinction process. Heat effects on foam degradation and fuel transport should be included in the above analysis in future works.

5.2.5. Role of Aqueous Film Formation in AFFF

Aqueous film formation is thought to be essential for forming an effective barrier to block the flow of fuel vapors from the pool surface to the fire, leading to rapid fire suppression. Tuve [5] reported that a fluorosurfactant only solution did not form an aqueous film on an n-heptane pool. However, Figure 27(a) shows that the Cap foam suppresses a heptane fire more rapidly than the rest of the formulations without the aqueous film formation on heptane. In an effort to correlate aqueous film formation to the bench-scale extinction results, spreading coefficient data were collected over heptanes (mixture of isomers, Tilley Chemical Co., Middle River, MD). Even though the film and seal test discussed under MilSpec tests in Table 11 shows the formation of an aqueous film on cyclohexane (except for Cap+TX100), one must measure the spreading coefficient for the same fuel used in extinction experiments. Because heptane is used in the bench-scale tests and gasoline in large-scale tests described in this paper, the film spreading coefficients were calculated for heptane and gasoline fuels.

The measured surface tension data in Table 12 show that the formulations containing a fluorocarbon surfactant have lower surface tensions than the individual hydrocarbon surfactants (Gluc215 and TX100) consistent with the values reported in the literature [28]. Also, mixtures of hydrocarbon and fluorocarbon (Cap) surfactants have a lower interfacial tension with heptane (1-3 mN/m) than Cap, which has an interfacial tension above 5 mN/m consistent with previous reports. More importantly, the fluorocarbon solution (Cap) has a negative spreading coefficient on heptane indicating a lack of aqueous film formation and is consistent with the observation of the

lack of a film on an n-heptane pool surface reported by Tuve [5]. In contrast, Cap+Gluc215 has a positive spreading coefficient on heptane indicating aqueous film formation on a heptane pool. Regardless of the spreading coefficients, both Cap and Cap+Gluc215 formulations extinguished a heptane pool fire effectively as shown in Figure 27. For gasoline, Table 13 shows positive spreading coefficient data for the Cap and Cap+Gluc215 solutions consistent with the film and seal test results reported in Table 11. However, Cap has a smaller spreading coefficient than Cap+Gluc215 and yet, Cap and Cap+Gluc215 extinguished the fire in 23 and 26 seconds respectively as shown in Table 11. Therefore, there appears to be no direct or consistent correlation between spreading coefficients and fire extinction for the six formulations listed in Table 10. However, direct measurements of aqueous film under fire conditions are needed to quantify its contribution to fire extinction and are very difficult to perform.

Table 12. Measured surface tensions and interfacial tensions between heptane and different surfactant formulations, and Buckeye 3% at 16°C. The film-spreading coefficient given by Eq. (1) was calculated using the measured surface tension of heptane, 20.4 mN/m at 16°C [53].

Foam	Surface Tension (mN/m)	Interfacial with Heptane (mN/m)	Spreading Coefficient (calculated, heptane)
Cap+TX100	16.8 ± 0.5	2.9	0.7
Cap+Gluc215	16.7 ± 0.5	1.9	1.8
Cap	15.3 ± 0.5	5.2	-0.1
Gluc215	31.1 ± 0.5	2.9	-13.6
TX100	27.8 ± 0.5	2.4	-9.8
Buckeye 3%	16.4 ± 0.5	1.5	2.5

Table 13. Measured interfacial tensions between cyclohexane, gasoline, and two formulations: Cap and Cap+Gluc215. The film spreading coefficient given by Eq. (1) was calculated using the measured surface tension of cyclohexane and gasoline: 23.9 and 21.5 mN/m respectively at 18°C [53].

Foam	Interfacial with Cyclohexane (mN/m)	Interfacial with Gasoline (mN/m)	Spreading Coefficient (calc, cyclo)	Spreading Coefficient (calc, gasoline)
Cap+Gluc215	1.9	1.0	5.3	3.8
Cap	5.6	3.3	3.0	2.9

5.3. QSAR and EPA Suite Modeling Results

The approach and modeling methods are described in Section 4.12. The results are described here. Information gathered on each surfactant investigated is recorded in the following tables. The goal is to use the data to generate a general understanding of the environmental risk of each surfactant. The values generated by EPI Suite for the charged head groups are unreliable because the training sets of molecules used to create the algorithms used by EPI Suite were largely neutral, nonpolar molecules. The positively charged head group (ammonium group) typically imparts greater toxicity. Thus, cationic surfactants were not modeled at this time because of their known toxicity to organisms. Most of the surfactants listed currently are used as detergents, so these chemicals are assumed to have low environmental risk. Because of the assumed low risk, little information is found in databases like TOXNET.

Chemical Properties. Surfactants with high boiling points and low vapor pressure have low volatility. Low volatility limits the ability of the surfactant to undergo long-range atmospheric transport. Octanol-water partitioning (log Kow) relates to the partitioning of the surfactants in the environment. High log Kow values indicate that the surfactant will preferentially sorb to soils and sediments, as well as to biota, with a smaller fraction remaining dissolved in water. The Kow partition coefficient also serves as a predictor of bioaccumulation, another property to be aware of during environmental risk assessment. Bioconcentration Factor (BCF) and Bioaccumulation Factor (BAF) both estimate the ability of a chemical to bioaccumulate in tissues of organisms. High BCF/BAF values should be avoided to lower the environmental risk of the final formula. Biodegradability is a strongly desired property for the chemicals under consideration. Ready biodegradability (generally tested under aerobic conditions) indicates the surfactants will not be persistent in environmental systems, lowering overall risk. One of the biggest issues associated with fluorinated components in AFFFs is their inability to be degraded biologically.

Acute and Chronic Toxicity. Acute and chronic toxicity data are reported to give an impression of the relative toxicity of each surfactant. Values are reported as LC50 (Lethal Concentration to kill 50% of the population), LD50 (Lethal Dose to kill 50% of the population) and EC50 (Half maximal effective concentration). The difference between the three measures is small. While LC50 relates to the concentration (in water) for the test exposure, LD50 values are the dose given to animals. The EC50 is used to report any type of effect, but in this case only adverse effects (death or reproductive effects) are reported.

A chemical is considered “very toxic” if LC50 or EC50 values are ≤ 1 mg/L, “toxic” if > 1 mg but ≤ 10 mg/L, and “harmful” if the LC50 or EC50 is > 10 mg/L but ≤ 100 mg/L (Globally Harmonized System of Classification and Labeling of Chemicals). Chronic toxicity refers to long lasting effects.

The NOEL and NOEC (No observed effect level and no observed effect concentration respectively) both indicate the lowest tested concentration of a chemical, which did not cause a response in the organism.

Silicone Surfactants. No structures were available for the silicone surfactants (Siltech Silsurf J208 and Helena Sillwet L77), thus, making them unusable for EPI Suite modeling. The only source of information for most of them was provided by the manufacturers themselves (Table 14). The very limited information provided classifies these as acutely nontoxic and biodegradable (Table 14); however, no data were provided to support these conclusions.

In addition to the surfactants listed, several silicone-based surfactants are proposed for synthesis in this project. Since these structures do not exist, no data are available on their properties. Because the head groups are charged, properties estimations are unreliable; however, it is possible to examine the effects of changing the non-polar tail on properties. By directly comparing the EPI Suite output for tail types and lengths, several general trends were observed. Increased silicone-methyl group density generally resulted in increased log Kow values (greater potential

Table 14. Commercial silicone-based surfactants.* All information provided by the chemical manufacturers.

Product Name:	Siltech Silsurf J208	Helena Silwet L77
Description	Polydimethylsiloxane polymer ¹	Polyalkyleneoxide modified heptamethyltrisiloxane
European Community No.	614-822-8	NA
CAS No.	68937-54-2	proprietary
bioaccumulation potential	none	NA
biodegradation potential	degrades in soil	readily biodegradable
acute toxicity to fish	No adverse effects	NA
Rat LD50 (mg/kg)	NA	2,330
Rabbit LD50 (mg/kg)	NA	2,640

¹ECHA

LD50= Lethal Dose to kill 50% of the population

- Not included in the table are Siltech Silphos J208, Siltech Silquat A0, Siltech Silteric A0, Dow FZ7604, and Dow FZ-2123. These were not included because information on these surfactant could be found from the manufacturer or any other database.

bioaccumulation and partitioning in general) and lower (more toxic) LC/EC50 values. Silicone tails with high amounts of methylation and branching may also be more resistant to biodegradation.

Nonionic Surfactants. The properties of nonionic (polysaccharide, polyglucoside, and polyethoxylate) surfactants are better predicted than for the three other groups stated in the proposal. Chemical property information from chemical manufacturers or databases (Table 15), when available, and that predicted by EPI Suite (Table 16) are in generally good agreement. Water solubility is high while KOW and bioaccumulation factors are low for all but AzkoNobel Ethomeen (Table 16). In general, EPI Suite indicates that the longer the ethoxylate (polar) chain, the lower the log Kow and bioaccumulation factor and the higher the LC50/EC50 (lower toxicity). EPI Suite predicts two of the five surfactants (Tergitol TMN-6 and Ethomeen) are not readily biodegradable (Table 16), whereas there is no information from manufacturers (Table 15a and b). Tergitol 15-S-7, while being readily biodegradable, has a high bioaccumulative potential with an estimated BCF of 34.66 (Table 16) and a value over 3,000 in ECHA database (Table 15a and b).

Table 15b. Additional chemical property information, and biological effects data provided by chemical manufacturers and found in databases. If no notation is provided for the source of the information, the data comes directly from the manufacturer of the surfactant.

Descriptor	Huntsman Ecoteric 7700	Triton CG-425	AzkoNobel Ethomeen	Tergitol 15-S-7	Tergitol TMN-6
Chronic toxicity to fish (NOEC/NOEL)	NA	1.8 NOEC (analog, 4 weeks) ²	NA	0.47	NA
Acute toxicity to algae/ cyanobacteria EC50 (mg/L)	6 (algae)	37(algae) ¹ 47 (algae) ²	NA	2.011 (algae)	NA
Chronic toxicity algae/ cyanobacteria NOEC (mg/L)	NA	2 algae (72hr) ²	NA	NA	NA
Microorganism EC50 (mg/L)	NA	NA	NA	824 (activated sludge respiration inhibition test) 391	NA
toxicity to terrestrial organisms (not arthropods)	NA	654 (LC50 mg/kg earthworm) ¹	NA	EC50= 14.82 mg/kg sed dw (assumed from daphnia data) ¹	NA

¹ECHA; ²Chem View; ³ECHA; NA = not available

EC50= Half maximal effective concentration

LC50= Lethal Concentration to kill 50% of the population

LD50= Lethal Dose to kill 50% of the population

NOEC mg a.i./L= no observed effects concentration mg active ingredient/liter

NOEL = no observed effects level

As for acute toxicities toward fish, Ethomeen is classified as very toxic while the Tergitols are classified as toxic (Table 15 and 16). Tergitol 15-S-7 is harmful to aquatic invertebrates and Tergitol is toxic to invertebrates (Table 16a and b). Triton CG-425 and Tergitol TMF-6 are toxic to algae (Table 15 a and b), while Tergitol 15-S-7 is harmful to algae (Table 16a and b). In terms of chronic toxicity, Ecoteric 7700 and Tergitol 15-S-7 are toxic with long lasting effects to algae (Table 15a and b). Due to their high BCFs and their acute and chronic toxicities, the use of Tergitol 15-S-7, Tergitol TMN-6, and Ethomeen should be avoided.

Table 16a. Estimated chemical properties from EPI Suite for nonionic surfactants. Results generated by EPI Suite predict chemical properties and biological impacts based on the chemical structure.

Descriptor	Huntsman Ecoteric 7700	Triton CG-425	AzkoNobel Ethomeen	Tergitol 15-S-7	Tergitol TMN-6
Log octanol water partition coefficient (Kow)	0.93	1.42	6.2975	3.266	3.65
Water solubility (mg/L)	770.2	683.6	0.06762	41.92	23.5
Log octanol-air partition coefficient (Koa)	12.8	12.6	16.3	18.4	11.7
Henry's Law constant	1.8E-14	1.5E-13	1.3E-15	3.0E-21	1.7E-10
Organic carbon-water partition coefficient (Koc)	0.729	5.087	2190	48.78	182.3
Bioaccumulation Factor (BAF)	2.254	2.124	47.03	34.66	77.44

Table 16b. Additional estimated chemical properties from EPI Suite for nonionic surfactants. Results generated by EPI Suite predict chemical properties and biological impacts based on the chemical structure.

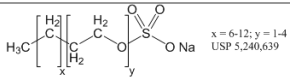
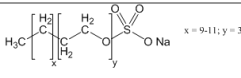
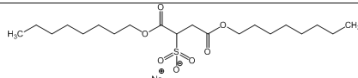
Descriptor	Huntsman Ecoteric 7700	Triton CG-425	AzkoNobel Ethomeen	Tergitol 15-S-7	Tergitol TMN-6
Biodegradation potential	YES	YES	NO	YES	NO
Acute toxicity fish LC50 96 hr (mg/L)	NA	NA	NA	30.4*	8.5
Acute toxicity aquatic invertebrates LC50 48 hr (mg/L)	NA	NA	NA	19.4*	5.6
Acute toxicity algae/ cyanobacteria EC50 96 hr (mg/L)	NA	NA	NA	23.4*	7.9

NA= Not available

* Indicates the values are not reliable, but are rough estimations.

Anionic Surfactants. The anionic (sulfated, sulfonated) surfactants are more water soluble and more biodegradable than dioctyl sulfosuccinate (DOSS) (Table 17). The bioaccumulation potential of the ether sulfate is below measurement while that of the others is low (BCF <5). The properties were not estimated by EPI Suite since the polar head groups are charged. In terms of toxicity, the alkyl ether sulfate is acutely toxic to fish, while Witcolate 1276 and DOSS are harmful to fish (Table 17). All three anionic surfactants are acutely harmful to aquatic invertebrates (Table 17). The Witcolate 1276 is considered harmful to algae/cyanobacteria (Table 17).

Table 17. Chemical properties and biological effects data for anionic surfactants provided by chemical manufacturers and found in database search.* If no notation is provided for the source of the information, the data comes directly from the manufacturer of the surfactant.

Descriptor	Alpha Foamer Ammonium Alkyl Ether Sulfate	AzkoNobel Witcolate 1276	Dioctyl sulfosuccinate sodium salt (DOSS)
Name	Alcohols, C8-10, ethoxylated, sulfates, ammonium salts ¹	Product is inactive	Dioctyl sulfosuccinate sodium salt
Structure			
European Community No.	500-233-2 ¹	221-416-0 ¹	209-406-4
CAS No.	68891-29-2	3088-31-1	577-11-7
Molecular formula	range	C16H34O6SNa	C20H37NaO7S
Melting Point (°C)	25	NA	153 ²
log Kow	0.96	NA	NA
Water Solubility (mg/L at 20°C)	>3,800	NA	NA
Biodegradation potential	Readily biodegradable	measurable degradation in sea water ²	66.4% after 28 d not readily biodegradable ²
Bioaccumulation potential	None ¹	No Bioaccumulation Potential ¹ Low potential (BAF=5) ²	BCF=3.8
Acute toxicity fish LC50 (mg a.i./L), LD50 (g/kg)	LD50 <5 LC50 7.1 ¹ (Danio rerio)	LC50=49 (zebra fish) LC50=46 ¹ (Oryzias latipes)	LC50=49 (zebra fish) LC50 = 37 (bluegills) LC50 = 28 ² (trout)
Acute toxicity aquatic invertebrates EC50 mg a.i./L or LC50 mg/L	EC50 91 (daphnia, read across from C8-10, 1-2.5EO) ¹	LC50=7.2-15.4 ¹ <i>Artemia salina</i>	<i>Daphnia magna</i> EC50=10.3 <i>Daphnia magna</i> EC50 = 36.2 ²
Acute toxicity to algae/cyanobacteria NOEC or EC50 (mg a.i./L)	NOEC 31.3 (algae) EC50 >100 ¹	EC50= 100 ¹	Stimulatory effect, not inhibitory ²
Acute toxicity microorganisms EC50 (mg/L)	>10,000 ¹ (<i>Pseudomonas putia</i> , 16 hr)	NA	NA
toxicity to terrestrial macroorganisms except arthropods NOEC (mg a.i./L)	750 ¹ (<i>Eisenia fetida</i>)	NA	NA
Acute toxicity rat LD50 (mg/kg)	NA	NA	Not acutely toxic 1900 ³
Toxicity to rabbit	NA	NA	Not acutely toxic

¹ECHA, ²ChemView, EC50= Half maximal effective concentration, LC50= Lethal Concentration to kill 50% of the population, LD50= Lethal Dose to kill 50% of the population, NA = not available, NOEC mg a.i./L= no observed effects concentration mg active ingredient/liter, NOEL = no observed effects level, *Not included in the table are Tergitol 4, AN Witcolate WAQ, AN Witcolate 1050, AN Witcolate LES-60C. These were not included because no information on these surfactant could be found from the manufacturer or any other database.

The available information on the surfactants in the original proposal is limited and only a few surfactants are eliminated including, Tergitol 15-S-7, Tergitol TMN-6, and Ethomeen from advanced research. The information given is largely based on “read-across” approaches with data generated for structurally similar materials, and not from empirically gathered data. Each resource has limitations, which makes the information inadequate for complete understanding of the potential risks of each surfactant. More information needs to be acquired through experiments before confident risk assessments can be made.

5.4. Fluorine-free Commercial Surfactants

Commercial surfactants were chosen for two purposes; (1) to rank and identify top performing surfactants based on the foam degradation by fuel, fuel transport through foam, foam spread, and fire extinction time, (2) to establish a correlation among foam degradation, fuel transport, and fire extinction and examine the hypothesis that reducing fuel transport reduces fire extinction time.

We selected non-fluorocarbon surfactants that are reported or advertised to have good foam-forming properties and that may group into structurally related sets of surfactants, even if they were not designed for firefighting purpose. This enabled us to look for structure-property correlation for guidance toward the more effective surfactant candidates. We selected two categories of hydrocarbon and siloxane surfactant systems. Siloxane surfactants are the more promising category on the basis of a lower surface tension but more challenging as the chemical structures of the commercial siloxane surfactants are complex and generally proprietary. We performed a broad literature search and developed contacts with surfactant industry over a period of time to identify structurally related surfactants to the extent the industry is willing. Specifically, we conducted a number of consultations with a chemists at Dow-Corning Inc., SilTech Inc., and Colonial Chemical Co., who provided some of their silicone surfactants and related technical information. We chose surfactant structures because of varying number of hydrocarbon, siloxane, and oxy-ethylene units.

By their nature, commercial surfactants can only allow a broader variation in chemical structure. We can explore the molecular structure effects semi-quantitatively within a given type (siloxane or hydrocarbon surfactants); linear versus branched tails, single versus multiple tails, ionic versus non-ionic head groups, etc. Head group is polar or hydrophilic and gets adsorbed on the water side of an air bubble in the foam. The tail is relatively non-polar or hydrophobic and gets adsorbed on the air side of the bubble.

5.4.1. Selection of Commercial Surfactant Structures

We selected a group of five non-ionic siloxane surfactants with identical trisiloxane tails and closely related head groups of different average length (a distribution of lengths exist) as shown in Figure 32. They are Silwet L77 from Momentive Inc., GelestSiH6185 from Gelest Inc., and 67A, 501W, and 502W from Dow-Corning Inc. as shown in Figure 32. 67A and 502W have poly oxy-ethylene head groups with hydroxyl terminal unit. Silwet L77 and 501W also have poly oxy-ethylene head group but have methyl terminal unit as shown in Figure 32. The other three are grafted siloxane surfactants, and have multiple siloxane tails and heads as shown in Figure 32. They are 193A from Dow-Corning Inc. and SilsurfJ208 from Siltec Inc. The eighth surfactant, SilphosJ208, is similar to SilsurfJ208 but is anionic as shown in Figure 32.

Similarly, Figure 33 shows three hydrocarbon surfactants with an alkane tail of similar lengths (six to twelve carbons) but different polar head groups; Alpha Foamer (Stepan Inc.) has an oxy-ethylene connected to the sulfonate head group unlike sodium dodecyl sulfonate (SDS, Aldrich Co.), and Glucopon215UP (BASF) has a glucoside head group having numerous hydroxyl units, which are non-ionic. The other hydrocarbon surfactants have different number of oxyethylene head groups and different hydrocarbon tails; Tergitol 15-S-7 (Dow Chemical) has two alkane tails and Tergitol TMN6 (Dow Chemical) has pendant methyl groups on the two tails as shown in Figure 33.

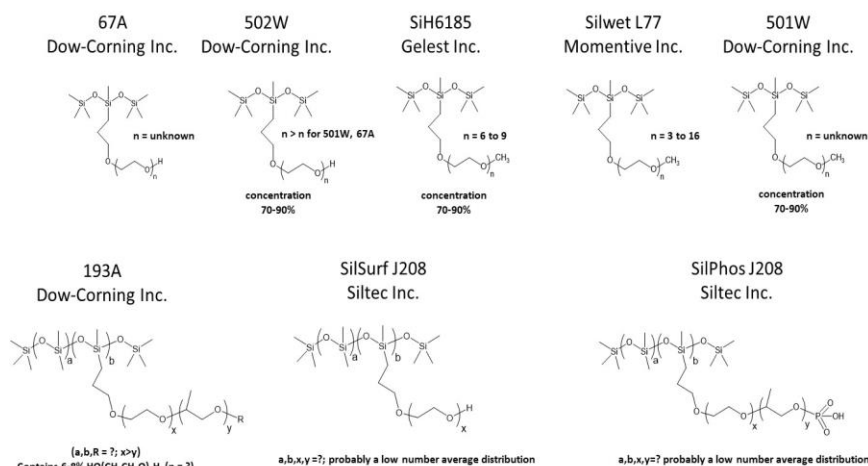


Figure 32. Top row: All have identical trisiloxane tails with unspecified distribution of oxyethylene units in the head group terminated with a hydroxyl unit. 502W has larger head than 501W and 67A. Other three are similar but have head groups terminated with a methyl unit. **Bottom row:** Grafted surfactants with multiple tails and heads, but differ in the number of siloxane, oxy-ethylene and oxy-propylene units, non-ionic. Silphos is similar but has an anionic head group.

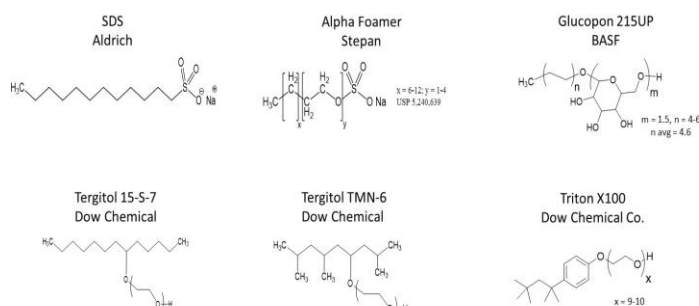


Figure 33. Top row: SDS and Alpha Foamer differ by an oxy-ethylene unit in the head group; Alpha Foamer has a distribution of chain lengths including the dodecyl similar to SDS's tail. Glucopon has slightly smaller length (octane) tail and a glucoside head group. **Bottom row:** Tergitols have twin hydrocarbon tails and similar head groups containing different length poly oxy-ethylene units. Tergitol TMN6 also has pendant methyl units. Triton is branched with phenyl linker.

We also conducted measurements on commercial fluorine-free foam, RF6 (Rehealing Foam 6%, Lot#506166, August 2005, Solberg Inc.), which is ICAO certified and sold in Europe. RF6 failed the 28 ft² pool fire extinction test of U.S. Milspec, and the 6% concentrate is highly

viscous to adapt to Navy's existing hardware [4]. It contains multiple surfactants and additives with a proprietary composition.

5.4.2. Commercial Surfactants - Solution Properties

Aqueous solutions of surfactants only and surfactant mixtures (formulations) were prepared. The formulations were prepared by replacing Capstone1157 in the RefAFFF composition shown in Table 6. We measured surface tensions for these solutions to determine the critical micelle concentration (CMC). We typically used well above the CMC values to prepare the solutions for foam degradation, fuel transport, and fire extinction testing.

The surface tension of aqueous solutions of commercial surfactants were measured using DuNoy ring apparatus at different dilutions of a stock solution containing 2 weight % surfactant. In the case of formulations, stock solution was prepared using 2 weight % of the total surfactant (1.2 % candidate + 0.8 % Glucopon + 2% DGBE by volume). Figure 34 shows the measured surface tension values from which CMC values were determined by fitting two straight lines at small and large values of the concentration, and finding the intersection of the two lines.

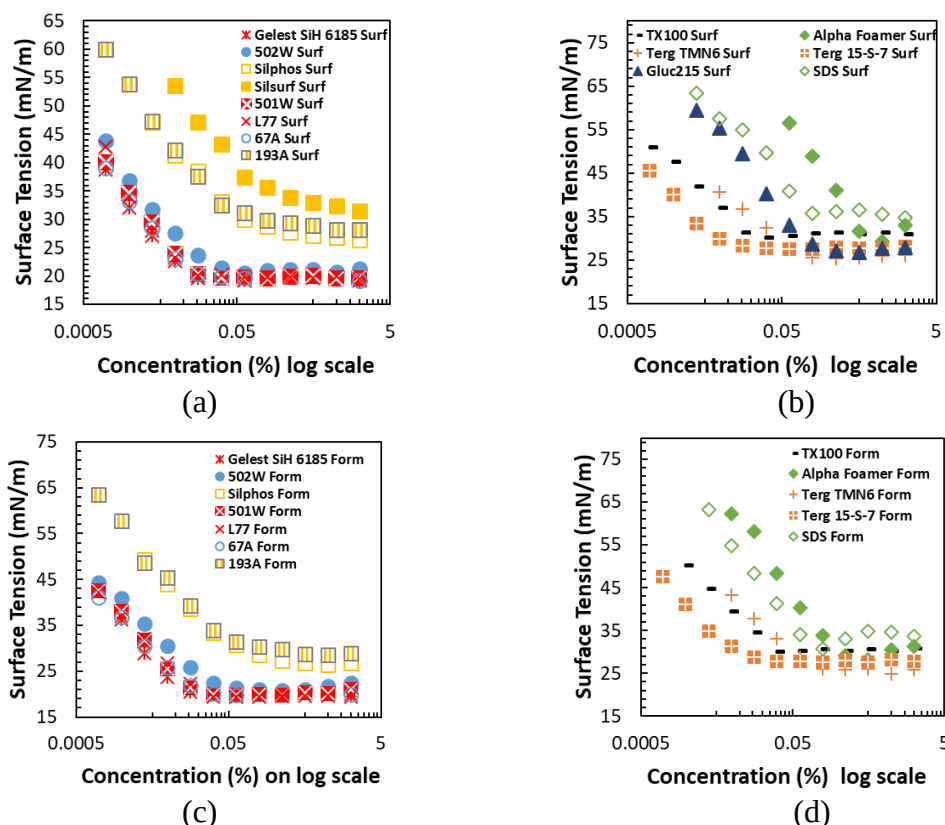


Figure 34. Surface tension versus concentration plots for commercial (a) individual siloxane surfactant solutions, (b) individual hydrocarbon surfactant solutions, (c) siloxane formulations with Gluc215, and (d) hydrocarbon formulations with Gluc215.

The surface tensions are 35 mN/m or less above CMC, which are a fraction of 1 volume %. As one might expect, the formulations have CMC values typically less than that of individual surfactant solutions. We prepared most solutions 2 to 10 times greater than their CMC values.

5.4.3. Commercial Surfactants – Foam/Fuel Interaction Dynamics

Figures 35 and 36 show percent change in foam height with time for foams generated with a surfactant by itself in water and with the surfactant replacing the fluorocarbon surfactant, Capstone 1157, in the RefAFFF formulation in Table 6. The foams were generated and allowed to flow directly on to a heptane pool to an initial thickness of 4-cm at 1000 mL/min foam generation rate. The heptane pool was heated by a water bath to maintain a temperature of 60 °C, but the foam itself was not heated externally. Degradation time is the time for complete disappearance of the foam layer (lifetime).

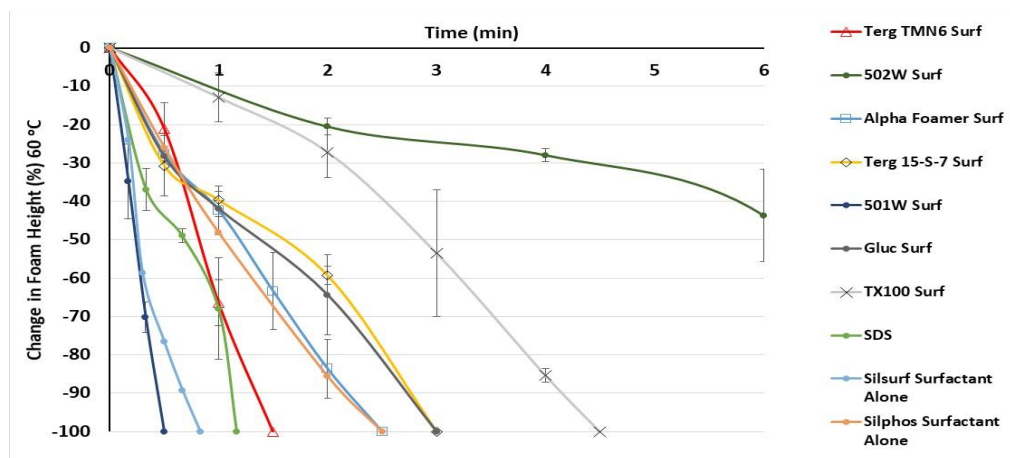


Figure 35. Percent change in foam height for foams generated using individual surfactants.

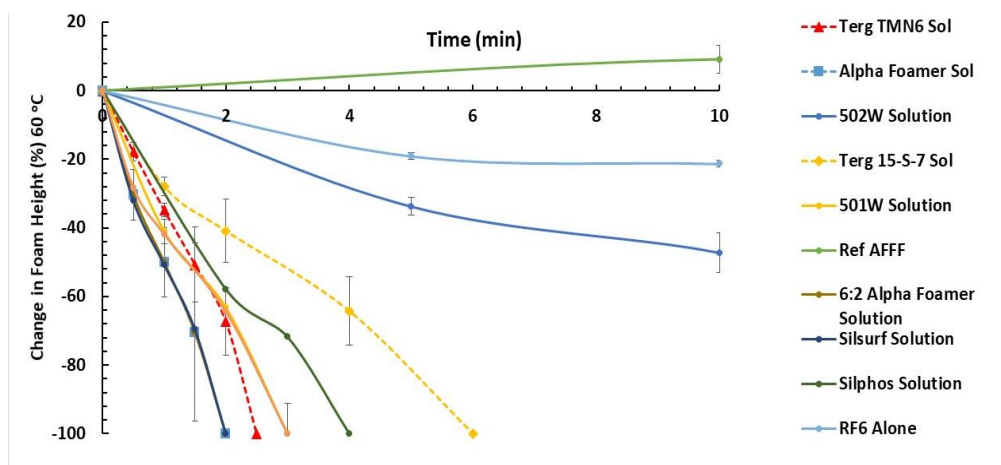


Figure 36. Percent change in foam height for foams generated using surfactant-mixture formulations. Alphafoamer was prepared as 6:2 ratio with Glucocon215 CS UP unlike the rest of the formulations which are 3:2 ratio.

Figures 35 and 36 show that surfactant formulations have longer life times than the individual surfactant solutions. The surfactant 502W siloxane from Dow Silicones Inc. has the longest lifetime among the foams examined. Even though RF6 has even longer lifetime, its high viscosity prevents it from being a drop-in surfactant formulation.

Figures 37 and 38 show mole flux of heptane vapor transported through a foam layer for foams generated with a surfactant by itself in water and with the surfactant replacing the fluorocarbon surfactant, Capstone 1157, in the RefAFFF. The foams undergo degradation during the measurement inside a closed flux chamber because the foams were placed on hot (60 °C) heptane pool. The foam lifetimes are typically higher than in the degradation measurements shown above, which are in an open beaker. The humidity is expected to be higher in a closed flux container. Pool area was 19.6 cm² and initial foam layer thickness was 4 cm, total nitrogen flow of 600 mL/min (500 mL/min through the flux chamber and 100 mL/min by-pass flow) to FTIR. Transport time is defined as the time at which fuel flux is 4.4×10^{-9} mole/cm²/s corresponding to 193 ppm heptane measured by FTIR. A fuel concentration of 193 ppm in the nitrogen flow through FTIR corresponds to the lower flammability limit (1 vol. %) at the pool surface as calculated based on 29 vol% vapor pressure on bare heptane that resulted in 5675 ppm in the nitrogen flow through the FTIR.

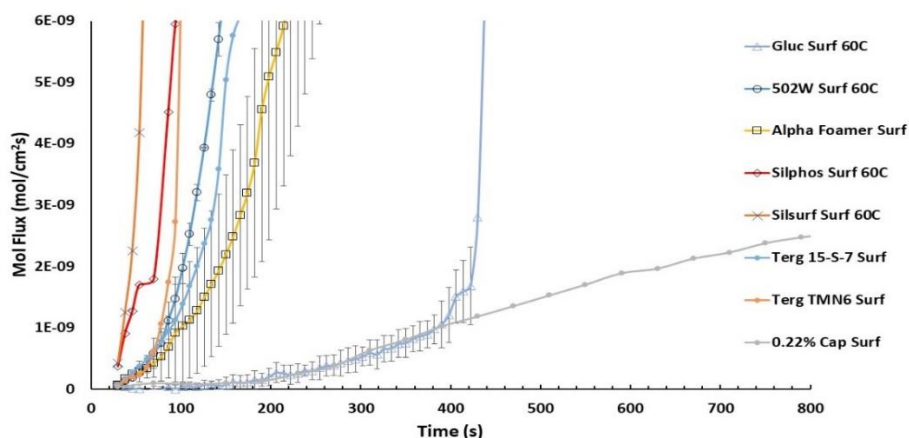


Figure 37. Fuel vapor flux with time for foams generated with individual surfactants.

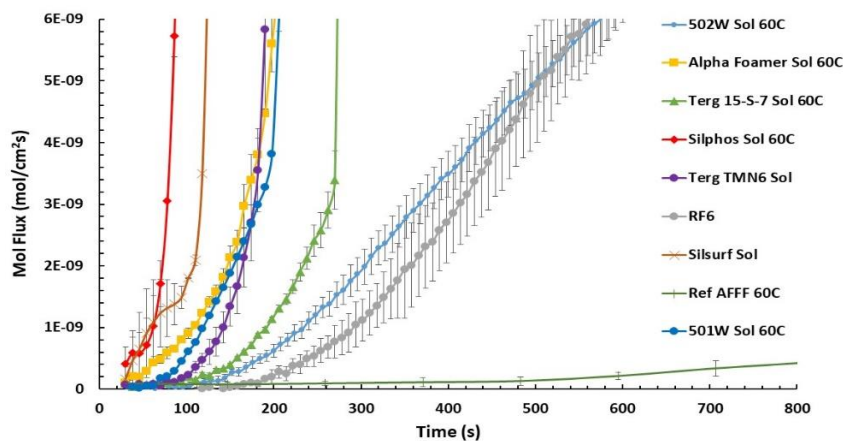


Figure 38. Fuel vapor flux with time for foams generated with surfactant-mixture reformulations.

Figure 37 shows that Glucopon 215 CS UP of BASF has the smallest fuel transport rate among the commercial foams including 502W. But, Figure 38 shows that the 502W formulation and RF6 have the smallest transport rates. The 502W formulation's transport flux is even smaller than the Glucopon surfactant by itself. It is possible that combining Glucopon 215 CS UP with 502W in the 502W formulation reduced the fuel flux further due to increased foam stability shown

in Figure 36. A similar effect can be seen between Capstone1157 surfactant by itself shown in Figure 37 and RefAFFF shown in Figure 38.

Foam degradation and fuel transport rate with time were also measured for additional commercial siloxanes and hydrocarbon surfactants as discussed in Figures 39 to 42 below.

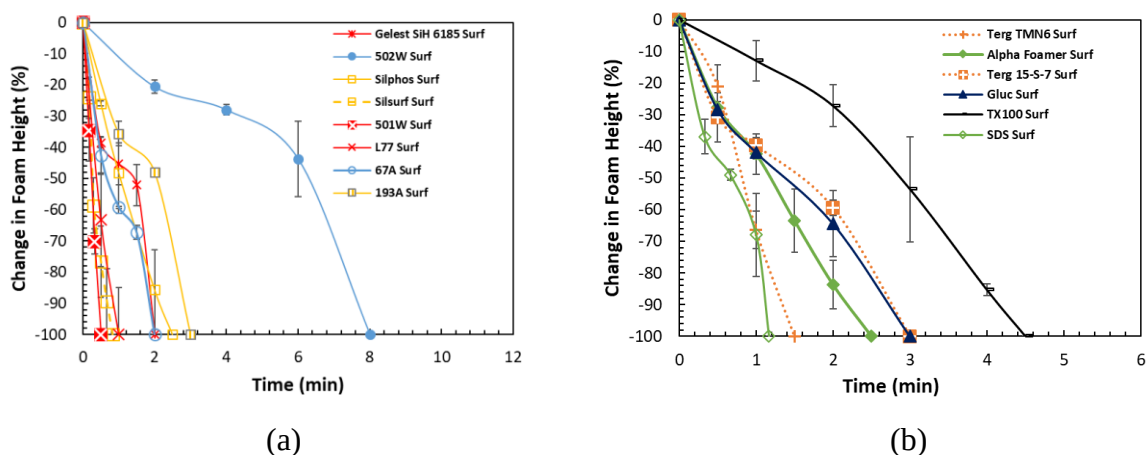


Figure 39. Percent change in foam height for foams generated using (a) individual siloxane surfactants and (b) individual hydrocarbon surfactants.

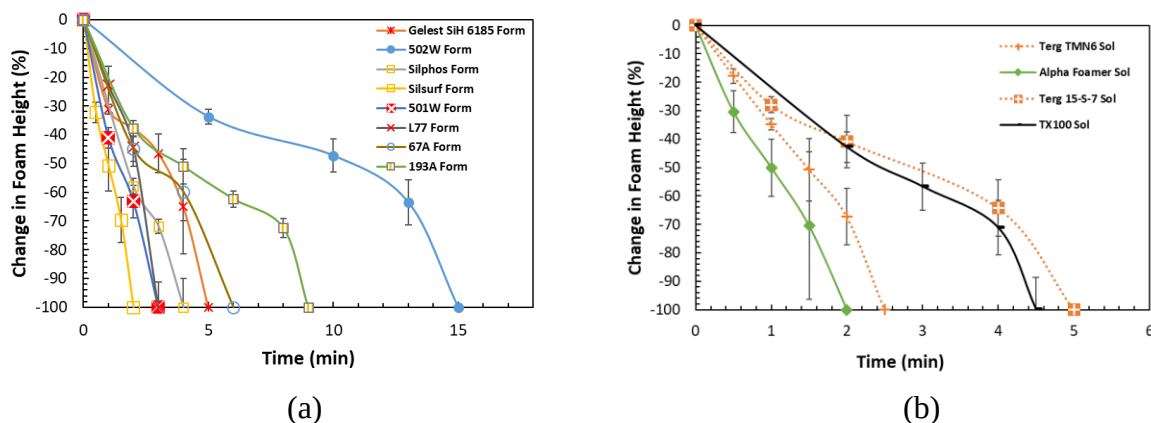


Figure 40. Percent change in foam height for foams generated using (a) siloxane surfactants in a formulation with Gluc215, and (b) hydrocarbon surfactants in a formulation with Gluc215. SDS formulation not plotted. Alphafoamer was prepared as a 6:2 ratio with Gluc215 unlike the others which are at a 3:2 ratio.

Gluc215 has a lifetime of 3 minutes and many of the siloxanes have lifetimes below that as well in Figure 39. However, the formulations show longer lifetimes than the individual components in Figure 40 due to synergism between siloxane surfactants and Gluc215. The highest degree of synergism is seen with the 502W:G215 mixture.

Figures 41 shows that Glucocon 215 CS UP of BASF has the smallest fuel transport rate among the commercial foams and 502W did not. The hydrocarbon surfactants alone appear to have

slower fuel transport than the siloxane surfactants. However, when put in a mixture with Gluc215, the siloxane formulations have slower transport than the hydrocarbon formulations. Figure 42

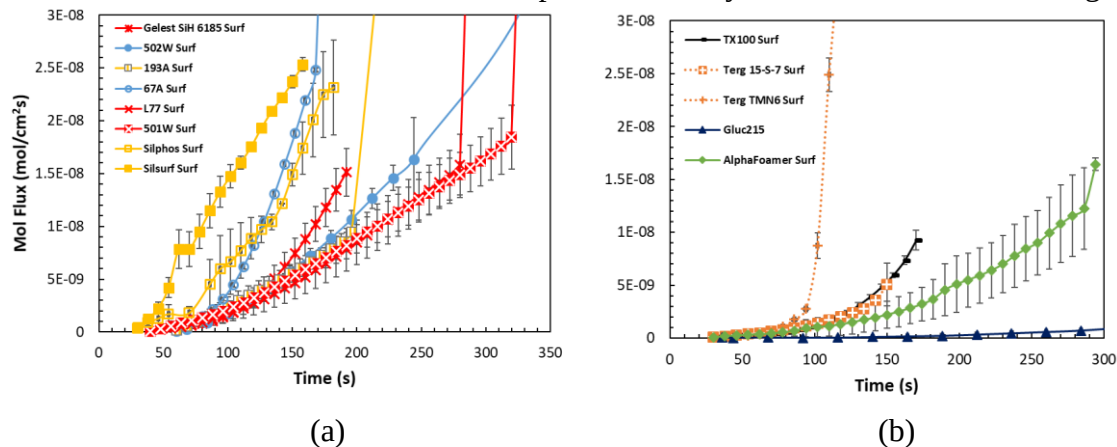


Figure 41. Fuel vapor flux with time for foams generated with different surfactants (a) individual siloxane surfactants and (b) individual hydrocarbon surfactants. SDS surfactant is not plotted.

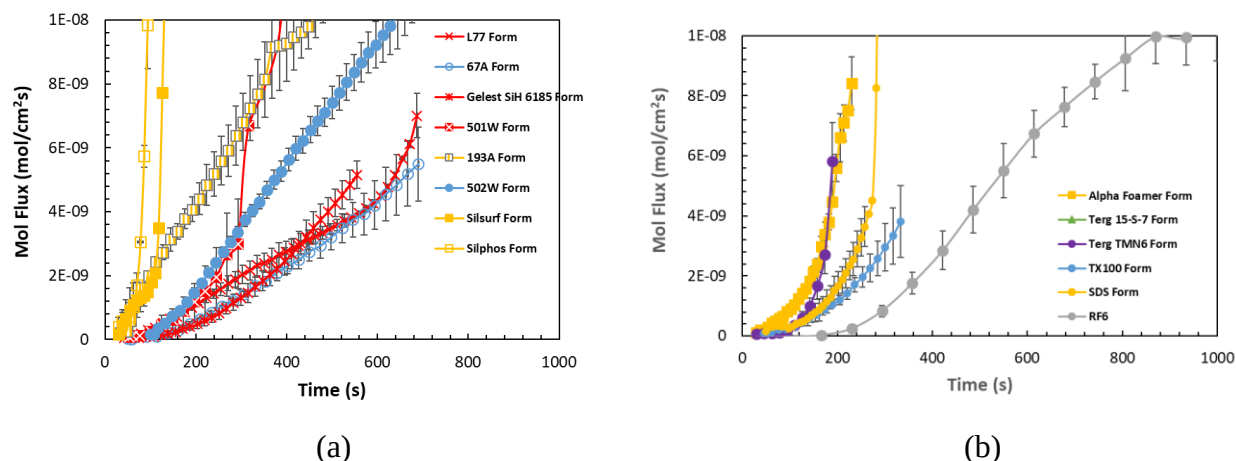


Figure 42. Fuel vapor flux with time for foams generated with different surfactant formulations (a) siloxane surfactant formulations with Gluc215 and (b) hydrocarbon surfactant formulations with Gluc215. Alphafoamer formulation is in a 6:2 ratio with Gluc215 while all others are in a 3:2 ratio.

shows that the 502W formulation and RF6 have the smallest transport rates. While synergism was seen in foam lifetime, none of the formulations have comparable or reduced fuel transport rates compared to the Gluc215 surfactant individually. This is surprising as the Capstone surfactant showed synergistic fuel transport with Gluc215. However, the data is promising as the 502W formulation has a long foam lifetime compared to other siloxane surfactants and a fuel transport rate comparable to RF6, a commercially available product.

5.4.4. Commercial Surfactants - Heptane Pool Fire Extinction

We initially conducted fire extinction on a 19-cm diameter heptane pool fire and found that most commercial surfactants could not extinguish the fire and no quantitative measurements could be made. We conducted fire extinction experiments for the surfactants shown in Figure 35 to 37

on a 12-cm diameter heptane pool fire. Most of them are expected to perform poorly compared to the RefAFFF, but the interest here is to see if a correlation develops in Figure 43 so that new surfactants could be developed based on the knowledge gained from the commercial surfactants.



Figure 43. A pool (12-cm diameter, n-heptane liquid, 2-cm lip) fire extinction by foam applied at the center at a constant flow rate; from 30-sec pre-burn to extinction.

Figure 43 shows a 12-cm diameter heptane pool fire with a constant foam flow rate, from 30 s pre-burn to extinction. The foam spread from the center to the edges covering the entire pool. During and after spreading, a foam layer of increasing thickness continues to build eventually causing extinction. When the foam flow rate was too low, the foam was unable to cover the pool completely, and in some cases the foam receded after covering the pool initially. This is especially true for foams that have higher degradation rates in Figure 35 and 36. Also, we noticed fire on top of the foam covered regions of the pool because the foam layer was not thick enough to block the fuel vapor supply to the fire above the foam surface. As the foam flow rate was increased, spreading occurred faster and fire extinction time decreased depending on the surfactant system employed. Some surfactants, with very high foam degradation rates in Figure 35, did not extinguish the fire in a reasonable time (90 s to 150 s) even when the foam flow was increased. Typically, foam supply was continued up to 150 s, if the foam layer appeared to be spreading or growing. But, if there appeared to be a steady state in the pool coverage by the foam layer or foam was receding, the foam supply was stopped at 60 to 90 s.

Figures 44 and 45 show measured fire extinction time with foam flow rate applied at the center of heptane pool at a constant foam flow rate. Fire extinction time increased as the foam flow rate is decreased. The foam flow rates, where the fire did not extinguish in 120 s are shown as symbols placed along the x-axis in Figures 44 and 45. We found that 501W and SilsurfJ208 surfactant solutions were unable to cover the 12-cm diameter pool even at a high foam flow rate (2500 mL/min), but the Silsurf covered a larger area of the pool consistent with the fuel transport and degradation rates shown in Figure 35 to 38. We also found that Tergitol 15-S-7 and TMN6 were unable to extinguish the fires at foam flow rates from 1000 to 3300 mL/min as shown above. The extinction with Tergitol TMN6 was inconclusive because we noticed extinction only at a foam flow rate of 1440 mL/min. The results for Tergitol TMN6 were complicated by the fact that the drained solution from the foam formed a whitish emulsion layer that settled just below the fuel layer. These results appear to be not consistent with the foam properties shown in Figure 35-38, and may need further investigation.

Figures 44 and 45 show that extinction time decreases as the foam flow rate is increased and the surfactant's effectiveness at suppressing the fire depends on foam application rate. Figure

44 shows TritonX100 and 502W are relatively more effective than the other surfactants in suppressing the fire especially at low foam flow rates. RF6 is more effective at low flow rates than at high foam flow rates. Surprisingly, TritonX100 with DGBE solvent has comparable effectiveness with RF6 and 502W formulation. The 501W formulation has the highest fire extinction time.

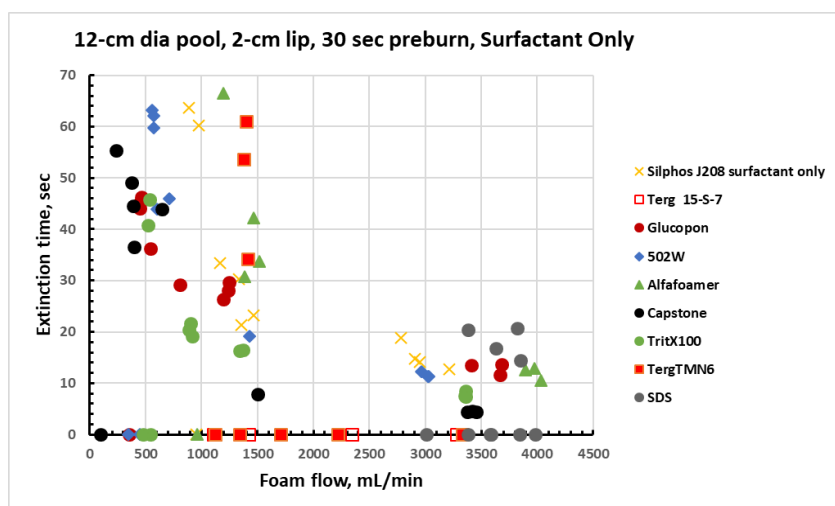


Figure 44. Extinction time with foam flow rate for foams generated with individual surfactants. A 6:2 Alpha Foamer to Glucopon ratio was used for extinction while 3:2 ratio was used in Figures 36 and 38. Foams applied at the center of the pool.

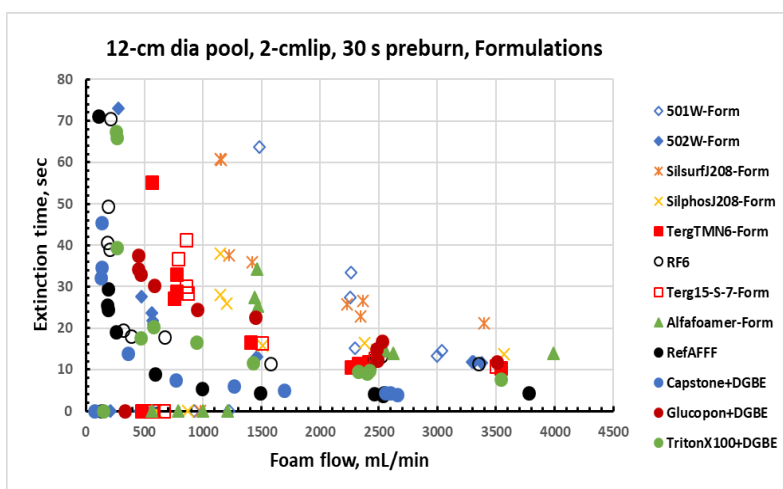


Figure 45. Extinction time with foam flow rate for foams generated with surfactant-mixture formulations. Foams applied at the center of the pool.

5.4.5. Correlate Foam/Fuel Interaction Dynamics with Fire Extinction

Table 18 shows relative degradation and transport times and extinction times at 500 mL/min foam flow rate calculated from the data shown in Figures 35 to 41.

Table 18. Fire extinction time for foams generated by different surfactant solutions.

Surfactant	Extinction time, s	Transport time, s	Degradation time, s	CMC, g/L	Concentration/CMC
RefAFFF	12	3619	3800	0.05	10
Capstone1157+DGBE	12	2790	2700	0.033	7.3
RF6	17	478	1620	N/A	N/A
502WForm	25	448	840	0.018	6.7
Capstone1157	38	2710	2100	0.031	7.3
Glucopon215UP	40	433	190	0.072	2.8
TritonX100	44	138	270	0.012	42
Tergitol TMN6Form	70	182	150	0.07	7.1
502W	70	126	500	0.016	6.0
Tergitol 15-S-7Form	No extinction	272	360	0.0086	6.0
501WForm	No extinction	198	195	0.01	6.8
AlfafoamerForm	No extinction	190	195	0.13	13.9
Alfafoamer	No extinction	190	150	0.38	3.4
Tergitol 15-S-7	No extinction	142	195	0.009	6.0
SilsurfForm	No extinction	122	115	0.1	7.0
Tergitol TMN6	No extinction	94	90	0.07	6.0
SilphosJ208	No extinction	86	135	0.04	7.5
SilphosForm	No extinction	78	250	0.125	2.0
SDS	No extinction	67	67	0.04	10.6
SilsurfJ208	No extinction	57	45	0.07	0.2
501W	No extinction	20	20	0.09	6.0
67A (0.5%)	N/A	76	120	--	--
Glucopon215UP+DGBE	N/A	470	260	0.072	6.3
TritonX100+DGBE	N/A	130	180	0.012	42
Angus 3%	N/A	158	780	N/A	N/A

Figures 35 and 36 showed foam lifetimes when a 4-cm thick foam layer degraded completely for fluorinated and fluorine-free surfactants and their formulation mixtures. Relative degradation rate is calculated by dividing the lifetime for RefAFFF with that of a fluorine-free surfactant candidate. Fuel transport time is defined as the time taken for the surface concentration to reach 1 vol %, which is just below the lower flammability limit for heptane and is calculated from Figures 37 and 38. The concentration of 1 vol. % at the surface corresponded to 193 ppm concentration in the nitrogen gas flow carrying the fuel vapors to FTIR because of the nitrogen dilution. Relative transport rate is defined as the transport time for RefAFFF divided by the transport time for a candidate fluorine-free surfactant.

Figure 46 shows the relative transport rate against the relative degradation rate for surfactants by themselves and as part of the reference formulation. By definition, a value of 1 corresponds to the measured rates for RefAFFF, whose values are given in Table 18. The data for different surfactants fall at different distances away from the origin and represent increasing rates of fuel transport and foam degradation. Figure 46 shows that the siloxane surfactant based 502W formulation (502WForm) is the closest to RefAFFF among the surfactants examined to date. The 502W formulation has transport and degradation rates comparable to that of a commercial fluorine-free foam, RF6, which is an important milestone to achieve; 502W is not viscous unlike RF6 concentrate. Figure 46 also shows that the fuel transport rate and degradation rates for 502WForm are 8 and 4.5 times higher than those for RefAFFF respectively.

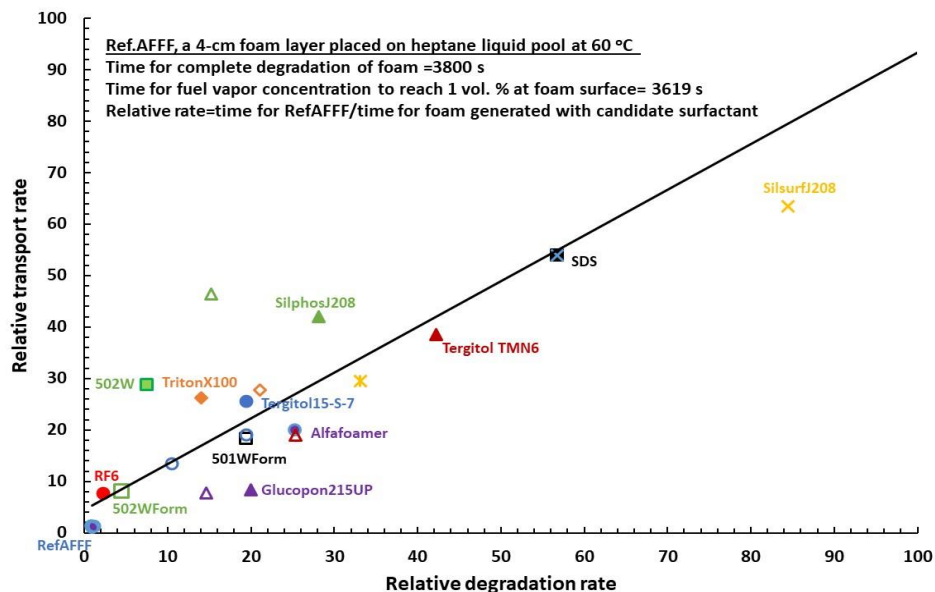


Figure 46. Fuel transport rate versus degradation rate relative to RefAFFF. Open and solid symbols represent data taken for foams generated with surfactant as a part of the formulation (e.g. 502WForm) and surfactant alone (e.g. 502W); same color symbol is used for a given surfactant.

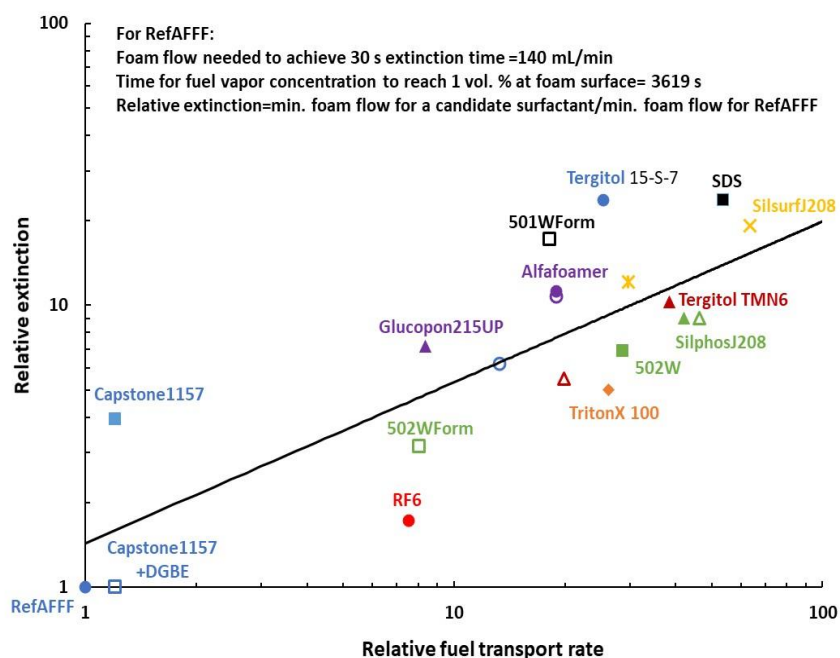


Figure 47. Fire extinction for 12-cm diameter heptane pool versus fuel transport rate. Open and solid symbols for formulations and surfactants only respectively.

Figure 46 enables comparison of the effects of variations in chemical structures shown in Figures 32 and 33 and ranking of the surfactants. Figure 35 shows a dramatic difference between 502W and 501W (surfactant only measurements), which degraded so quickly (< 30 s) that repeatable measurements could not be made. As formulations, 502W and 501W also show significant difference in fuel transport rate and degradation rate. These differences in foam

properties suggest that the differences in surfactants' structures shown in Figure 32, namely the larger length oxy-ethylene head of 502W compared to that of 501W, could be one of the causes (we also found that foam generated using 67A surfactant with a hydroxyl terminal group was unable to extinguish the bench-top fire, further measurements on 67A are in progress) in addition to the differences in polydispersity and purity. Silphos had smaller transport and degradation rates compared to Silsurf. This could be due to Silphos's anionic head group and a different length oxy-ethylene and ox-propylene units compared to Silsurf. In general, the data suggest that polarity and structural differences in the head group of the siloxane surfactants appear to have significant effect on foam's properties.

Among the hydrocarbon surfactants shown in Figure 33, Alpha Foamer has a distribution of oxy-ethylene units ranging from 1 to 4 in the head group unlike SDS. Figure 46 shows significant reduction in foam's fuel transport and degradation rates over SDS, again confirming the positive effect of oxy-ethylene units in the head group similar to the silicone surfactants discussed above. Glucopon 215UP has larger head having numerous hydroxyl units, which might have led to further reduction in both fuel transport and foam degradation properties over those with Alpha Foamer surfactant. The Tegitols shown in Figure 33 appear to be somewhat unique. Figure 46 shows that Tergitol 15-S-7 had significantly smaller degradation and transport rates for the foam than Tergitol TMN6. But, it is difficult to separate the effects of the pendant methyl groups from the effects of different number of oxy-ethylene units in Tergitol TMN6's structure relative to the structure of Tergitol 15-S-7.

The surfactants can be ranked based on the values of foam flow rate at which the extinction time becomes relatively long. Figure 47 shows the foam flow rate needed for fire extinction time of 30 s (12-cm dia. pool) relative to that for RefAFFF versus the relative transport rate. The smaller the foam flow rate needed for a 30 s extinction time, the more efficient is extinction. Figure 47 shows a power law correlation between relative foam extinction and the relative transport rate with an exponent of 0.6. The scatter among the data points is partially attributed to significant and uneven degradation of the foam layer by the heptane fuel during the fuel flux measurements; some of the foams degraded quickly before fuel flux could be measured reliably.

In general, the surfactants in Figure 47 follow the trends shown in Figure 46. Extinction was not observed with 501W, but 502W extinguished the fire, as expected from Figure 46. Similarly, SilphosJ208 had superior extinction performance to SisurfJ208 as shown in Figure 46. Also, Alpha Foamer had faster extinction than SDS. Glucopon 215UP performed better than Alpha Foamer. In Figure 47, 501W, SilsurfJ208, SDS are farther from RefAFFF (at origin) similar to those in Figure 46. RF6, Capstone, 502WFormulation are closest to RefAFFF as in Figure 46. Rest of the surfactants fall between the two groups in Figure 47 as in Figure 46. Alpha Foamer formulation's extinction performance is comparable to Alpha Foamer surfactant solution as expected, because 6:2 Alpha Foamer to Glucopon was used for extinction while 3:2 was used in Figure 46. Capstone 1157 appears to have synergism with DGBE that makes it an exception to the general trend. The combined solution extinguished the fire as fast as the RefAFFF. The transport rate for 502WForm and RF6 are close but the extinction times are significantly different because of slower foam spread rate for 502W.

5.5. Invention of an Effective Siloxane-Glycoside Mixture

Figures 46 and 47 identified siloxane surfactants, especially 502W formulation, as a potential fluorine-free surfactant formulation for further development. We developed a formulation by substituting the fluorocarbon surfactant in the RefAFFF formulation described in Table 19 with a commercial siloxane-polyoxyethylene surfactant [44]. The siloxane surfactant has large siloxane tail and slender polyoxyethylene head while the alkylpolyglycoside surfactant has a large glycoside head and a slender alkane tail. The interactions between siloxane's and glycoside's head and tail structures in the surfactants mixture can affect foam stability in the presence of fuel, fuel diffusion through a foam layer, foam properties and fire suppression. We investigated synergistic effects due to such interactions and the effects of polyglycoside head size of the hydrocarbon surfactant on foam stability and heptane fire suppression [44].

Aqueous foams generated from commercial Siloxane-polyoxyethylene and alkyl polyglycoside surfactants were characterized individually and as mixtures in a formulation. The results showed significantly smaller fire extinction times for the surfactant mixtures than for either of the individual components exhibiting a synergistic fire extinction rather than following the law of averages; 5 times enhancement in extinction performance. The measured foam degradation rate with the foam exposed to a hot heptane pool also showed a similar synergism. The reduced foam degradation rate resulted in a reduced fuel vapor transport for longer times and a more rapid fire extinction for the siloxane-glycoside mixture. By increasing the hydrophilicity with increased size of the polyglycoside head, the synergistic effect was enhanced. Both benchtop (19 cm diameter) and large scale (6 ft diameter) heptane pool fire extinction with the siloxane-glycoside surfactant mixture showed that the extinction time was 1.5 times that of an equivalent AFFF formulation containing a fluorosurfactant in place of the Siloxane surfactant at a fixed foam application rate ($22 \text{ L m}^{-2} \text{ min}^{-1}$). An understanding of the molecular interactions at the interface causing the synergistic effects may lead to improved siloxane-glycoside systems and other novel surfactant systems with performance matching that of fluorocarbon surfactants.

5.5.1. Siloxane-Glycoside Mixture Compositions

It is crucial to have a complete sets of data for the same formulations because it allows us to relate the solution and foam properties to the extinction performance and determine those properties that have a significant impact on fire extinction. Table 19 shows the compositions of three Siloxane-Gluc formulations and the RefAFFF formulation used for making the foams. The percentages of surfactants and DGBE refer to the amounts of the surfactant concentrates and DGBE supplied by the respective manufacturers. The surfactant concentrations shown in Table 19 for the Siloxane formulations are two and half (3:2 Siloxane-Gluc215) to ten times (2:3 Siloxane-Gluc225 and 2:3 Siloxane-Gluc600) the respective CMC values, and the RefAFFF is 5 times the CMC value. CMC values are described later in the paper. Increasing the concentrations of the siloxane and glycoside surfactants to 0.3% and 0.2% respectively in 3:2 Siloxane-Gluc215 formulation shown in Table 19 did not result in a significant change ($< 10\%$) in fire extinction, degradation, and transport properties in the bench scale measurements possibly because they are significantly higher than CMC.

Table 19. Fluorine-free Siloxane surfactant formulations and fluorinated RefAFFF formulation. The values shown under each column are volume percentages of the individual components (or concentrates) in distilled water. The formulations were used for foam generation, property and fire performance measurements [44].

2:3 Siloxane-Gluc225	2:3 Siloxane-Gluc600	3:2 Siloxane-Gluc215	3:2 Cap-Gluc215 (RefAFFF)
0.2 % 502W	0.2 % 502W	0.075% 502W	0.3% Capstone
0.3% Glucopon 225 DK	0.3% Glucopon 600 CS UP	0.05% Glucopon 215 CS UP	0.2% Glucopon 215 CS UP
0.5% DGBE	0.5% DGBE	0.5% DGBE	0.5% DGBE

5.5.2. Evaluation of Siloxane-Glycoside – Bench Scale

Figure 48 presents time-lapse images of this fire suppression over a 19 cm diameter heptane pool fire using a foam application rate of 1000 mL min^{-1} [44]. At 0 seconds, the foam is introduced to the pool fire surface after the pool has been burning for 60 seconds. Within the first 5 seconds of foam application, a significant suppression is not observed in all cases in Figure 48b, 43g, and 43l. After 10 seconds of foam application, Figures 48c and 48h show that the 3:2 Cap-Gluc215 (RefAFFF) formulation extinguished most of the fire (knockdown) similar to a commercial AFFF (Buckeye), while the Siloxane-Gluc225 formulation did not suppress the fire to the same degree as shown in Figure 48m. After 15 seconds, Figures 48d and 48i show complete extinction while Figure 48n shows that Siloxane-Gluc225 suppressed most of the fire (knockdown). Finally, Figure 48o shows that Siloxane-Gluc225 took longer (20 seconds) to completely extinguish the fire unlike the other two fluorinated foams, 3:2 Cap-Gluc215 and Buckeye 3%, which took 12 and 16 seconds respectively for complete extinction. For the two fluorinated foams and the fluorine-free foam, we noticed fire persisting for a few seconds above the foam even in the regions of the pool covered with the foam and also subsequent to complete coverage of the pool by the foams. In the case of the two fluorinated foams, we found that the fire persists above the foam layer for as long as 50% of the extinction time and may underscore the significant role the foam layer plays in fire extinction relative to any “aqueous film” layers that may exist underneath the foams. Also, the persistent fire above the foam layer may be indicative of that the fuel vapor emanating from the hot pool surface permeates through the foam layer feeding the fire above. The fuel transport through the foam ceases as the foam layer thickens due to continued application of the foam, resulting in fire extinction due to lack of the fuel supply. During the extinction process, foam also degrades and delays building a thick foam layer. This can be noticed at very slow foam application rates, where the foam was unable to cover the pool despite continuous application of the foam for a long time (up to 6 min) because foam was degraded by the hot fuel and the fire. At high flow foam application rates subsequent to the fire extinction, we also noticed that the residual foam layer disappeared quickly with time especially for the fluorine-free foams. Thus, high fuel transport and high foam degradation can increase the minimum volume of foam (or minimum foam layer thickness) needed to extinguish a fire, which is a performance measurement of a given formulation (For example, MilSpec requires a 2.6 m^2 (28 ft^2) fire to be put out in 30 s using less than 7.57 L (1 gallon) of

surfactant solution, which translates to 37.85 to 75.7 L (5 to 10 gallons) of foam depending on the expansion ratio).

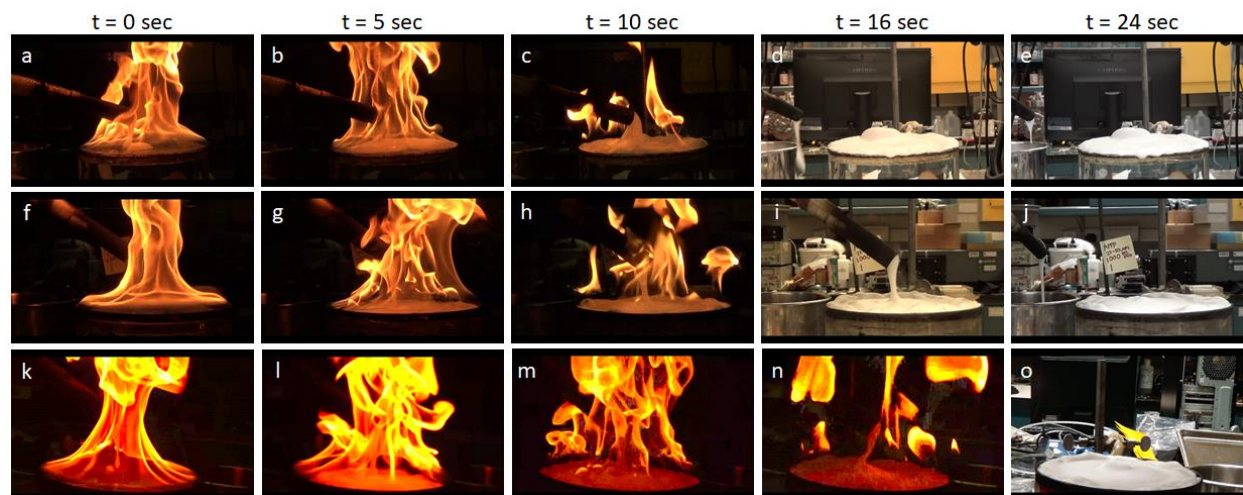


Figure 48. Time-lapse images of Buckeye (a-e), RefAFFF or 3:2 Cap-Gluc215 (f-j), and Siloxane-Gluc225 (k-o) foams extinguishing a benchtop (19 cm diameter) heptane pool fire at a foam application rate of 1000 mL min^{-1} at the center of the pool. Images are taken at times 0, 5, 10, 16, and 24 s during extinction.

In Figure 49, we show extinction times measured for 19-cm diameter bench top and 1.83 m (6 ft) diameter large scale heptane pool fires as functions of foam application rate per unit area (flux) of the pool. The 1.83 m (6 ft) pool fire test is same as the MilSpec MIL-F-24365F [4] but with heptane fuel instead of gasoline. For the benchtop, we compare fire extinction times for the Siloxane-Gluc225 surfactants formulation (red solid square), RefAFFF (black solid circle), and the commercial AFFF (Buckeye 3%, black solid diamond) foams. As the foam application rate is decreased, the extinction time increases and reaches extinction times greater than 180 seconds when the foam application is stopped and the fire is extinguished by placing a tray over the pool. The RefAFFF and the Siloxane-Gluc225 formulations could not extinguish the flame within 180 seconds at foam application rate below 5.9 and $9.7 \text{ L m}^{-2} \text{ min}^{-1}$ respectively. The extinction times for the siloxane formulation are closer (< 1.5 times that of RefAFFF) to the AFFFs at large foam application rates. For the 1.83 m (6 ft) diameter heptane pool fire, we compare the extinction times for the Siloxane-Gluc225 formulation at fixed solution flow rates of 7.6 and 11.4 L min^{-1} (2 and 3 gallons per minute) which correspond to 18.6 and $22.2 \text{ L m}^{-2} \text{ min}^{-1}$ of foam flow rates respectively. The foam flow rates are calculated by multiplying the measured liquid flow rates with the measured expansion ratio values. We also compare the extinction times for the Siloxane-Gluc225 formulation with that of RefAFFF formulation for the 1.83 m (6 ft) diameter heptane fire in Figure 49. The extinction times are 45 and 30 seconds for the Siloxane-Gluc225 and RefAFFF respectively at a fixed foam flux of about $22 \text{ L m}^{-2} \text{ min}^{-1}$. Thus the extinction times for the siloxane formulation are within 1.5 times those for the RefAFFF, consistent with the bench-scale data for the same foam flux. Despite significant differences in the foam generation and foam properties between the bench and large scales, the fire extinction data are surprisingly consistent possibly because the surfactant-fuel interactions and the foam application rate per unit area have more significant effects. Although the foam application rate $22 \text{ L m}^{-2} \text{ min}^{-1}$ is about the same for the two formulations, the solution application rate 11.4 L min^{-1} (3 gallon/min, expansion ratio 5.1) is higher

for the Siloxane-Gluc225 than 7.57 L min^{-1} (2 gallon per min, expansion ratio 7.5) for the RefAFFF because of the differences in the foam expansion ratio in the large scale testing. The foam expansion ratio of Siloxane-Gluc225 decreases from 6.4 to 5.1 as the solution flow rate increases from 7.57 to 11.36 L min^{-1} (2 gpm to 3 gpm) during the large scale foam generation.

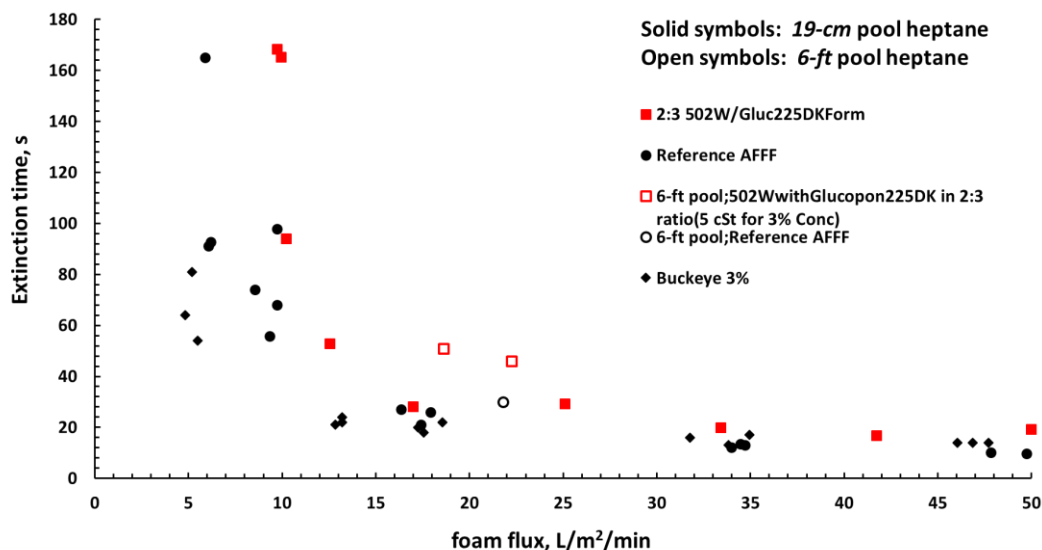


Figure 49. Bench-scale (19 cm dia.) and large scale (1.83 m or 6 ft dia.) extinction of heptane pool fire showing extinction times of Siloxane-Gluc225 surfactant formulation relative to the RefAFFF and commercial formulation (Buckeye 3%) at different measured foam application rates; For the 1.83 m (6 ft) fire, the foam and liquid flux values correspond to 7.57 to 11.36 L min^{-1} (2 and 3 gallons per min) solution flow rates [44].

5.5.3. Metal versus Glass Wall Effects and Expired 502W Concentrate

Figure 50 compares fire extinction and pool coverage time profiles using stainless steel container versus glass container for the fuel pool. The stainless steel container has much higher thermal conductivity even though it is slightly smaller in diameter than the glass container. The metal container may conduct heat away from the edges where the flame is very hot. At the container edges, fuel vapors mix with the entrained fresh air with high combustion rate and heat release rate. Figure 50a and b do not show a significant effect on extinction and coverage times due to the container material.

Figure 50c shows variation in DOWSIL 502W samples provided in kind by Dow Chemical Co. The samples provided by Dow are in closed containers and have expiration dates as indicated in Figure 50c. We noticed a precipitate at the bottom of the closed container past the expiration date 06/19/2020. We performed gasoline fire extinction tests on a sample before and after expiration date. We took only the liquid sample (not precipitate) from the top of the container without shaking for the gasoline fire test shown in Figure 50c. The liquid part of the expired sample appears to have slightly smaller extinction times than the unexpired, homogeneous, fresh samples.

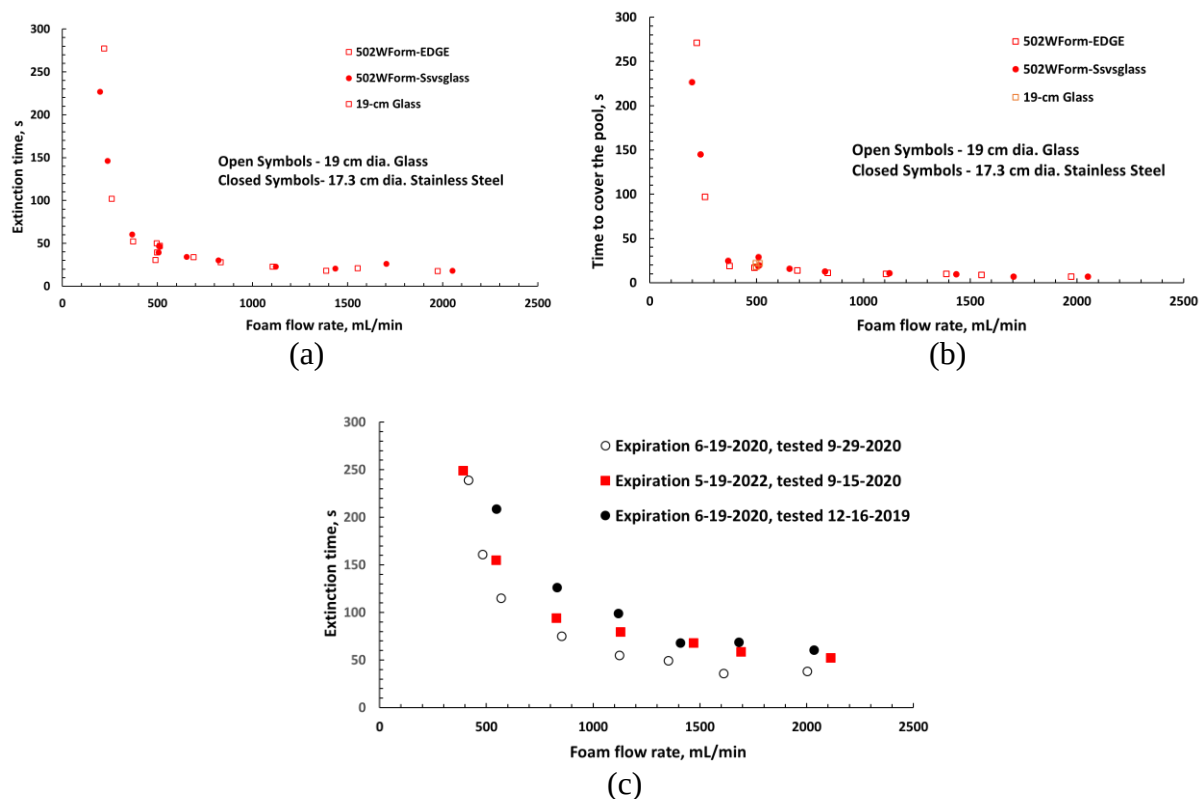


Figure 50. Effect of metal versus glass walls on heptane fire (a) extinction time and (b) pool coverage time versus foam application rate for 502WForm (502W:Glucopon225DK 2:3 ratio). Foams were deposited at the center of the pool and at the pool edge (labeled EDGE). (c) Effect of expired versus fresh samples of 502W on gasoline fire extinction time versus foam application rate with foams deposited at the edge of the pool.

5.5.4. Evaluation of Siloxane-Glycoside – Large Scale

We focused on a subset of five metrics in the MilSpec standard MIL-F-24385 to evaluate the Siloxane-Gluc225 and the RefAFFF formulations [44]. We measured five parameters and compared with passing criteria, which are based on gasoline fuel rather than the heptane. The parameters measured were (1) 2.6 m² (28 ft²) pool fire extinction time, (2) burnback time, (3) film and seal, (4) expansion ratio, and (5) 25% drainage time, and are described in MilSpec standard MIL-F-24385. The results are shown in Table 20.

Both 90% and 100% extinction times decrease as the foam flow rate is increased as shown in Table 20. At a fixed foam flow rate of about 56.8 L min⁻¹ (15 gpm) shown in row 3 and columns 3 and 4 of Table 20, the 90 and 100% extinction times for the Siloxane-Gluc225 are less than or equal to a factor of 1.5 times those for RefAFFF. However, at a fixed solution flow rate of 7.57 L min⁻¹ (2 gpm), the extinction times differ by as much as a factor of two as shown in columns 2 and 4. The factor 1.5 times is consistent with the bench-scale data as shown in Figure 49. One reason for the longer extinction time for Siloxane-Gluc225 is the larger foam degradation rate, as indicated by the smaller burnback time of 338 s for the siloxane formulation compared to 981 s for the RefAFFF as shown in columns 2 and 4. Foam is applied for a total of 90 s including

Table 20. Comparison of Siloxane-Gluc225 formulation at 7.57 and 11.36 L min⁻¹ (2 and 3 gpm) and with RefAFFF at 11.36 L min⁻¹ (2 gpm) liquid application rate for 6-ft diameter MilSpec pool fire using heptane as the fuel instead of gasoline¹[44].

MilSpec Test with Heptane fuel	2:3 Siloxane-Gluc225		RefAFFF 3:2 Cap/Gluc215	Criteria (based on gasoline)
Liquid flow rate L min ⁻¹ (gpm)	7.57 (2)	11.36 (3)	7.57 (2)	7.57 (2)
Foam flow rate ² L min ⁻¹ (gpm)	48.4 (12.8)	57.9 (15.3)	56.8 (15)	N/A
90% extinction (s)	43	26	21	N/A
Extinction (s)	51	45	30	<30
Burnback (s)	338	424	981	>360
Film and seal	N/A	N/A	PASS	PASS
Expansion ratio	6.4	5.1	7.5	5-10
25% Liquid Drainage (s)	198	198	251	>150
Average bubble size (μm)	220±111	140±30	170±30	N/A
3% concentrate viscosity, 20°C (cP)	5.3	5.3	3.2	>2
3% concentrate viscosity, 5°C (cP)	7.4	7.4	4.7	<20
Solution viscosity, 20°C (cP)	1.14	1.14	1.12	N/A
Spreading coefficient on cyclohexane ³ , (mN m ⁻¹) at 20°C	-0.4	-0.4	6.4	>3
Interfacial tension on cyclohexane, (mN m ⁻¹) at 20°C	2.2	2.2	1.9	N/A
Surface tension (mN m ⁻¹) at 20°C	22.4	22.4	16.7	N/A
3% concentrate refractive index	1.371	1.371	1.362	>1.363
CMC (% volume of total surfactant concentrates)	0.05	0.05	0.1	N/A
3% concentrate pH	6-8	6-8	6-8	7-8.5

¹The MilSpec typically requires unleaded, alcohol-free, gasoline fire suppression rather than heptane fire.

²Foam flow rate is the specified liquid flow rate multiplied by the measured foam expansion ratio.

³Surface tension of cyclohexane is 25 mN m⁻¹ at 20°C.

extinction, therefore the expected burnback time for the siloxane formulation is 544 s, after correcting for the shorter foam application time following fire extinction and for the difference in the expansion ratios. The measured burnback time of 338 s for the siloxane-Gluc225 is significantly smaller than the expected 544 s indicating significantly greater foam degradation.

The data in Table 20 show that the increased foam flow rate decreases the extinction time. The foam flow rate can be increased by increasing the foamability or the expansion ratio as well as by increasing the solution flow rate. Other properties especially the viscosity of the concentrate are within MilSpec criteria. This is important because many commercial fluorine free concentrates to date have viscosities well above the MilSpec criteria.

5.5.5. Synergistic Effects on Fire Suppression

The reason for relatively good fire suppression performance of the Siloxane-Gluc225 formulation is the synergism between the Siloxane and Glycoside surfactants. This is especially indicated by the smallest foam flow rate at which a formulation can extinguish the fire in a given time (e.g., 180 seconds) [44]. Figure 51 depicts the synergism where the surfactant mixture can extinguish the fire at a much smaller foam application rate than the individual surfactant solutions rather than an intermediate foam flow rate, which is expected following the law of averages. Figure 51 shows the bench scale heptane pool fire extinction data for 3:2 Siloxane-Gluc215 formulation composition listed in Table 19 and for the three individual surfactant solutions (0.45% Glucopon 215 CS UP, 0.1% siloxane 502W, 0.5% siloxane 502W, 0.5% Glucopon 225 DK, 0.5% Glucopon 600 CS UP all with 0.5% DGBE in distilled water). Gluc215 could not extinguish the fire even at a very high foam flow rate (2100 mL min^{-1} or $74 \text{ L m}^{-2} \text{ min}^{-1}$ within 180 s) as shown by the data points (open squares) on the x-axis, which represent no extinction. Similarly, 502W siloxane surfactant solution also could not extinguish the fire below a high value of the foam flow rate (1550 mL min^{-1} or $54.7 \text{ L m}^{-2} \text{ min}^{-1}$) as represented by the data points (solid green circles) on the x-axis. But, when both the surfactants are combined in a 3:2 ratio the foam extinguished the fire at significantly smaller foam flow rate (in 197 s at 453 mL min^{-1} or $16 \text{ L m}^{-2} \text{ min}^{-1}$) as indicated by the data (red solid squares) for Siloxane-Gluc215 (composition 0.075% 502W, 0.05% Gluc215, and 0.5% DGBE) exhibiting synergism. Similar results are shown for Siloxane-Gluc225DK and Siloxane-Glucopon600UP mixtures.

Figure 51 also shows the effect of varying Glucopon surfactant's head size and the number of OH functional groups on heptane pool fire extinction because of the synergistic effects. The head size is varied from $x=0.4$, 0.5, and 0.7 using commercially available Glucopon 600 CS UP, Glucopon 215 CS UP, and Glucopon 225 DK respectively while keeping the composition fixed (0.2% 502W, 0.3% Glucopon, and 0.5% DGBE). Gluc600 has slightly longer alkyl tail than Gluc215 and Gluc225. Increasing the hydrophilicity of the hydrocarbon surfactant increases the synergistic effect, and reduces the foam flow rate where the extinction time is 180 s in Figure 51. The synergistic extinction between 502W and Glucopon surfactants is unique because for most other commercial surfactants that we examined, the extinction times fell between the extinction times of the individual surfactant following the law of averages. The synergism is responsible for the high extinction performance of the siloxane formulation.

The synergistic extinction between 502W siloxane and Glucopons relates to the synergistic foam degradation, which is shown in Figure 52a. Again, Figure 52a shows that the surfactant mixture exhibits smaller foam degradation rate than the rates for the individual surfactants rather than an intermediate value, which is expected following the law of averages. Figure 52a shows percent change in foam layer thickness (initial thickness of 4-cm) on top of a hot heptane pool with time due to fuel vapor induced degradation. The foams generated from 0.5% Glucopon 215 CS UP with 0.5% DGBE and 0.1% 502W with 0.5% DGBE degraded in 240 and 480 s respectively.

The foam generated from Siloxane-Gluc215 (0.075% 502W, 0.05% Glucopon 215 CS UP, and 0.5% DGBE) degraded completely in a much longer time (900 s) compared to the degradation

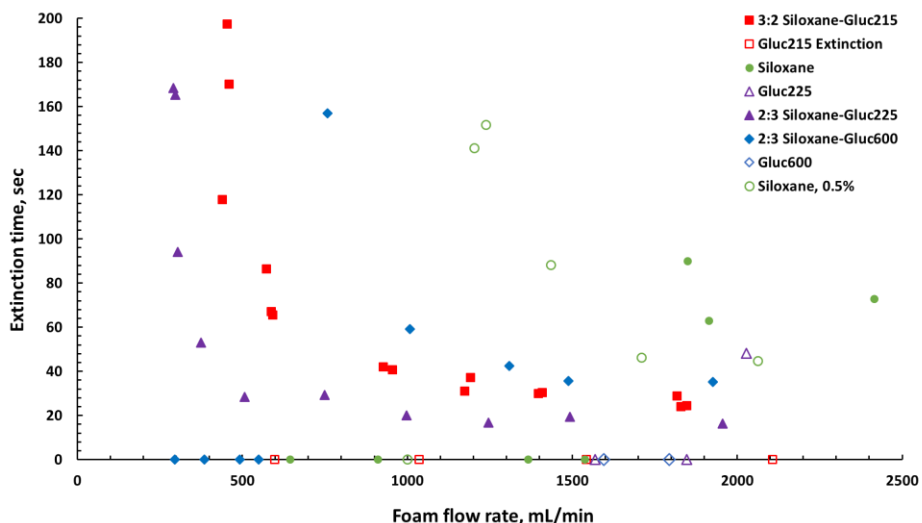


Figure 51. Bench-scale (19-cm dia.) extinction of heptane pool fire showing extinction time of Siloxane-Gluc mixtures listed in Table 19 relative to the solutions of individual components, which also contain 0.5% DGBE. The data points shown along the x-axis represent no extinction data after 180 s of foam application [44]. Foams applied at the center of the pool.

times of the individual surfactants. Figure 52a also shows degradation data for the individual surfactant solutions of Gluc600 and Gluc225 and their mixtures with 502W. They also show synergistic effects like those described for Siloxane-Gluc215. Furthermore, as the glycoside head size of the Glucopon is increased, the degradation rate is reduced for the glycoside mixtures with the siloxane surfactant. The synergism is increased by increasing the hydrophilicity of Glucopon's head group as shown by the foam degradation for Siloxane-Gluc600, Siloxane-Gluc215, and Siloxane-Gluc225 formulations in Figure 52a. The number of OH functional groups increased from $x=0.4$, 0.5 to 0.7 by switching from Gluc600, Gluc215 to Gluc225 as shown in Figure 17; Gluc600 has slightly longer alkyl tail. The exact mechanisms for the increased foam stability are not well understood. However, it is possible that the increased hydrophilic interactions between the polyoxyethylene and glycoside head groups may have reduced the surfactant solubility in heptane resulting in increased foam stability over the individual surfactants. Figure 52a shows that the foam generated from Siloxane-Gluc225 formulation degraded completely in 1380 s versus 900 s for the foam generated from Siloxane-Gluc215 (in a 3:2 ratio), and 500 s for Siloxane-Gluc600. Siloxane-Gluc225 has the smallest degradation rate but is still significantly higher than the RefAFFF as shown in Figure 52a. For comparison, commercial AFFF (Buckeye 3%) and RefAFFF degrade completely in time periods that are 1.7 (2400 s) and 2.6 times (3600 s) longer respectively than the time (1400 s) for Siloxane-Gluc225.

Figure 52b shows that the fuel permeation rate through foam follows roughly the law of averages and does not show the synergistic effects observed in foam degradation at small times for all three Siloxane-Gluc surfactant combinations. For example, below 450 s, the fuel flux for foam generated from Siloxane-Gluc215 lies between those for foams generated from the individual surfactants. However, the synergism exhibited in foam degradation in Figure 52a prolongs the

foam life time and suppresses the fuel flux shown in Figure 52b at long times. At longer than 450 s, the surfactant mixture Siloxane-Gluc215 has a smaller fuel flux than the individual surfactants, which exhibit a steep rise in fuel flux because of differences in the foam degradation rate. Thus,

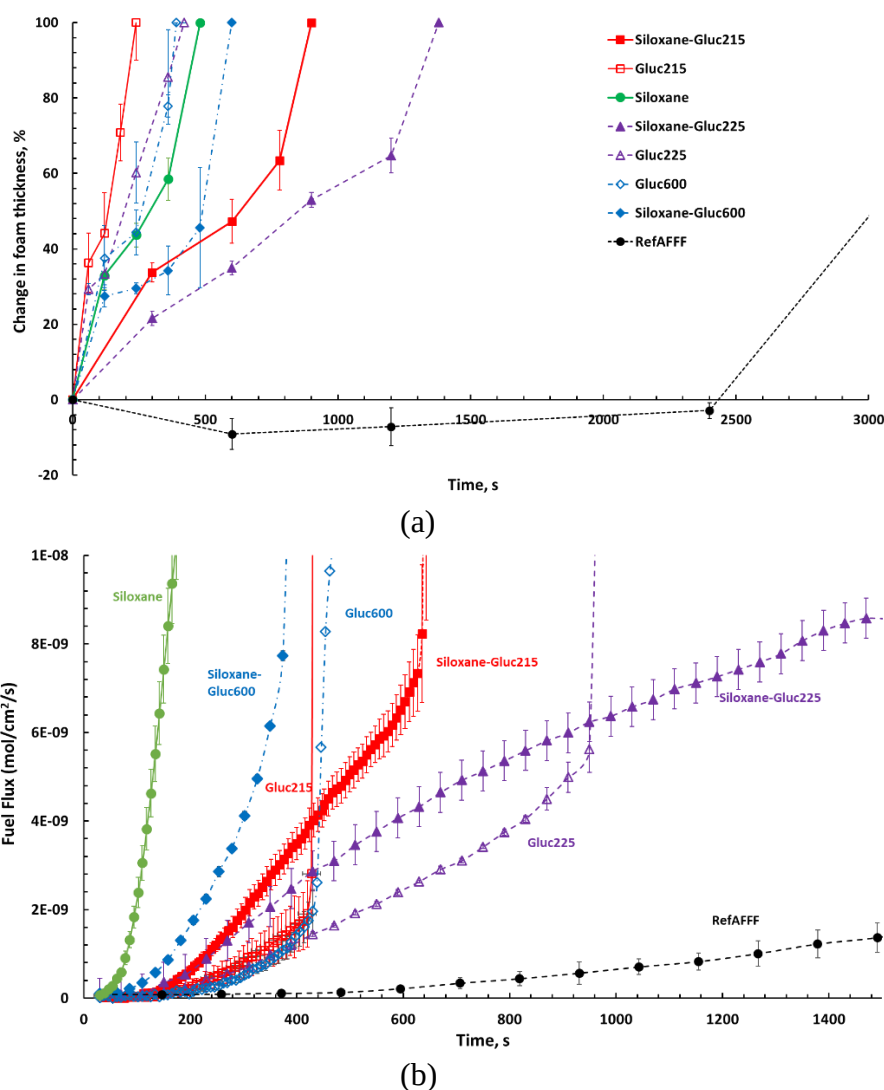


Figure 52. Measured rates for a 4 cm thick (initial thickness) foam layer covering heptane pool at 60°C with time for the Siloxane-Gluc225, Siloxane-Gluc600, and Siloxane-Gluc215 listed in Table 19, and for the individual surfactant components (0.5% Gluc215, 0.5% Gluc225, 0.5% Gluc600, and 0.1% 502W. All four solutions contain 0.5% DGBE.): (a) foam degradation, (b) heptane vapor permeation rate through the foam. Error bars represent one standard deviation calculated between three trials [44].

the synergism in degradation leads to a dramatic reduction in fuel transport rate for the three surfactant mixtures compared to foams generated with individual surfactants because of the increased lifetimes of the foams for the mixtures. Even though the fuel flux is smaller for Gluc225 than for Siloxane-Gluc225 mixture at short times, Siloxane-Gluc225 lasts longer (>1750 s) than Gluc225 (980 s) and the trend reverses. For comparison, commercial AFFF (Buckeye 3%) and RefAFFF have a heptane flux of 0.4 (2.7×10^{-9} mole cm^{-2} s^{-1}) and 0.1 (7×10^{-10} mole cm^{-2} s^{-1})

times that of Siloxane-Gluc225 (6.6×10^{-9} mole $\text{cm}^{-2} \text{s}^{-1}$) respectively at 1000 s. The reduction in degradation and fuel transport rates decreases the fire extinction times for the mixtures over the individual surfactants shown in Figure 51. The foams lasts longer in the fuel transport apparatus because it is closed and the water vapor is relatively more contained than in the open degradation apparatus. This is especially true for Gluc225 which lasts greater than 980 s in the transport apparatus but less than 400 s in the degradation apparatus. But, Figure 52b shows a steep rise in fuel flux to 1×10^{-8} mole $\text{cm}^{-2} \text{s}^{-1}$ in less than 200 s for the Siloxane foam. It take much longer than 200 s for the foam to degrade completely and for the fuel flux to reach that of bare heptane's fuel flux (not shown in Figure 52b). The reason the Siloxane foam's fuel transport curve rises rapidly in Figure 52b is that the heptane vapors travel through the foam very quickly and not because of a significant reduction in foam layer thickness. Thus, the Siloxane foam seems to have significantly higher fuel transport than Gluc225 foam and the Gluc225 foam has only a slightly higher degradation rate than the Siloxane foam. However, the combination of Siloxane with Gluc225 suppresses the foam degradation dramatically and as a result the fuel transport is also suppressed at long times. It is also interesting that the three Glucopons have very similar fuel transport rate profiles at small times (<400 seconds). The fuel transport rate depends on the fuel concentration in surfactant solution which may depend on the micelle size and number density because most of the fuel is expected to reside inside the micelles. Micelle size can affect the diffusion rate. The exact mechanisms of fuel and micelle transport in the presence of a surfactant remain unclear. During fire extinction, as the foam is applied continuously on to a burning fire, the foam spreads and foam layer thickness increases with time. The thickness (foam volume) needed to extinguish the fire varies between 0.5 to 2 cm depending on the foam application rate, rate of foam degradation by the fuel vapor, fuel vapor permeation rate, and foam spread rate. Foam's ability to resist fuel vapors from coalescing and permeating through the bubbles plays a crucial role in foam degradation, fuel permeation, and foam spread.

If a foam spreads too slowly, it can increase the extinction time because complete coverage of the pool surface is necessary, but not sufficient, to extinguishing a fire. Figure 53 shows the time to cover a burning heptane pool with foam, which is delivered at the center of the bench-scale pool at a constant flow rate for the Siloxane-Gluc225 and the RefAFFF formulations listed in Table 19. As the foam flow decreases the foam spread time increases as expected. Also shown are the fire extinction times for comparison. The foam spread times are about half the extinction times at high foam flow rates for both the formulations. As the foam flow rate is decreased, the foam spread times become greater than half, but still remain smaller than, the fire extinction times likely because foam degrades significantly due to longer exposure to the hot pool and fire. In addition to foam degradation, foam spread also depends on the rheological properties and the expansion ratio, which increases as the foam flow rate decreases in our foam generation apparatus as discussed later.

Fluorocarbon surfactants differ significantly from the fluorine-free surfactants in their hydrophobic and oleophobic interactions with water and fuel leading to superior foam properties and fire performance. However, combining two fluorine-free non-ionic surfactant structures in a mixture can exhibit synergistic effects leading to superior performance over the individual components. We showed that a commercial siloxane surfactant with a polyoxyethylene head group when combined with a certain commercial alkane surfactant with polyglycoside head group exhibited quicker (4.7 times smaller extinction time at 1200 mL min^{-1} foam flow rate) fire extinction of a heptane pool fire than the individual components. This was due to synergistic

reduction in foam degradation rate (3.5 times longer time at 100% foam degradation caused by the heptane vapors generated by the hot fuel pool for the mixed surfactant formulation over the individual surfactants. Despite the lack of a similar synergism in fuel transport rates through a

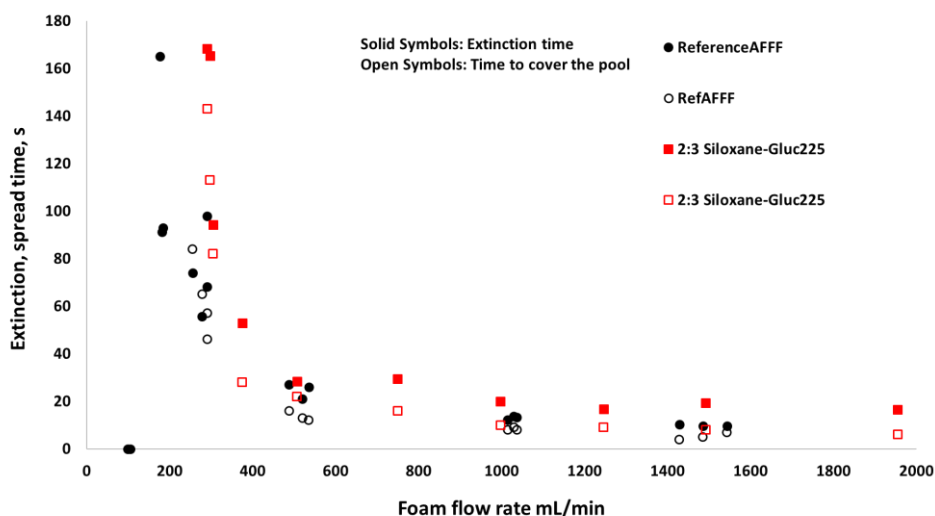


Figure 53. Comparison of foam spread time to cover the pool surface during the heptane pool fire suppression with the fire extinction time at different foam application rates for the bench-scale pool. Foam is delivered at the center of the pool at a constant flow rate and allowed to spread. Spread times (open symbols) and extinction times (closed symbols) are shown for Siloxane-Gluc225 and RefAFFF listed in Table 19. Data points on x-axis ($y=0$) show flow rates where fire was not extinguished in 180 s [44].

foam layer, the fuel transport rates are suppressed for longer time for foams generated with the surfactant mixture because of the enhanced foam stability. The molecular interactions between the two surfactants' hydrophilic head groups (poly oxyethylene and poly glycoside) and precise mechanisms of the synergism are unclear. However, increasing the number of $-OH$ functional groups by increasing the size of the polyglycoside head, reduced the foam degradation and the fire extinction time further. Indeed, small differences in the size ($x=0.4, 0.5$, and 0.7) of polyglycoside head had a significant effect on foam stability. Similarly, we hypothesize that varying the size of oxyethylene head of siloxane surfactant can also affect the degree of synergism. It is possible that the stronger interaction between the two head groups may have suppressed the surfactant solubility in heptane resulting in increased foam stability near the foam-fuel interface. Previously, we showed that the fuel destabilizes the foam near the foam-fuel interface causing coalescence of bubbles in a cascading effect leading to rapid degradation. Similarly, the micelle size and micelle number density can affect the fuel concentration and diffusivity, which may affect the fuel transport. The large tail and slender head of the branched-trisiloxane surfactant and vice-versa for the glycoside surfactant may enable bilayer vesicle formation providing stability to the bubble lamellae and resistance to the fuel. The mechanisms of transport for the individual versus combined surfactants are unclear and may not be limited to trisiloxane-glycoside systems. The synergism between siloxane and glycoside structures resulted in a factor of 5 enhancement in foam stability and fire extinction performance demonstrating the key role played by the interactions between the surfactant structures and fuel in extinction. A basic understanding of the mechanisms

of synergism can lead to an approach based on synthesizing synergistic molecules, which can result in performance matching that of fluorocarbon surfactants.

We found that the fire extinction time for NRL's siloxane surfactant formulation to be less than 1.5 times that of an equivalent AFFF formulation containing a fluorocarbon surfactant for both the bench (19 cm diameter) and 1.83 m (6 ft) diameter heptane pool-fires at a fixed foam application rate ($22 \text{ L m}^{-2} \text{ min}^{-1}$). The viscosity of NRL's siloxane-formulation concentrate is within the MilSpec criteria unlike many commercial fluorine-free firefighting-foam concentrates. Foam's resistance to fuel vapors from hot pool play crucial role in designing firefighting surfactants and foams. Foam's resistance depends on specific surfactants and their interactions with a specific fuel at air-water and fuel-water interfaces, and micelles. The difference in fire extinction between the Siloxane-Glycoside and RefAFFF formulations was due to differences in foam degradation and fuel vapor transport rates rather than the differences in surface tension (dynamic and static) or aqueous film formation, bubble size distributions and coarsening, foam spread rates, and liquid drainage rates for the foam application rates studied. However, fluorocarbon and fluorine-free surfactants can have very different effects on bubble sizes, coarsening, and liquid drainage when hot fuel is present and need to be studied further. Single lamella studies are needed to directly relate surfactant and fuel effects to a bubble lamella stability. Solution and foam properties measured especially in the presence of hot fuel cannot be ignored because they may become the controlling factors for fire extinction depending on the specific surfactant system and the fuel under consideration, and the foam generation methods used.

5.6. Environmental Impact of Siloxane-Glycoside Formulation

The approach and methods for the evaluation of environmental impact are described in section 4.13. Here, we describe the test results.

5.6.1. Test Conditions

The hardness and alkalinity of the laboratory control water (moderately hard-reconstituted water for *C. dubia* and *P. promelas* tests) ranged from 96-104 and 80-84 mg/L as CaCO_3 , respectively. The hardness and alkalinity of the laboratory control water (OECD algae media for *R. subcapitata* test) was 32 and 32 mg/L as CaCO_3 , respectively. Throughout the tests, water quality chemistries were measured in "new" waters that were representative of freshly-prepared solutions, but before organism exposure, and in "old" waters from one replicate per treatment following 24-hrs of organism exposure. As shown in Table 21, the ranges of pH did not significantly differ in any exposures staying within ± 0.5 SU between minimum and maximum values. Dissolved oxygen concentrations also did not significantly differ and remained above 60% saturation. But it should be noted that measurements were only taken from control replicates, due to the inability to clean the DO probe if submerged in the test compounds. It has been noted that surfactants may cause low dissolved oxygen in waters, but data reported here are not able to address this question. Conductivity did vary between exposures, but the variability (typically an increase) was commonly observed between new and old measurements, even in the control waters. This demonstrates that biological processes (food and/or feces from the organisms) in the exposure waters were most likely contributing to conductivity variability, as opposed to the test substances. Acceptable temperatures ($25 \pm 2^\circ\text{C}$) were maintained in all tests.

Table 21. Exposure water quality during conduct of toxicity tests (all exposures).

Compound	Test	pH (SU) (range)	Conductivity (μ S/cm) (range)	Dissolved oxygen (mg/L) (range)
DOWSIL™ 502W Additive	<i>C. dubia</i> Acute	7.93 – 8.16	362 – 376	8.06 – 8.45
	<i>P. promelas</i> Acute	7.77 – 8.05	367 – 422	8.14 – 8.56
	<i>C. dubia</i> Chronic	7.74 – 8.41	358 – 401	8.25 – 9.69
	<i>P. promelas</i> Chronic	7.84 – 8.20	360 – 435	7.31 – 8.77
Butyl Carbitol	<i>C. dubia</i> Acute	7.52 – 8.10	364 – 550	8.15 – 8.50
	<i>P. promelas</i> Acute	7.72 – 8.16	367 – 647	8.09 – 8.58
	<i>C. dubia</i> Chronic	7.65 – 8.11	335 – 522	8.27 – 8.76
	<i>P. promelas</i> Chronic	7.71 – 8.13	359 – 509	8.04 – 8.77
Glucopon® 225 DK	<i>C. dubia</i> Acute	7.93 – 8.33	347 – 744	8.30 – 8.67
	<i>P. promelas</i> Acute	7.90 – 8.12	370 – 556	8.16 – 8.77
	<i>C. dubia</i> Chronic	7.80 – 8.05	353 – 484	8.26 – 8.74
	<i>P. promelas</i> Chronic	7.62 – 7.99	361 – 466	7.33 – 8.71

5.6.2. Exposure Concentrations - DOWSIL 502W Additive

As shown in Tables 22 to 25, DOWSIL™ 502W Additive exposure concentrations are reported under two categories: “new” and “old”. “New” waters were sampled directly from the freshly prepared solutions at test initiation or immediately prior to use for water-renewals (while homogenized, see Section 2.5). “Old” waters consisted of a composite of solutions obtained directly from test chambers following either 24 or 48 hrs of exposure, and at test termination. Homogeneity was maintained for all samples by keeping the beaker of water gentle mixed prior to sampling for each analysis.

When compared to nominal DOWSIL™ 502W Additive concentrations, concentrations in “new” solutions freshly prepared were highly variable, ranging from 48-156% of nominal (with one sample measuring 186% of nominal). Samples taken after 24 to 48 hrs of organism exposure under static exposures reflected decreases ranging from 0 to 64% of the concentrations measured in newly prepared waters. These variable results are consistent with previous work that identified challenges in maintaining constant concentrations in solutions due to partitioning of the surfactants to the air-water interface, adhesion to the surface of containers and other issues with homogeneity [54,55]. Due to a variety of factors, including surface area ratio of air/water of testing containers and unknown sorption to the cups used in testing, it is difficult to isolate the cause of the loss. This loss effects both the stability of the solutions over the course of the tests, as well as implies possible problems with the stability of the surfactants over time when stored prior to use in an AFFF formulation.

In addition to unknowns associated with the behaviors of the siloxanes in the testing vessels, the siloxanes may interact with the organisms in ways which decrease the observed concentrations over time. The organism may be metabolizing the surfactants in unidentified ways, or the surfactants may be partitioning onto the external integument of the organisms. This increases the difficulty in isolating the source of loss observed in the tests.

Background concentrations of DOWSIL™ 502W Additive in the control waters were below the limit of quantitation (LOQ of 0.02 mg/L). For statistical analysis of the biological data from the toxicity tests, control exposures were assigned a value of 0.01 mg/L (or half the LOQ).

Table 22. DOWSIL™ 502W Additive analysis during conduct of toxicity test – *C. dubia* Acute.

Test org	Test ID	Nominal Conc. (mg/L)	0 hr (new)	48 hr (old)	Average	Std Dev
			mg/L DOWSIL™ 502W Additive (measured)			
<i>C. dubia</i> <i>Acute</i>	AFFF 1312 CDA	0 ¹	< LOQ 0.02	< LOQ 0.02	0.01	0.0
		6.25	6.7	5.4	6.1	0.9
		12.5	13.4	9.6	12	2.7
		25	30	21	26	6
		50	60	45	53	11
		100	100	110	105	7

¹ Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=0.01 mg/L)

Table 23. DOWSIL™ 502W Additive analysis during conduct of toxicity test – *C. dubia* Chronic.

Test org	Test ID	Nominal Conc. (mg/L)	Day 0 (new)	Day 6 (new)	Day 7 (old)	Average	Std Dev
			mg/L DOWSIL™ 502W Additive (measured)				
<i>C. dubia</i> <i>Chronic</i>	AFFF 1335 CDC	0 ¹	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	0.01	0
		1.25	0.6	1.3	1.0	0.9	0.4
		2.5	1.5	2.4	2.1	2.0	0.5
		5	3.3	9.3 ²	3.5	5.3	3.4
		10	6.2	9.0	sample/ analytical error	7.6	2.0
		20	13.1	18.0	18.0	16.3	2.8

¹ Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=0.01 mg/L).

² Sample result verified by duplicate sample. Reported as measured.

Table 24. DOWSIL™ 502W Additive analysis during conduct of toxicity test – *P. promelas* Acute.

Test org	Test ID	Nominal Conc. (mg/L)	0 hr (new)	48 hr (old)	48 hr (new)	96 hr (old)	Average	Std Dev
			mg/L DOWSIL™ 502W Additive (measured)					
<i>P. promelas</i> Acute	AFFF 1327 PPA	0 ¹	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	0.01	-
		1.54	2.4	1.5	2.4	1.9	2.1	0.4
		2.18	3.1	2.2	3.4	2.4	2.8	0.6
		3.07	4.5	3.5	4.5	3.7	4.1	0.5
		4.34	5.8	4.8	6.2	5.4	5.6	0.6
		6.13	8.5	7.2	-	-	7.9	0.9

¹ Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=0.01 mg/L)

Table 25. DOWSIL™ 502W Additive analysis during conduct of toxicity test – *P. promelas* Chronic.

Test org	Test ID	Nominal Conc. (mg/L)	Day 0 (new)	Day 6 (new)	Day 7 (old)	Average	Std Dev
			mg/L DOWSIL™ 502W Additive (measured)				
<i>P. promelas</i> Short-term Chronic	AFFF 1342 PPC	0 ¹	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	0.01	0
		0.238	0.24	0.12	0.18	0.2	0.1
		0.475	0.55	0.37	0.38	0.4	0.1
		0.95	0.73	0.88	0.88	0.8	0.1
		1.9	1.69	2.00	0.73	1.5	0.7
		3.8	3.16	3.63	1.82	2.9	0.9

¹ Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=0.01 mg/L)

5.6.3. Exposure Concentrations - Butyl Carbitol

As shown in Tables 26 to 29, exposure concentrations are reported under two categories: “new” and “old”. “New” waters were sampled directly from the freshly prepared solutions at test initiation or immediately prior to use for water-renewals (while homogenized, see Section 2.5). “Old” waters consisted of a composite of solutions obtained directly from test chambers following either 24 or 48 hrs of exposure, and at test termination. Homogeneity was maintained for all samples by keeping the beaker of water gentle mixed prior to sampling for each analysis.

When compared to nominal butyl carbitol concentrations, concentrations in “new” solutions freshly prepared remained consistent, ranging from 76-127% of nominal. Samples taken after 24 to 48 hrs of organism exposure under static exposures reflected decreases ranging from 0 to 19% of the newly prepared waters. Unlike the DOWSIL 502W Additive concentration variability, butyl carbitol remained stable throughout the preparation of solutions and conduct of the toxicity tests.

Background concentrations of butyl carbitol in the control waters ranged were below the limit of quantitation (LOQ of 2.5 mg/L). For statistical analysis of the biological data from the toxicity tests, control exposures were assigned a value of 1.3 mg/L (or half the LOQ).

Table 26. Butyl Carbitol analysis during conduct of toxicity test – *C. dubia* Acute.

Test org	Test ID	Nominal Conc. (mg/L)	0 hr (new)	48 hr (old)	Average	Std Dev
			mg/L Butyl Carbitol (measured)			
<i>C. dubia</i> <i>Acute</i>	AFFF 1382 CDA	0 ¹	< LOQ 2.5	< LOQ 2.5	1.3	0
		350	391	411	401	14
		700	721	808	764	61
		1400	1733	1832	1782	70
		2800	3352	3726	3539	264
		5600	6630	7155	6893	371

¹ Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=1.3 mg/L)

Table 27. Butyl Carbitol analysis during conduct of toxicity test – *C. dubia* Chronic.

Test org	Test ID	Nominal Conc. (mg/L)	Day 0 (new)	Day 6 (new)	Day 7 (old)	Average	Std Dev
			mg/L Butyl Carbitol (measured)				
<i>C. dubia</i> <i>Chronic</i>	AFFF 1391 CDC	0 ¹	< LOQ 2.5	< LOQ 2.5	< LOQ 2.5	1.3	0
		125	121.3	113.4	119.2	118	4
		250	200	253	260	238	33
		500	509	505	514	509	4
		1000	1059	1093	1028	1060	33
		2000	1935	1959	1995	1963	30

¹Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=1.3 mg/L)

Table 28. Butyl Carbitol analysis during conduct of toxicity test – *P. promelas* Acute.

Test org	Test ID	Nominal Conc. (mg/L)	0 hr (new)	48 hr (old)	48 hr (new)	96 hr (old)	Average	Std Dev
			mg/L Butyl Carbitol (measured)					
<i>P. promelas</i> <i>Acute</i>	AFFF 1376 R PPA	0 ¹	< LOQ 2.5	< LOQ 2.5	< LOQ 2.5	< LOQ 2.5	1.3	0
		250	306	329	304	302	310	13
		500	442	447	467	474	457	16
		1000	756	911	827	928	855	80
		2000	1560	1401	1625	1674	1565	119
		4000	3495	3348	-	-	3421	104

¹Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=1.3 mg/L)

Table 29. Butyl Carbitol analysis during conduct of toxicity test – *P. promelas* Chronic.

Test org	Test ID	Nominal Conc. (mg/L)	Day 0 (new)	Day 6 (new)	Day 7 (old)	Average	Std Dev
			mg/L Butyl Carbitol (measured)				
<i>P. promelas</i> Short-term Chronic	AFFF 1386 PPC	0 ¹	< LOQ 2.5	< LOQ 2.5	< LOQ 2.5	< LOQ 2.5	0
		245	310	304	298	304	6
		490	462	444	411	439	26
		980	790	772	625	729	91
		1960	1605	1557	1414	1525	99
		3920	3404	-	3244 ^A	3324	113

¹ Control water with measurements below the limit of quantification (LOQ) were assigned a value of ½ the LOQ (=0.01 mg/L)

^A Concentration nominal 3920 mg/L: 100% mortality occurred on Day 1 and old sample was taken (shown in Day 7 (old) cell)

5.6.4. Biological Results

The biological results and endpoint summaries (NOEC, LOEC, LC50, EC20) in the single compound tests are summarized in Tables 30 to 35. Values with bold font represent a statistically significant concentration ($p < 0.05$) when compared to the dilution water control.

In the acute tests with *C. dubia* and *P. promelas*, test acceptability criteria for survival was met for survival in the control water for each test, exceeding the acceptability criteria of > 90 % (USEPA 2002).

In the chronic tests with *C. dubia*, control acceptability criteria (> 80 % survival and > 60% surviving females having 15 or more neonates) were met. Reproduction is reported as the total number of young per original female. In the *P. promelas* tests, control acceptability criteria (minimum of 80% survival and an average dry weight of surviving fish in control chambers of > 0.25 mg; USEPA 2002) were met. Mean dry biomass is reported as the total dry weight of all surviving organisms divided by the original number of organisms.

Significant effects on survival, reproduction, and growth were observed in all tests. Responses were sufficient to calculate NOEC, LOEC, and 10%, 20%, and 50% effect concentrations (LC/EC10, LC/EC20, LC/EC50).

For the mixture testing detailed in Section 3.5, each single compound test was conducted to calculate a median-lethal concentration (LC50) or sublethal 20% effect concentration (EC20). The LC50 and EC20 of each compound were classified as 1 Toxic Unit (TU).

Table 30. Acute toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, and Glucopon® 225 DK to the cladoceran, Ceriodaphnia dubia.

Compound	Test #	Nominal Conc. (mg/L)	Measured Conc. (mg/L)	% Survival		NOEC (mg/L)	LOEC (mg/L)	LC ₅₀ (95% CI) (mg/L)
				Average	Std Dev			
DOWSIL™ 502W Additive	AFFF 1312 CDA	0 (control)	0.01	100	0	12	26	24 (21 – 28)
		6.25	6.1	100	0			
		12.5	12	95	10			
		25	26	50	26			
		50	53	0	0			
		100	105	0	0			
Diethylene Glycol Butyl Ether (Butyl Carbitol)	AFFF 1382 CDA	0 (control)	1.3	95	10	1782	3539	2689 (2455 – 2946)
		350	401	100	0			
		700	764	100	0			
		1400	1782	100	0			
		2800	3539	10	12			
		5600	6893	0	0			
Glucopon® 225 DK	AFFF 1393 CDA	0 (control)	0 *	95	10	50	100	74 (67 – 83) Nominal
		12.5	12.5 *	100	0			
		25	25 *	100	0			
		50	50 *	95	10			
		100	100 *	10	20			
		200	200 *	0	0			

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not available.
Bolded font represents a statistically significant concentration (p < 0.05) when compared to the dilution water control.

Table 31. Acute toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, and Glucopon® 225 DK to the fathead minnow, Pimephales promelas.

Compound	Test #	Nominal Conc. (mg/L)	Measured Average Conc. (mg/L)	% Survival		NOEC (mg/L)	LOEC (mg/L)	LC ₅₀ (95% CI) (mg/L)
				Average	Std Dev			
DOWSIL™ 502W Additive	AFFF 1327 PPA	0 (control)	0.01	100	0	4.1	5.6	5.1 (4.8 – 5.4)
		1.54	2.1	100	0			
		2.18	2.8	100	0			
		3.07	4.1	87.5	9.6			
		4.34	5.6	20	18.3			
		6.13	7.9	0	0			
Diethylene Glycol Butyl Ether (Butyl Carbitol)	AFFF 1376R PPA	0 (control)	1.3	100	0	1630	3421	2321 (2243 – 2402)
		250	310	100	0			
		500	457	100	0			
		1000	855	100	0			
		2000	1630	97.5	5.0			
		4000	3421	0	0			
Glucopon® 225 DK	AFFF 1389 PPA	0 (control)	0 *	100	0	100 *	200 *	139 (131 – 147) Nominal *
		25	25 *	100	0			
		50	50 *	100	0			
		100	100 *	95	5.8			
		200	200 *	2.5	5.0			
		400	400 *	0	0			

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not developed.
Bolded font represents a statistically significant concentration (p < 0.05) when compared to the dilution water control.

Table 32. Chronic toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, and Glucopon® 225 DK to the cladoceran, Ceriodaphnia dubia.

Compound	Test #	Nominal Conc. (mg/L)	Measured Average Conc. (mg/L)	Survival (%)		Reproduction	
				Average	Std Dev	Average	Std Dev
DOWSIL™ 502W Additive	AFFF 1335 CDC	0 (control)	0.01	100	0	39.0	5.5
		1.25	0.9	100	0	39.5	5.4
		2.5	2.0	100	0	37.4	10.9
		5	5.3	100	0	38.5	4.8
		10	7.6	100	0	20.8	7.6
		20	16.3	60	51.6	2.0	2.5
Diethylene Glycol Butyl Ether (Butyl Carbitol)	AFFF 1391 CDC	0 (control)	1.3	90	31.6	33.6	12.3
		125	118	100	0	33.8	7.6
		250	238	100	0	34.2	3.8
		500	509	100	0	34.2	4.3
		1000	1060	100	0	16.5	7.6
		2000	1963	20	42.2	0	0
Glucopon® 225 DK	AFFF 1401 CDC	0 (control)	0 *	90	31.6	35.2	13.4
		8.8	8.8 *	90	31.6	38.5	11.5
		18	18 *	90	31.6	36.2	13.4
		35	35 *	100	0	28.7	10.9
		70	70 *	50	52.7	4.9	5.2
		140	140 *	0	0	0	0

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not developed.
Bolded font represents a statistically significant concentration ($p < 0.05$) when compared to the dilution water control.

Table 33. Endpoint Summary: C. dubia chronic toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK.

Compound	Test #	Survival			Reproduction			
		NOEC (mg/L)	LOEC (mg/L)	LC ₅₀ (95% CI) (mg/L)	NOEC (mg/L)	LOEC (mg/L)	EC ₁₀ (95% CI) (mg/L)	EC ₂₀ (95% CI) (mg/L)
DOWSIL™ 502W Additive	AFFF 1335 CDC	16.3	> 16.3	> 16.3 (N/A)	5.3	7.6	5.4 (3.6 – 8.0)	6.3 (4.7 – 8.6)
Diethylene Glycol Butyl Ether (Butyl Carbitol)	AFFF 1391 CDC	1060	1963	1561 (1379 – 1767)	509	1060	773 (N/A) ^A	857 (N/A) ^A
Glucopon® 225 DK	AFFF 1401 CDC	70 Nominal	140 Nominal	75 (57 – 101) Nominal	35 Nominal	70 Nominal	29 (23 – 37) Nominal	34 (29 – 41) Nominal

^A TRAP identified as inadequate partial effects to determine error estimates.
N/A = Not reportable

Table 34. Short-term chronic toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, and Glucopon® 225 DK to the fathead minnow, *Pimephales promelas*.

Compound	Test #	Nominal Conc. (mg/L)	Measured Average Conc. (mg/L)	Survival (%)		Mean Dry Biomass (mg)	
				Average	Std Dev	Average	Std Dev
DOWSIL™ 502W Additive	AFFF 1342 PPC	0 (control)	0.01	85.0	12.9	0.3038	0.0396
		0.238	0.2	85.0	10.0	0.3043	0.0459
		0.475	0.4	90.0	8.2	0.3378	0.0356
		0.95	0.8	82.5	9.6	0.3575	0.0276
		1.9	1.5	85.0	12.9	0.2953	0.0507
		3.8	2.9	62.5	18.9	0.2035	0.0896
Diethylene Glycol Butyl Ether (Butyl Carbitol)	AFFF 1386 PPC	0 (control)	1.3	100	0	0.3467	0.0378
		245	304	97.5	5.0	0.3325	0.0478
		490	439	100	0	0.3312	0.0128
		980	729	97.5	5.0	0.2615	0.0227
		1960	1525	100	0	0.0808	0.0021
		3920	3324	0	0	0	0
Glucopon® 225 DK	AFFF 1396 PPC	0 (control)	0 *	87.5	5.0	0.2545	0.0241
		10	10 *	92.5	5.0	0.2813	0.0134
		20	20 *	100	0	0.3085	0.0396
		40	40 *	80	8.2	0.2650	0.0272
		80	80 *	92.5	9.6	0.2083	0.0180
		160	160 *	10.0	14.1	0.0083	0.0102

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not available.

Table 35. Endpoint Summary: *P. promelas* chronic toxicity of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK.

Compound	Test #	Survival			Growth (as mean dry biomass)			
		NOEC (mg/L)	LOEC (mg/L)	LC ₅₀ (95% CI) (mg/L)	NOEC (mg/L)	LOEC (mg/L)	EC ₁₀ (95% CI) (mg/L)	EC ₂₀ (95% CI) (mg/L)
DOWSIL™ 502W Additive	AFFF 1342 PPC	2.9	> 2.9	> 2.9 (N/A)	1.5	2.9	1.5 (0.4 – 5.5)	2.0 (0.8 – 4.8)
Diethylene Glycol Butyl Ether (Butyl Carbitol)	AFFF 1386 PPC	1525	3324	2240 (2209 – 2272)	729	1525	559 (489 – 638)	693 (621 – 772)
Glucopon® 225 DK	AFFF 1396 PPC	80 Nominal	160 Nominal	122 (112 – 136) Nominal	40 Nominal	80 Nominal	68 (42 – 109) Nominal	77 (64 – 91) Nominal

5.6.5. Environmental Impact of Mixture

Commercial end-use AFFF formulations are typically a mixture of cationic/anionic surfactants, hydrocarbon solvents, and water. To date most assessments of these materials have been based on the evaluation of the individual mixture components and assumptions regarding any potential interactive effects, i.e., additivity. In an effort to characterize and quantify potential interactive toxicant effects that may result from the use of an end-use formulation of an AFFF, a series of acute and chronic toxicity tests with the prescribed mixture of three compounds: DOWSIL™ 502W additive, diethylene glycol butyl ether (butyl carbitol), and Glucopon® 225 DK were conducted. The composition of the mixture recipe was developed by NVRL (formulation in Table 36) and is intended to represent a possible “typical” end-use fluorine-free AFFF formulation (from Hinnant et al. 2018). These data should help to clarify if the current approach used in evaluating mixture toxicity, i.e., additivity, is appropriate.

Table 36. Mixture Recipe of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK.

Compound	Measurements (Mixture composition per NVRL)	Concentration in final mixture
DOWSIL™ 502W Additive	8 grams	2000 mg/L
Diethylene Glycol Butyl Ether (Butyl Carbitol)	12 grams	3000 mg/L
Glucopon® 225 DK	20 grams	5000 mg/L
Water (lab reconstituted water)	4 Liters	

The toxicity tests were performed following a toxic unit (TU) approach [56] with the goal of determining whether the mixture was less than-additive (less toxic), additive (equally toxic), or more-than-additive (more toxic) than its individual components. The nominal toxic units defined in the testing were as follows: 1 TU = LC50 (median-lethal concentration) of each individual component for acute testing and 1 TU = EC20 (20% sublethal effect concentration) of each individual component from chronic testing (Table 37). The mixture is shown as individual toxic units (per compound) and the sum of toxic units contained in the mixture (Tables 38 and 39).

Table 37. Toxic Units (TU) of DOWSIL™ 502W Additive, Butyl Carbitol, and Glucopon® 225 DK to the cladoceran, *Ceriodaphnia dubia* and the fathead minnow, *Pimephales promelas*.

Compound	Acute TU (LC ₅₀)		Chronic TU (EC ₂₀)	
	<i>C. dubia</i>	<i>P. promelas</i>	<i>C. dubia</i>	<i>P. promelas</i>
DOWSIL™ 502W Additive	24	5.1	6.3	2.0
Diethylene Glycol Butyl Ether (Butyl Carbitol)	2689	2321	857	693
Glucopon® 225 DK	74 (nominal)	139 (nominal)	34 (nominal)	77 (nominal)

LC50 = Median-lethal concentration

EC20 = 20% effect concentration of reproduction (*C. dubia*) and growth (*P. promelas*)

Table 38. Compound mixture recipe and Toxic Units – Acute testing.

Compound	Measurements (Mixture composition per NVRL)	Concentration in final mixture	Acute TU = LC50 (mg/L) (single compound)		Acute TU in mixture	
			<i>C. dubia</i>	<i>P. promelas</i>	<i>C. dubia</i>	<i>P. promelas</i>
DOWSIL™ 502W Additive	8 grams	2000 mg/L	24	5.1	83.3	392.2
Diethylene Glycol Butyl Ether (Butyl Carbitol)	12 grams	3000 mg/L	2689	2321	1.1	0.8
Glucopon® 225 DK	20 grams	5000 mg/L	74	139	67.6	36.0
Water (lab reconstituted water)	4 Liters				SUM (TU) 152	SUM (TU) 429

Table 39. Compound mixture recipe and Toxic Units – Chronic testing.

Compound	Measurements (Mixture composition per NVRL)	Concentration in final mixture	Chronic TU = EC20 (mg/L) (single compound)		Chronic TU in mixture	
			<i>C. dubia</i>	<i>P. promelas</i>	<i>C. dubia</i>	<i>P. promelas</i>
DOWSIL™ 502W Additive	8 grams	2000 mg/L	6.3	2.0	317.5	1000.0
Diethylene Glycol Butyl Ether (Butyl Carbitol)	12 grams	3000 mg/L	857	693	3.5	4.3
Glucopon® 225 DK	20 grams	5000 mg/L	34	77	147.1	64.9
Water (lab reconstituted water)	4 Liters				SUM (TU) 468	SUM (TU) 1069

5.6.5.1. Mixture Analytical Chemistry

Samples of test solutions were collected during the conduct of the toxicity testing and provided to the OSU Field Lab for analytical determination of measured concentrations of DOWSIL™ 502W additive and Diethylene Glycol Butyl Ether (Butyl Carbitol), while Glucopon® 225 DK is reported as nominal.

Measured concentrations in the mixture “stock” were within 70 to 96% of nominally added for DOWSIL™ 502W and 100 to 122% for butyl carbitol (Table 40). These mixture stock solutions were used in the preparation of the test solutions (described in Section 2.5), which are reported in Tables 41 to 44.

As was also observed in the single compound tests with DOWSIL™ 502W Additive, measured concentrations compared to nominal “new” solutions were highly variable. In the case of the acute test with *C. dubia* (Table 41), measured concentrations were only 9 to 27% of nominal. After 24 or 48 hrs of exposure, concentrations decreased by approximately 50% in the higher exposures, but in the lower exposures actually showed measured increases, up to a 2-fold increase. Similarly, in the acute test with *P. promelas* (Table 42), measured concentrations were only 14-53% of nominal, and after 48-hrs decreased anywhere from 7 to 89% while certain samples showed an increase (also in one case almost doubling). In the chronic tests, measured concentrations were still variable, but somewhat closer to nominal, with one series ranging from 75-113% of nominal. The observed variability is further proof of the challenging nature of this substance, as explained in Section 3.2.

Measured concentrations of butyl carbitol were more variable in the acute mixture tests, ranging from 35-67% of nominal for one test and 46-73% of nominal for the other acute test. These were lower recoveries than those observed in the single compound tests. The recoveries of butyl carbitol in the chronic mixture tests were more typical, ranging from 78-123% of nominal. In addition, decreases of concentrations over time were less pronounced than those observed with DOWSIL™ 502W Additive. After 24 or 48 hrs of exposure, butyl carbitol concentrations decreased up to 47% in certain cases, but also had slight increased measurements up to 39%. Although variability in measured concentrations were reported, concentrations of butyl carbitol remained significantly more stable than those of DOWSIL™ 502W Additive. Due to the high variability in the measured concentrations, statistical analysis was performed under various iterations (nominal and measured), as discussed in Section 3.5.3

Table 40. Analytical chemistry analysis of mixture.

Compound	Concentration in final mixture	Stock 7/13/20	Stock 7/15/20	Stock 7/29/20	Stock 7/30/20	Stock 8/4/20	Stock 8/5/20	Stock 1/19/21	Minimum % of nominal	Maximum % of nominal
		mg/L								
DOWSIL™ 502W Additive	2000 mg/L	1920	1710	1640	1390	1390	1650	1650	70	96
Diethylene Glycol Butyl Ether (Butyl Carbitol)	3000 mg/L	2446	2471	3333	3000	3667	3333	2960	100	122
Glucopon® 225 DK	5000 mg/L	Not measured								

Table 41. Analytical chemistry analysis of mixture during conduct of toxicity test – C. dubia Acute (Test ID: AFFF 1406 CDA).

Compound	MIXTURE Nominal Conc. (mg/L)	Measured Conc. (mg/L)			
		0 hr (new)	48 hr (old)	Average	SD
DOWSIL™ 502W Additive	0 (control)	< LOQ 0.02	< LOQ 0.02	0.01	0
	1.32	0.12	0.31	0.21	0.13
	2.63	0.38	0.70	0.54	0.23
	5.27	1.26	0.55	0.91	0.50
	10.53	2.85	1.38	2.12	1.04
	21.07	2.53	1.12	1.83	1.00
Diethylene Glycol Butyl Ether (Butyl Carbitol)	0 (control)	< LOQ 0.01	< LOQ 0.01	0.005	0
	1.97	0.68	0.62	0.6	0.04
	3.95	2.30	2.12	2.2	0.1
	7.91	4.54	3.84	4.2	0.5
	15.8	8.50	9.40	8.9	0.6
	31.6	21.2	15.8	18.5	3.8
Glucopon® 225 DK	0 (control)				
	3.29 *				
	6.58 *				
	13.18 *				
	26.34 *				
	52.68 *				

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not available.

Table 42. Analytical chemistry analysis of mixture during conduct of toxicity test – *P. promelas* Acute (Test ID: AFFF 1405 PPA).

Compound	MIXTURE Nominal Conc.	Measured Conc. (mg/L)					
		0 hr (new)	48 hr (old)	48 hr (new)	96 hr (old)	Average	SD
DOWSIL™ 502W Additive	0 (control)	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	0.01	0
	0.58	0.0833	0.154	0.172	0.107	0.13	0.04
	1.17	0.321	0.234	0.567	0.529	0.41	0.16
	2.33	0.762	0.602	0.70	0.451	0.63	0.14
	4.67	2.46	0.275	1.51	2.37	1.65	1.01
	9.32	2.70	0.705	-	-	1.70	1.41
Diethylene Glycol Butyl Ether (Butyl Carbitol)	0 (control)	< LOQ 0.01	< LOQ 0.01	< LOQ 0.01	< LOQ 0.01	0.005	0
	0.87	0.57	0.40	0.51	0.48	0.5	0.1
	1.75	1.07	0.69	1.02	0.66	0.9	0.2
	3.5	2.09	1.68	2.56	1.35	1.9	0.5
	7	3.24	3.22	3.31	2.55	3.1	0.4
	14	7.38	7.51	-	-	7.4	0.1
Glucopon® 225 DK	0 (control) *						
	1.46 *						
	2.92 *						
	5.83 *						
	11.67 *						
	23.3 *						

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not available.

Table 43. Analytical chemistry analysis of mixture during conduct of toxicity test – *C. dubia* Chronic (Test ID: AFFF 1411 CDC).

Compound	MIXTURE Nominal Conc.	Measured Conc. (mg/L)				
		Day 0 (new)	Day 6 (new)	Day 7 (old)	Average	SD
DOWSIL™ 502W Additive	0 (control)	< LOQ 0.02	0.01	0.01	0.01	0
	1.07	0.68	1.21	0.90	0.93	0.27
	2.14	1.15	2.23	2.07	1.82	0.58
	4.27	2.39	3.68	4.20	3.42	0.93
	8.54	4.39	6.37	5.88	5.55	1.03
	17.09	6.07	-	13.2 (day 2 old)	9.64	5.04
Diethylene Glycol Butyl Ether (Butyl Carbitol)	0 (control)	< LOQ 0.01	< LOQ 0.01	< LOQ 0.01	0.005	0
	1.6	1.67	1.33	1.83	1.6	0.3
	3.2	3.33	3.67	2.67	3.2	0.5
	6.4	5.00	7.86	5.71	6.2	1.5
	12.8	11.7	13.3	10.0	11.7	1.7
	25.6	25.0	-	25.0 (day 2 old)	25.0	0.0
Glucopon® 225 DK	0 (control)					
	2.68 *					
	5.35 *					
	10.69 *					
	21.36 *					
	42.72 *					

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not available.

Table 44. Analytical chemistry analysis of mixture during conduct of toxicity test – *P. promelas* Chronic (Test ID: AFFF 1410 PPC).

Compound	MIXTURE Nominal Conc.	Measured Conc. (mg/L)				
		Day 0 (new)	Day 6 (new)	Day 7 (old)	Average	SD
DOWSIL™ 502W Additive	0 (control)	< LOQ 0.02	< LOQ 0.02	< LOQ 0.02	0.01	0
	0.47	0.27	0.30	0.28	0.28	0.02
	0.93	0.55	0.92	0.60	0.69	0.20
	1.87	1.19	1.64	1.49	1.44	0.23
	3.74	2.45	3.32	2.59	2.79	0.47
	7.48	3.65	-	3.91 (Day 2 old)	3.78	0.18
Diethylene Glycol Butyl Ether (Butyl Carbitol)	0 (control)	< LOQ 0.01	< LOQ 0.01	< LOQ 0.01	0.005	0
	0.7	0.57	0.57	0.79	0.6	0.1
	1.4	1.71	1.29	1.00	1.3	0.4
	2.8	2.35	2.65	2.65	2.6	0.2
	5.6	5.63	5.00	5.00	5.2	0.4
	11.2	10.0	-	8.75 (Day 2 old)	9.4	0.9
Glucopon® 225 DK	0 (control)					
	1.17 *					
	2.34 *					
	4.68 *					
	9.36 *					
	18.7 *					

* Nominal concentrations used for Glucopon® 225 DK as analytical method to measure concentrations is not available.

5.6.5.2. Mixture Water Chemistry

Water chemistries measured during the mixture tests were similar to those measured in the single compound tests. The hardness and alkalinity of the laboratory control water (moderately hard-reconstituted water for *C. dubia* and *P. promelas* tests) ranged from 96-104 and 80-84 mg/L as CaCO₃, respectively. The hardness and alkalinity of the laboratory control water (OECD algae media for *R. subcapitata* test) was 32 and 32 mg/L as CaCO₃, respectively. Throughout the tests, water quality chemistries were measured in “new” waters that were representative of freshly-prepared solutions, but before organism exposure, and in “old” waters from one replicate per treatment following 24-hrs of organism exposure. As shown in Table 45, the ranges of pH did not significantly differ in any exposures staying within ± 0.5 SU between minimum and maximum values in the *C. dubia* and *P. promelas* tests but did increase in the algae tests. An increase in pH is due to photosynthesis and the growth of the algae and was more apparent in the control exposure when compared to the mixture exposures which had inhibited growth. Dissolved oxygen concentrations also did not significantly differ and remained above 60% saturation. But it should be noted that measurements were only taken from control replicates, due to the inability to clean the DO probe if submerged in the test compounds. It has been noted that surfactants may cause low dissolved oxygen in waters, but data reported here are not able to address this question. Conductivity did vary between exposures, but the variability (typically an increase) was commonly observed between new and old measurements, even in the control waters. This demonstrates that

biological processes (food and/or feces from the organisms) in the exposure waters were most likely contributing to conductivity variability, as opposed to the test substances. Acceptable temperatures ($25 \pm 2^{\circ}\text{C}$) were maintained in all tests.

Table 45. Exposure water quality during conduct of toxicity tests (all exposures).

Compound	Test	pH (SU) (range)	Conductivity ($\mu\text{S}/\text{cm}$) (range)	Dissolved oxygen (mg/L) (range)
Mixture	<i>C. dubia</i> Acute	7.81 – 8.04	359 – 393	8.24 – 8.28
	<i>P. promelas</i> Acute	7.80 – 8.04	354 – 502	7.46 – 8.43
	<i>C. dubia</i> Chronic	7.54 – 8.13	351 – 450	8.18 – 8.75
	<i>P. promelas</i> Chronic	7.72 – 8.13	354 – 432	7.47 – 8.58
	<i>R. subcapitata</i> Chronic	7.53 – 9.34	361 - 466	Not measured

5.6.5.3. Mixture Biological Results

The biological results and endpoint summaries (NOEC, LOEC, LC50, EC20) on a toxic unit basis in the mixtures tests with *C. dubia* and *P. promelas* are summarized in Tables 46 to 49.

Control acceptability criteria was met in both the acute and chronic tests with *C. dubia* and *P. promelas*,

Effects of mixtures can be quantified under three effects:

- Less than additive = Less Toxic as a mixture
 - o Sum of TUs is greater than 1 (> 1)
- Additive: Non-interactive = No difference in toxicity as a mixture
 - o Sum of TUs is 1 (~ 1)
- More than additive = More Toxic as a mixture
 - o Sum of TUs is less than 1 (< 1)

Due to some of the variability in measured concentrations, specifically in the acute tests, as discussed in Section 3.5.1, analysis was performed on both a nominal and measured basis for the acute toxicity tests. As shown in Table 46 with acute toxicity to *C. dubia*, the mixture resulted in a more-than-additive effect on survival, whether based upon nominal or measured concentrations. Because DOWSIL™ 502W contributed significantly more to the toxic units of the mixture, the lower than nominal measured values of DOWSIL™ 502W resulted in lower TUs, reducing the total TU even further. This was also the case in the acute testing with *P. promelas*, as shown in Table 47, where nominally the mixture was additive, but due to the low DOWSIL™ 502W measured values, total TUs were lower than nominal, resulting in a more-than-additive endpoint.

Table 46. Acute toxicity of the Mixture to the cladoceran, *Ceriodaphnia dubia*.

Test ID	Compound	NOMINAL			MEASURED			SURVIVAL					
		Nominal Conc. (mg/L)	Nominal Toxic Units	Nominal Sum of TUs	Average Measured Conc. (mg/L)	Measured Toxic Units	Measured Sum of TUs	Survival % - Average	Survival % – Std Dev	NOEC TU	LOEC TU	LC ₅₀ TU	Effect
AFFF 1406 CDA	DOWSIL™ 502W Additive	0	0	0	0.01	0.0004	0.0004	100	0	0.4 (nominal)	0.8 (nominal)	0.67 (0.59 – 0.77) (nominal)	More-than-additive (nominal)
		1.32	0.055	0.10	0.21	0.009	0.05	100	0				
		2.63	0.110	0.20	0.54	0.023	0.11	100	0				
		5.27	0.220	0.40	0.91	0.038	0.22	100	0				
		10.53	0.440	0.80	2.12	0.088	0.45	25	19.2				
		21.07	0.880	1.60	1.83	0.076	0.80	0	0				
	Diethylene Glycol Butyl Ether (Butyl Carbitol)	0	0		0.005	0.00002				0.22 (measured)	0.45 (measured)	0.37 (0.33 – 0.42) (measured)	More-than-additive (measured)
		1.97	0.0007		0.6	0.0002							
		3.95	0.0015		2.2	0.0008							
		7.91	0.0029		4.2	0.0016							
		15.8	0.0059		8.9	0.0033							
		31.6	0.0118		18.5	0.0069							
	Glucopon® 225 DK (nominal)	0	0		0 *	0							
		3.29	0.044		3.29 *	0.044							
		6.58	0.089		6.58 *	0.089							
		13.18	0.178		13.18 *	0.178							
		26.34	0.356		26.34 *	0.356							
		52.68	0.712		52.68 *	0.712							

* Due to the lack of analytical method to quantify Glucopon® 225 DK concentrations, nominal concentrations were used.

As the chronic tests had less variability in measured concentrations compared to nominal, the biological endpoints are reported as measured values only. Chronic exposure of *C. dubia* to the mixture resulted in an additive effect (Table 48), while chronic exposure of *P. promelas* resulted in a less-than-additive effect (Table 49).

The chronic test with *R. subcapitata*, was only performed with the mixture and not the individual components and is summarized in Table 50 with the endpoints expressed as a sum of the components (mg/L as mixture) and is used as a comparison to the other organisms in Table 51. The exposure:response curve from the test was lacking a sufficient number of partial effects and was characterized for exploratory use only, as per the TRAP statistical model. Even with this qualifier, an effect concentration with confidence intervals was able to be calculated.

Control acceptability criteria was met with an algal density increasing by a factor of at least 16 within the test period, the mean coefficient of variation for section-by-section specific growth rates did not exceed 35%, and the coefficient of variation of average specific growth rates during the whole test period did not exceed 7%. In addition, quality control checks verifying cell density in relation to absorbance were within $\pm 20\%$ of expected density based upon calibration curves developed at test initiation, demonstrating that quantifying cell density using spectrophotometric absorbance (at 684λ) was acceptable.

Table 47. Acute toxicity of the Mixture to the fathead minnow, *Pimephales promelas*.

Test ID	Compound	NOMINAL			MEASURED			SURVIVAL					
		Nominal Conc. (mg/L)	Nominal Toxic Units	Nominal Sum of TUs	Average Measured Conc. (mg/L)	Measured Toxic Units	Measured Sum of TUs	Survival % - Average	Survival % - Std Dev	NOEC TU	LOEC TU	LC ₅₀ TU	Effect
AFFF 1405 PPA	DOWSIL™ 502W Additive	0	0	0	0.01	0.002	0.002	97.5	5.0	0.5 (nominal)	1 (nominal)	1.02 (0.91 – 1.14) (nominal)	Additive (nominal)
		0.58	0.114	0.125	0.13	0.0255	0.04	100	0				
		1.17	0.229	0.25	0.41	0.0804	0.10	100	0				
		2.33	0.458	0.5	0.63	0.1235	0.17	100	0				
		4.67	0.915	1	1.65	0.3235	0.41	52.5	9.6				
		9.32	1.828	2	1.70	0.3333	0.51	0	0				
	Diethylene Glycol Butyl Ether (Butyl Carbitol)	0	0		0.005	0.000002				0.17 (measured)	0.41 (measured)	0.35 (0.32 – 0.39) (measured)	More-than-additive (measured)
		0.87	0.0004		0.9	0.0004							
		1.75	0.0008		1.7	0.0007							
		3.5	0.0015		3.3	0.0014							
		7	0.0030		6.6	0.0028							
		14	0.0060		13.8	0.0059							
	Glucopon® 225 DK (nominal)	0	0		0 *	0							
		1.46	0.010		1.46 *	0.010							
		2.92	0.021		2.92 *	0.021							
		5.83	0.042		5.83 *	0.042							
		11.67	0.084		11.67 *	0.084							
		23.3	0.168		23.3 *	0.168							

* Due to the lack of analytical method to quantify Glucopon® 225 DK concentrations, nominal concentrations were used.

Table 48. Chronic toxicity of the Mixture to the cladoceran, *Ceriodaphnia dubia*.

Test ID	Compound	NOMINAL			MEASURED			REPRODUCTION (neonates per original female)					
		Nominal Conc. (mg/L)	Nominal Toxic Units	Nominal Sum of TUs	Average Measured Conc. (mg/L)	Measured Toxic Units	Measured Sum of TUs	#neonates - Average	#neonates - Std dev	NOEC TU	LOEC TU	EC ₂₀ TU	Effect
AFFF 1411 CDC	DOWSIL™ 502W Additive	0	0	0	0.01	0.0016	0.0016	40.2	8.9	0.86	1.52	0.97 (0.84 – 1.12)	Additive
		1.07	0.170	0.25	0.93	0.148	0.23	43.3	3.9				
		2.14	0.339	0.5	1.82	0.289	0.45	40.6	13.1				
		4.27	0.678	1	3.42	0.543	0.86	37.0	13.7				
		8.54	1.356	2	5.55	0.881	1.52	10.2	8.3				
		17.09	2.712	4	9.64	1.530	2.82	0	0				
	Diethylene Glycol Butyl Ether (Butyl Carbitol)	0	0		0.005	0.00001							
		1.6	0.002		1.6	0.002							
		3.2	0.004		3.2	0.004							
		6.4	0.007		6.2	0.007							
		12.8	0.015		11.7	0.014							
		25.6	0.030		25.0	0.029							
	Glucopon® 225 DK (nominal)	0	0		0 *	0							
		2.68	0.079		2.68 *	0.079							
		5.35	0.157		5.35 *	0.157							
		10.69	0.314		10.69 *	0.314							
		21.36	0.628		21.36 *	0.628							
		42.72	1.256		42.72 *	1.256							

* Due to the lack of analytical method to quantify Glucopon® 225 DK concentrations, nominal concentrations were used.

Table 49. Short-term Chronic toxicity of the Mixture to the fathead minnow, *Pimephales promelas*.

Test ID	Compound	NOMINAL			MEASURED			GROWTH (as mean dry biomass)					
		Nominal Conc. (mg/L)	Nominal Toxic Units	Nominal Sum of TUs	Average Measured Conc. (mg/L)	Measured Toxic Units	Measured Sum of TUs	Average - mg	Std dev - mg	NOEC TU	LOEC TU	EC ₂₀ TU	Effect
AFFF 1410 PPC	DOWSIL™ 502W Additive	0	0	0	0.01	0.005	0.01	0.3672	0.0453	0.78	1.52	1.29 (1.09 – 1.54)	Less than Additive
		0.47	0.235	0.25	0.28	0.142	0.16	0.3573	0.0346				
		0.93	0.465	0.5	0.69	0.345	0.38	0.3547	0.0313				
		1.87	0.935	1	1.44	0.720	0.78	0.3410	0.0256				
		3.74	1.870	2	2.78	1.392	1.52	0.1552	0.0219				
		7.48	3.740	4	3.78	1.890	2.15	0	0				
	Diethylene Glycol Butyl Ether (Butyl Carbitol)	0	0		0.005	0.000							
		0.7	0.0010		0.6	0.0009							
		1.4	0.0020		1.3	0.0019							
		2.8	0.0040		2.6	0.0037							
		5.6	0.0081		5.2	0.0075							
		11.2	0.0162		9.4	0.0135							
	Glucopon® 225 DK (nominal)	0	0		0	0.000							
		1.17	0.015		1.17 *	0.015							
		2.34	0.030		2.34 *	0.030							
		4.68	0.061		4.68 *	0.061							
		9.36	0.122		9.36 *	0.122							
		18.7	0.243		18.7 *	0.243							

* Due to the lack of analytical method to quantify Glucopon® 225 DK concentrations, nominal concentrations were used.

Table 50. Chronic toxicity of the Mixture to the green algae, *Raphidocelis subcapitata*.

Test ID	Compound	NOMINAL	MEASURED						GROWTH (as average specific growth rate)		Endpoints (mg/L mixture)			
		Nominal Conc. (mg/L)	0 hrs (new)	24 hrs (old)	48 hrs (old)	72 hrs (old)	Average (mg/L)	Background 72 hrs (old) No algae	Average - mg	Std dev - mg	NOEC	LOEC	EC ₁₀ (95% CI)	EC ₂₀ (95% CI)
AFFF 1432 RS	DOWSIL™ 502W Additive	0	<LOQ	<LOQ	<LOQ	<LOQ	0.01	<LOQ	1.715	0.052	14 (nominal)	36 (nominal)	35.2 (21.9 – 56.7) (nominal)	92.9 (45.0 – 191.9) (nominal)
		0.4	0.26	0.06	0.04	<LOQ	0.09	0.06	1.724	0.026				
		1.0	0.99	0.45	0.39	0.04	0.47	0.54	1.710	0.025				
		2.8	3.01	1.90	1.77	0.10	1.69	2.29	1.674	0.057				
		7.2	7.59	5.93	4.95	2.19	5.17	6.16	1.504	0.130				
		19.2	17.80	17.20	15.50	8.28	14.70	15.70	1.382	0.196				
	Diethylene Glycol Butyl Ether (Butyl Carbitol)	0	<LOQ	<LOQ	<LOQ	<LOQ	0.005	<LOQ			12.5 (measured)	32.6 (measured)	31.8 (19.6 – 51.6) (measured)	83.0 (39.1 – 176.1) (measured)
		0.6	0.5	0.5	0.7	0.5	0.6	0.5						
		1.5	1.1	1.2	1.2	1.2	1.2	1.3						
		4.2	3.8	3.6	4.3	3.6	3.8	3.5						
		10.8	10.7	10.6	7.6	8.7	9.4	7.8						
		28.8	23.2	23.3	21.3	23.0	22.7	21.4						
	Glucopon® 225 DK (nominal)	0 *	*	*	*	*	0 *	*						
		1.0 *	*	*	*	*	1.0 *	*						
		2.5 *	*	*	*	*	2.5 *	*						
		7 *	*	*	*	*	7 *	*						
		18 *	*	*	*	*	18 *	*						
		48 *	*	*	*	*	48 *	*						

* Due to the lack of analytical method to quantify Glucopon® 225 DK concentrations, nominal concentrations were used.

In order to compare the organisms tested, both nominal and measure concentrations of the mixture (as opposed to the toxic unit approach) were used in statistical analysis. As anticipated, chronic exposures resulted in greater toxicity (lower effect concentrations) than acute exposures (Table 51). Evaluation of the TU contributions of each component suggests that the majority of both acute and chronic toxicity was contributed by the DOWSIL 502W additive. Results of the single compound tests indicate that in the case of DOWSIL 502W additive, fish were found to be more sensitive than the invertebrate, *C. dubia*. Interestingly, the results of the mixture tests also suggest that fish were more sensitive than both the invertebrate and the algae; however, this may be expected since the TU analysis suggested that the DOWSIL 502W additive was anticipated to contribute the majority of the toxicity.

Table 51. Toxicity of the mixture to invertebrates, fish, and algae.

Species		Duration	Effect	Mixture: DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK (mg/L)	Method
Invertebrate	<i>C. dubia</i>	48 h (Acute)	LC ₅₀	44.3 (38.7 – 50.7) (nominal) 31.1 (27.2 – 35.5) (measured)	USEPA 2002a
Fish	<i>P. promelas</i>	96 h (Acute)	LC ₅₀	23.8 (21.3 – 26.5) (nominal) 20.1 (18.0 – 22.4) (measured)	USEPA 2002a
Invertebrate	<i>C. dubia</i>	7 d (Chronic)	EC ₂₀	24.6 (20.7 – 29.3) (nominal) 23.2 (19.7 – 27.3) (measured)	USEPA 2002b
Fish	<i>P. promelas</i>	7 d (Chronic)	EC ₂₀	12.6 (11.3 – 14.0) (nominal) 11.9 (10.4 – 13.6) (measured)	USEPA 2002b
Algae	<i>R. subcapitata</i>	72 h (Chronic)	EC ₂₀	92.9 (45.0 – 191.9) (nominal) 83.0 (39.1 – 176.1) (measured)	OECD 2011

As stated, the objective of this research was to develop a fluorine-free, firefighting surfactant formulation that meets the performance requirements of MIL-F-24385F and is an environmentally friendly drop-in replacement for current AFFFs. A candidate end-use AFFF formulation was developed by the US Naval Research Laboratory composed of DOWSIL™ 502W Additive, Butyl Carbitol, Glucopon® 225 DK and water.

In summary, acute and chronic toxicity tests were performed with the individual formulation components to establish “baseline” toxicity for the materials. Subsequently, tests were conducted with the candidate end-use AFFF formulation in an effort to characterize its toxicity

and to determine if “interactive effects” among the components modified the toxicity of the mixture from what would be expected based on simple “additive” interactions. Toxicity tests were conducted with the cladoceran, *Ceriodaphnia dubia*, the fathead minnow, *Pimephales promelas*, and the green algae, *Raphidocelis subcapitata*. All test exposure concentrations were analytically confirmed in the DOWSIL™ 502W Additive and the diethylene glycol butyl ether (butyl carbitol) studies. A high degree of variability characterized measured concentrations of the DOWSIL™ 502W Additive; however, these results are consistent with previous work that identified challenges in maintaining constant concentrations in solutions due to partitioning of the surfactants to the air-water interface, adhesion to the surface of containers and other issues with homogeneity [54,55]. Unlike the DOWSIL™ 502W Additive concentration variability, butyl carbitol concentrations remained stable throughout the preparation of solutions and conduct of the toxicity tests. Glucopon® 225 DK test concentrations were not measured due to a lack of an acceptable analytical technique; therefore, test results are reported on a “nominal” basis (Table 52).

Table 52. Acute (LC50) and chronic (EC20) values for individual constituents are shown for *C. dubia* and *P. promelas*.

Compound	<i>Ceriodaphnia dubia</i>		<i>Pimephales promelas</i>	
	LC ₅₀ (95% CI) (mg/L)	EC ₂₀ (95% CI) (mg/L)	LC ₅₀ (95% CI) (mg/L)	EC ₂₀ (95% CI) (mg/L)
DOWSIL™ 502W Additive	24 (21 – 28)	6.3 (4.7 – 8.6)	5.1 (4.8 – 5.4)	2.0 (0.8 – 4.8)
Diethylene Glycol Butyl Ether (Butyl Carbitol)	2689 (2455 – 2946)	857 (N/A) ^A	2321 (2243 – 2402)	693 (621 – 772)
Glucopon® 225 DK	74 (67 – 83) Nominal	34 (29 – 41) Nominal	139 (131 – 147) Nominal *	77 (64 – 91) Nominal

The candidate end-use AFFF formulation mixture did not contain equivalent amounts of each single compound, therefore the contribution of the individual components was a function of its relative toxicity and content in the mixture. A toxicity units (i.e., TU) based approach was implemented in assessing mixture toxicity. Biological endpoints were assessed to determine whether the mixture exhibited additive (no difference in toxicity as a mixture), less-than-additive (reduced toxicity as a mixture), or more-than-additive (increased toxicity as a mixture) effects. The acute studies (toxicity based upon 48-hr or 96-hr survival) demonstrated that the mixture tested had additive or more-than-additive effects. In the chronic tests (72 h or 7 d), the scenario resulted in additive or less-than-additive effects. When comparing each species based upon measured mixture concentrations, *P. promelas* and *C. dubia* were more sensitive to chronic exposures versus acute exposures, while the algae, *R. subcapitata* was the least sensitive to the mixture tested.

5.7. MD Simulation of Heptane-Water Interface

We aim to study surfactant monolayers to facilitate the process of searching new surfactant in order to replace the toxic fluorocarbon surfactants contained in firefighting foams using

molecular dynamics (MD) simulation. MD simulations mimic the physical movements of atoms (position and velocity) by numerically solving Newton's equations of motion subject to interatomic potentials (i.e. force field) on tens of nano-seconds scale. We developed experimentally validated MD models for a few examples of siloxane and hydrocarbon surfactants and developed an understanding of the differences with a fluorocarbon surfactant in air/water and heptane/water interfacial structures [35]. The validated MD models are used to develop new understanding of how variations in chemical structure impact interface structure and may give rise to new surfactant designs.

We examine the interfacial properties of a few commercially available hydrocarbon (sodium dodecyl sulfate, SDS, and hexadecyltrimethylammonium bromide, CTAB (or C₁₆TAB)) and siloxane (2,2,4-trimethyl-4-[(trimethylsilyl)oxy]-3,8,11,14,17,20,23,26,29,32-decaoxa-2,4-disilatrilacontane used to represent Silwet L77) surfactants and compare them with a commercial perfluorosurfactant (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid, PFOA) [35]. The simulation results demonstrate that the predicted values of surface area and surface tension agree reasonably well with experimental data and validate the methods including the CHARMM36 lipid force field used to simulate the surfactant molecules in foams. Moreover, the simulation results show that the Gibbs elasticity of perfluorocarbon and siloxane surfactants at air-water interface are greater than the two hydrocarbon surfactants considered in this study. High Gibbs elasticity and low surface tension may suggest higher stability of bubble surfaces packed with the fluorocarbon and siloxane surfactants to dilatation of the lamellae than those with the hydrocarbon surfactants. The heptane penetration distance into the heptane-water interface is also smaller for the fluorocarbon and siloxane surfactants compared to the two hydrocarbon surfactants [35].

Using the experimentally validated MD model, we varied the structure of surfactants and compare the interfacial properties in order to search possible good candidate that can be effective enough for fire suppression and be MilSpec-qualified [36]. From the MD simulations, the interfacial properties such as the surface area per molecule (A), interfacial thicknesses of water (d_w) and heptane (d_h), the heptane to surfactant ratio (hsr), the heptane surface number density ($hsnd$), the inverse of maximum surfactant number density ($msnd^{-1}$), the heptane volumetric number density ($hvnd$), hydrogen bond number per molecule ($hbnm$) and hydrogen bond number per Å² ($hbna$) are calculated [36]. The d_w and $hbnm$ are the properties of the hydrophilic head group, and d_h , hsr , $msnd^{-1}$, and $hvnd$ are the properties of the hydrophobic tail. The $hbnm$ is related to stability of the head group, while the hsr , $msnd^{-1}$ and $hvnd$ are related to heptane transport rate in the tail.

The key aspects of variation of structures that we are interested are tested, and the detail results are presented [36]. The key conclusions are that hydroxyl-capped trisiloxane have smaller heptane to surfactant ratio (hsr) and inverse of maximum surfactants number density ($msnd^{-1}$) than methoxyl-capped trisiloxane, which suggests that hydroxyl-capped trisiloxane is a better candidate. By varying the alkyl glucoside length n , the result that the alkyl glucoside with $n \geq 9$ would have lower $msnd^{-1}$ and $hvnd$, and also higher $hbnm$, which make $n \geq 9$ good candidate. The β - and (α,β -1 $\rightarrow$ 4)-alkylglucoside have significantly smaller hsr , $hvnd$, thus better candidate than the ones with α - and (α,β -1 $\rightarrow$ 6) linkage. The 2k3s and 2k3t have smaller $hvnd$ and greater $hbnm$ than other siloxanes which make them good candidate. The neutral charged or zwitterionic hydrocarbon surfactants have lower heptane number density than that of the charged ones. By

studying the commercial surfactants, we conclude that two Glucopon-based hydrocarbon surfactants g215 and g225 have very similar interface properties. Among the commercial surfactant, capstone and capstone/g215e have the minimum h_{vnd} which agrees with the experimental heptane diffusion rate of AFFF. Among the pure trisiloxane and trisiloxane/alkylglucoside studied, the H8 and H8/g225 have the minimum d_h , h_{sr} and also $msnd^{-1}$ and h_{vnd} .

5.7.1. MD Model Development and Validation

For developing and validating the MD model, we chose the chemical structures of the surfactants shown in Figure 54 [35]. The firefighting surfactants are chosen partly because experimental data for the interfacial properties are available or can be measured. The hydrocarbon surfactants SDS and CTAB at an air-water interface were simulated using MD previously [57] and serve as references to compare against the siloxane and the fluorocarbon surfactants. A validated model can be used to understand the effects of surfactant's structural changes on interface and film stability in future works.

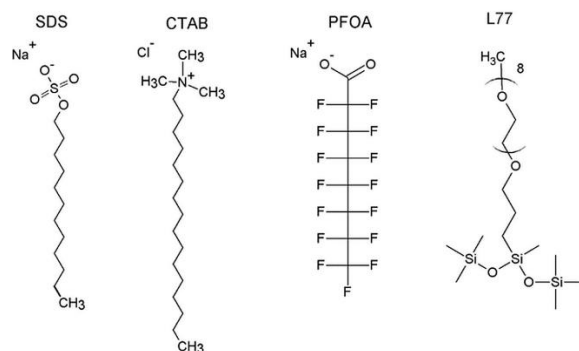


Figure 54. The chemical structures of hydrocarbon surfactants SDS and CTAB, perfluorocarbon surfactant PFOA, and siloxane surfactant L77. For CTAB (or C₁₆TAB), as the parameter for the free bromide ion is not available in CHARMM force field, the bromide is replaced by chloride in our MD simulations [35].

Figure 55e-h show a comparison of MD predictions with the experimental data using Gibbs-equation (GE₂). The results show good agreement between MD and GE₂ for the hydrocarbon and fluorocarbon surfactants SDS (Figure 55e) and PFOA (Figure 55g) respectively. Figure 55e-h also show good agreement between MD predictions and direct experimental measurements (labeled EXP) of surface area per molecule at saturation and surface tension reported in the literature [58, 59, 60-63]. However, there are quantitative differences between MD predictions and GE₂ for the hydrocarbon and trisiloxane surfactants CTAB and L77 (Figure 55f and 56g respectively) possibly due to high sensitivity to the calculation of slope using a polynomial fit of the experimental data.

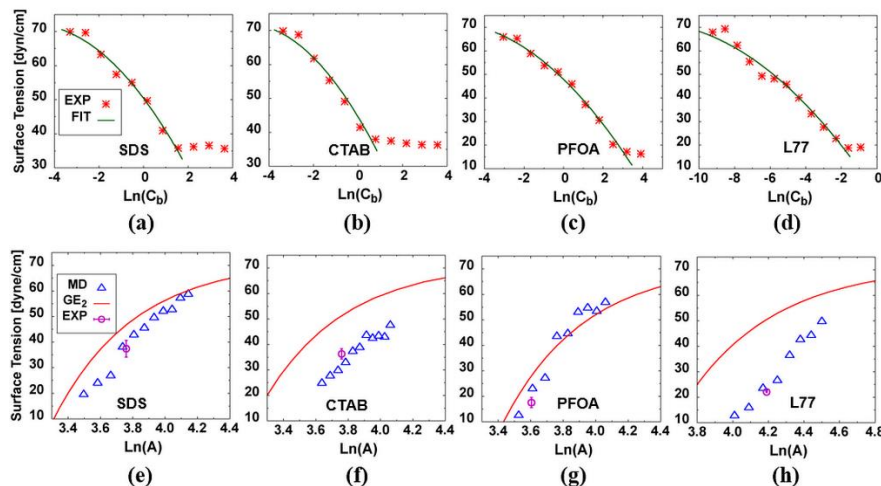


Figure 55. (a)-(d) Experimental measurements of surface tension versus concentration (mole/m³) of surfactant in the bulk solution and 2nd order polynomial fit to the experimental data to calculate area per molecule A using Gibbs-equation. The uncertainty for each experimental surface tension measurement is 0.5 dyne/cm. (e)-(h) Comparison of surface tension versus surface area per molecule calculated from Gibbs equation (GE_2) with MD-predictions. The purple data indicate the direct measurement of surface area per molecule and surface tension at saturation for SDS [60], CTAB [61], PFOA [58, 51], and L77 [63]. For consistency, all MD predicted surface tension values including that of pure water are adjusted by 19.0 dyne/cm higher to correct for the TIP3P water model [35].

5.7.1.2. Gibbs Elasticity (E) and Most Probable Surface Area per Molecule (A_m)

The Gibbs elasticity E of a film describes the strength of the intermolecular interactions between surfactant molecules at an interface. It is an indication of the capability of a monolayer to resist change in surfactant packing or area per molecule due to stretching of the interface, which is a measure of the film stability. E is given by

$$E = d\gamma/d(\ln A), \quad (2)$$

where γ is the surface tension and A is the surface area per molecule of surfactant. E can be determined from MD simulations, which are shown in Figure 56. Figure 56a shows the MD predictions for surface tensions of different surfactants that were already shown in Figure 55e-h. Figure 56a also shows a third order polynomial (with the negative coefficient of the highest order) fitted to the MD predictions of surface tension by

$$y = -|a|x^3 + bx^2 + cx + d, \quad (3)$$

where x is the natural logarithm of surface area per molecule A , y is the surface tension, and a , b , and c are the parameters obtained from fitting.

The trisiloxane has large A values because of its branched tail as one may expect. The surface tension curve is very steep for PFOA among the surfactants studied. As the logarithm of surface area increases, the surface tension increases, trending in an “S” shape. Then by taking the derivative of the fitted polynomial, E was obtained as a function of $\ln(A)$ as shown in Figure 56b. Figure 56b shows downward opening parabolas with maxima for different surfactants. The A value corresponding to the maximum Gibbs elasticity (E_m) is defined as the most probable surface area per molecule A_m . The maximum E indicates an interface’s capacity to increase surface tension in

response to imposed surface dilatation, therefore at this point the surfactant is most stable and resists surface dilatation or surfactant concentration fluctuations by retaining a uniform packing. The E_m and A_m values obtained from Figure 56b are shown in Figure 56c. Figure 56c shows that the E_m value predicted by MD simulation for CTAB monolayer was 64.6 dyne/cm at 25.0 °C, and agrees well with experimental value of 61.0 dyne/cm measured at 23.0 °C [61]. Experimental measurements of E_m for the other three surfactants were not available to our knowledge. The MD simulations show that the fluorocarbon surfactant PFOA has the greatest E_m (119.4 dyne/cm) and thus it is most stable, the siloxane surfactant L77 has an intermediate E_m value (90.9 dyne/cm), while hydrocarbons SDS (75.5 dyne/cm) and CTAB have the lowest values of E_m among the four surfactants. A surfactant is adsorbed on lamellae of bubbles within the foam structure. In foam stability experiments, foams are generated from different surfactants and degradation rates of a foam layer are measured with time. The order of the Gibbs elasticity values predicted by MD for different surfactant monolayers are qualitatively consistent with the foam stability measurements for SDS, perfluorocarbon surfactants and hydrocarbon surfactants.

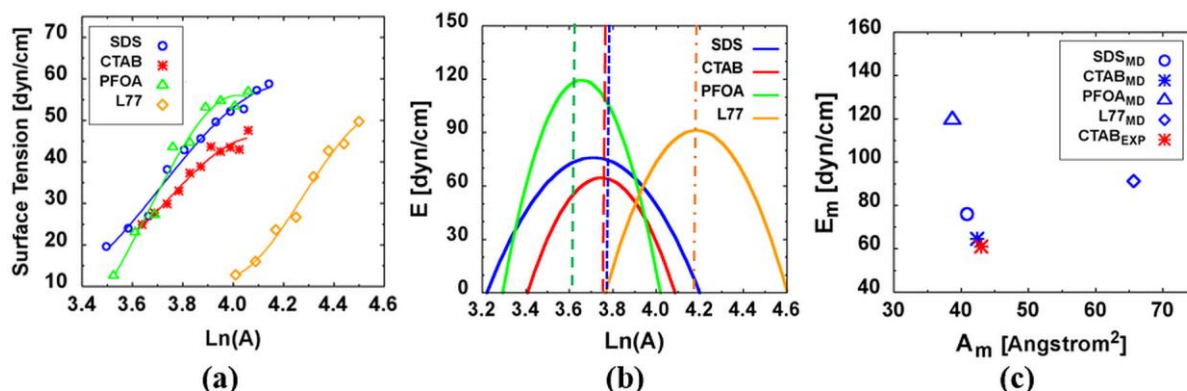


Figure 56. (a) The MD predictions for surface tension as functions of surface area per molecule, A , along with 3rd order polynomial fits (solid lines) for calculating maximum Gibbs elasticity, E_m . The uncertainty for each experimental surface tension measurement is 0.5 dyne/cm. (b) The MD-predicted Gibbs elasticity as functions of $\ln(A)$. The vertical lines indicate the experimental values for surface area per molecule [58, 59, 61, 63]. (c) The most probable surface area at maximum Gibbs elasticity of surfactant monolayer obtained from MD simulations compared with experimental values of E_m and A_m for CTAB surfactant monolayer [35].

5.7.1.3. MD Predictions versus Experiments for A_m and γ_m

The MD predictions of A_m were compared with experimental data [58, 59, 61, 63-65] and the MD simulation results of Jang et al. [57] in Figure 57a [35]. The results show that the A_m obtained from simulations agree reasonably well with experiments, with deviations less than 3.0 Å² for all four surfactants. The area of siloxane surfactant L77 is significantly larger than both the hydrocarbons, SDS and CTAB, and the fluorocarbon PFOA due to the long oxyethylene chain in the head group and also the bulky tri-siloxane group in the tail. PFOA has the smallest area due to its small head group (Figure 54). Zhuang et al. [66] showed that with the same tail, the surface area increases as the size of the head group increases; with the same head group, the surface area decreases as the hydrocarbon chain length increases due to stronger hydrophobic interaction of the tails. Therefore, the surface areas of SDS and CTAB are close because CTAB has a larger head group (trimethylamine) and longer hydrocarbon tail than SDS.

Figure 57b shows that the surface tension at saturation (γ_m) corresponds to E_m and A_m in Figure 56c. Small differences in the most stable surface area per molecule A_m can lead to rather large differences in the surface tension especially for PFOA which has the steepest curve as shown in Figure 56a. For PFOA, the predicted surface tension is noticeably higher than experimental values (Figure 57b). Nevertheless, the good agreement between the MD predictions for A_m and γ_m with the experimental data shows that our method based on the maximum in E_m for determining A_m and γ_m works well for the surfactants studied in this work. The A_m values from our calculations of the air-water interface using C36FF agree well with previous calculations of Newton black films by Jang and Goddard [57] for SDS and CTAB using DREIDING force-field as shown by blue bars in Figure 57a. Rusanov et al. [67] developed a thermodynamic model for thin and thick films relating Gibbs elasticity and disjoining pressure. The model predicts a peak in elasticity as the surfactant concentration approaches CMC. Their model predictions suggest that E_m corresponds to CMC consistent with the comparisons shown in Figure 57b. The A_m we defined represents the most stable packing, and requires the highest energy and force and it corresponds to E_m .

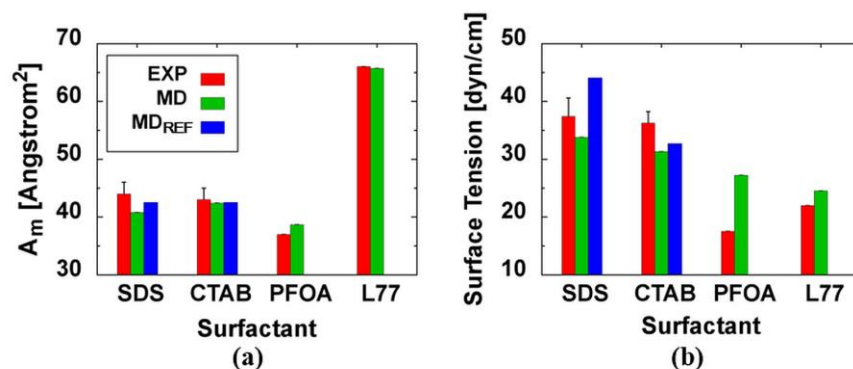


Figure 57. Comparisons of (a) the most stable surface area per molecule A_m , (b) surface tensions at saturation γ_m , MD predicted with the experimental data (EXP) for SDS [59], CTAB [59], PFOA [58], and L77 [61], and MD simulation results reported in the literature [57] (MD_{REF}) [35].

5.7.2. MD Predictions for Trisiloxane and Alkylpolyglycoside Surfactants

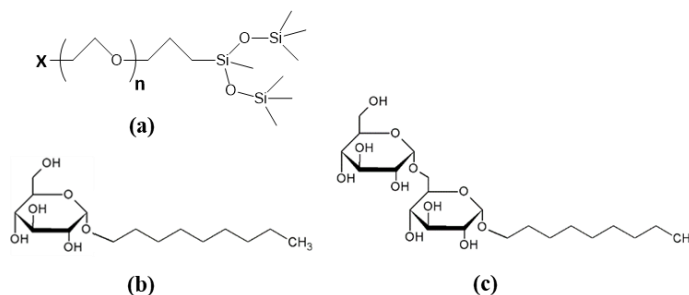


Figure 58. (a) Chemical Structure of polyoxyethylenated trisiloxane (existing in commercial trisiloxane 502W), X is OH, n is oxyethylene length in the range between 2 to 20 (b) alkylglucoside 1g9 with one glucoside head group and hydrocarbon length of 9 and (c) alkyl glucoside 2g9 with two glucosides head group 1→6 glucoside linkage and hydrocarbon length of 9 [36].

The chemical structure of polyoxyethylenated trisiloxane surfactant and hydrocarbon surfactant with one and two glucoside head group are shown in Figure 58. Three types of

monolayer systems with total of 36 molecules per monolayer are simulated; (1) a pure trisiloxane with a terminal hydroxyl (OH) group and varied oxyethylene length ($n=3\sim 20$ at 25 °C, and $n=4\sim 20$ at 60 °C), (2) a two-component trisiloxane/1g9 and trisiloxane/2g9 systems with varied oxyethylene length of trisiloxane ($n=2\sim 20$ at 25 °C), (3) a three-component trisiloxane/1g9/2g9 systems with varied oxyethylene length of trisiloxane ($n=2\sim 20$ at 60 °C). The experimental measurement shows that the fire suppression performance is best when the ratio of trisiloxane to Glucopon is 2:3, which is applied in the simulations. In the two-component systems, the molecular number ratio of trisiloxane:1g9 and trisiloxane:2g9 is 2:3, i.e. in each monolayer, there are 14 trisiloxane, and 22 1g9 or 22 2g9. Glucopon 225 is a commercial Glucopon with one and two glucoside head, and hydrocarbon tail ranges from 8~10, the averaged value 9 is used in our simulation. The average number of glucosides in Glucopon 225 is 1.7, which gives ratio of 1g9:2g9=3:7. Therefore, to mimic Glucopon 225 behavior in the three-component systems, in each monolayer, the numbers of trisiloxane, 1g9, and 2g9 are 14, 7, and 15, respectively. Also, 1g9:2g9=1:1 for Glucopon 215, in each monolayer of the three-component systems, the numbers of trisiloxane, 1g9, and 2g9 are 14, 11, and 11, respectively.

5.7.2.1. MD Predicted Surface Area per Molecule (A)

The surface area per molecule is calculated by dividing total cross-sectional area by the total number of surfactant 36, i.e. $A = A_{tot}/36$ [36]. Previous studies reported that the ratio of surface area per molecule of polyoxyethylenated surfactant (A) and the square root of oxyethylene unit number ($\sqrt{n}$) is constant, i.e., there is the correlation $A = k \times \sqrt{n}$ for specific type of surfactant at air/water interface [68, 58]. For example, the value of k for a polyoxyethylenated hydrocarbon surfactant $C_{12}H_{25}(OC_2H_4)_nOH$ is between 21.7-24.8 at 25 °C. As shown in Figure 59a, for hydroxyl-capped polyoxyethylenated trisiloxane at heptane/water interface, there is a similar linear correlation that $A = k \times \sqrt{n} + b$, where k and b values are 9.2 ± 0.1 and 48.4 ± 0.5 at 25 °C, and they are 10.6 ± 0.3 and 47.3 ± 1.0 at 60 °C, respectively. Moreover, with the same

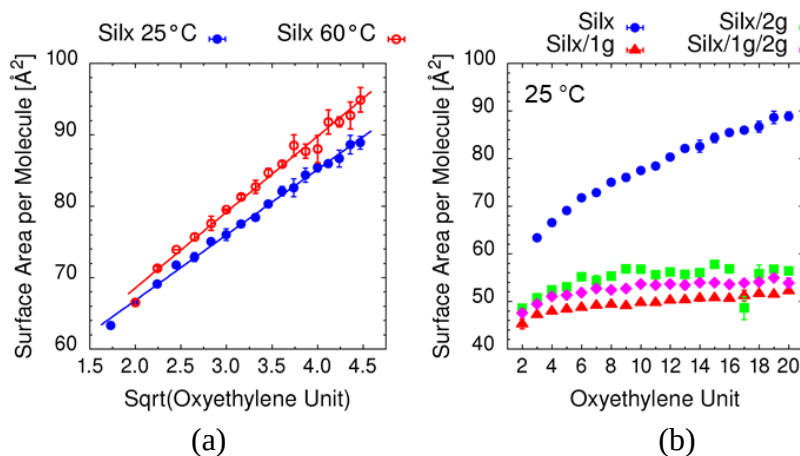


Figure 59. (a) The surface area per molecule of pure trisiloxane at 25 °C and 60 °C as function of square root of oxyethylene length. (b) The surface area per molecule of pure trisiloxane, trisiloxane/1g9, trisiloxane/2g9, and trisiloxane/1g9/2g9 at the heptane/surfactant-monolayer/water interface at 25 °C as function of trisiloxane oxyethylene length [36].

oxyethylene unit number n , the surface areas of pure trisiloxane at 60 °C are generally greater than the values at 25 °C due to more atomic movement at higher temperature. The differences are slightly greater at high oxyethylene length. The surface area per molecule A of pure trisiloxane

increases as n increases, while for trisiloxane/1g9 and trisiloxane/2g9, the A increase slightly and then level off. The A of pure trisiloxane are much greater than the values of trisiloxane/1g9 and trisiloxane/2g9, and the difference is greater at large n at 25 °C (Figure 59b). Similar trend is observed in pure trisiloxane and three-component trisiloxane/1g9/2g9 systems at 60 °C. It suggests that pure trisiloxane is much more sensitive to oxyethylene length than the mixture systems when n is large.

5.7.2.2. MD Predictions for Interfacial Thickness

Mass density profile of each component (trisiloxane, alkylglucoside, water, and heptane) is calculated based on atomic number density of each individual atoms [36]. The heptane/surfactant-monolayer/water system in the normal z direction are divided into small bins with bin size 0.2 Å, and then add up the bins of same molecule to obtain the atomic number density of each component. Based on atomic mass, the mass density profile for each component are obtained as shown in Figure 60a. Then, the interfacial thicknesses of water (d_w) and heptane (d_h), and also the heptane to surfactant ratio in the interface (hsr) are calculated based on the mass density profile. Interfacial thickness of water d_w is defined as the distance between the 10% to 90% mass density of water. Interfacial thickness of heptane d_h is defined as the distance between the 10% to 90% mass density of heptane, as shown in Figure 60b. The hsr is the ratio of number of heptane molecule to number of surfactant molecule in the interface, which is the region between 10% and 90 % of the bulk heptane density.

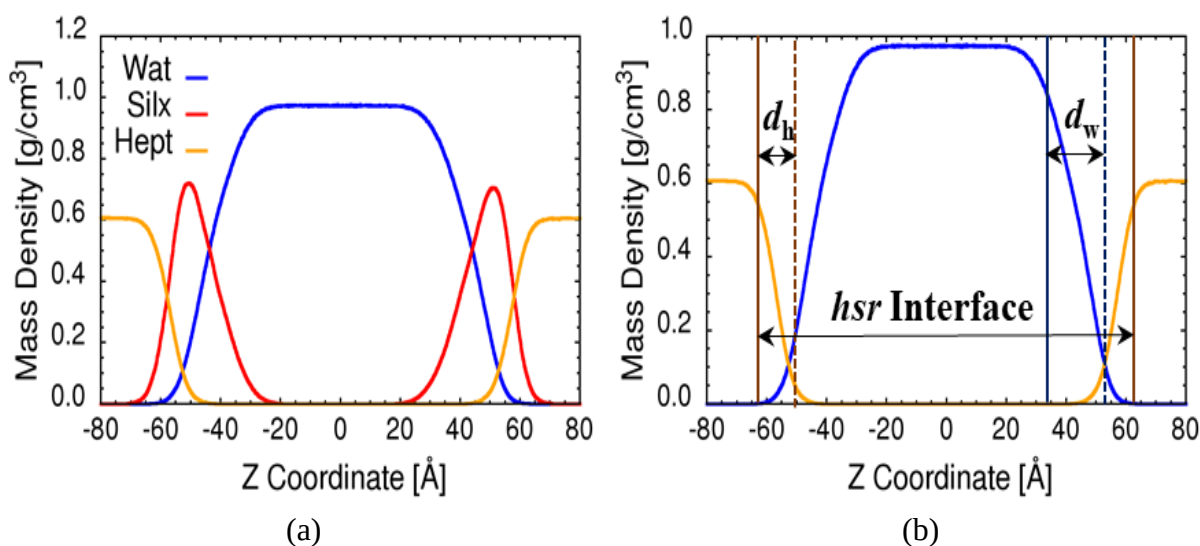


Figure 60. (a) Mass density profile, and the interface used to calculate interfacial thicknesses and heptane to surfactant ratio (hsr) of trisiloxane H8 at 60 °C (b) Schematic plots indicating the definition of interfacial thicknesses of water, heptane and hsr interface, respectively [36].

The interfacial thickness of water d_w increases as trisiloxane oxyethylene n increases as expected at both 25 °C (Figure 61a) and 60 °C. The d_w of pure trisiloxane are very similar at 25 °C and 60 °C which indicate weak temperature dependence. The pure trisiloxane have the greatest d_w , while the two-component trisiloxane/1g9 and trisiloxane/2g9 and the three-component trisiloxane/1g9/2g9 have similar and smaller d_w . Generally, the interfacial thickness of heptane d_h of all systems increases slightly with n when $n \geq 9$, but the n dependence is weak. Unlike the d_w , the d_h of pure trisiloxane are smaller at 25 °C than 60 °C which indicate strong temperature

dependence. The pure trisiloxane have generally smaller d_h than trisiloxane/1g9, trisiloxane/2g9, and trisiloxane/1g9/2g9 at large n (Figure 61b), the difference is greater at 2g9 at 60 °C.

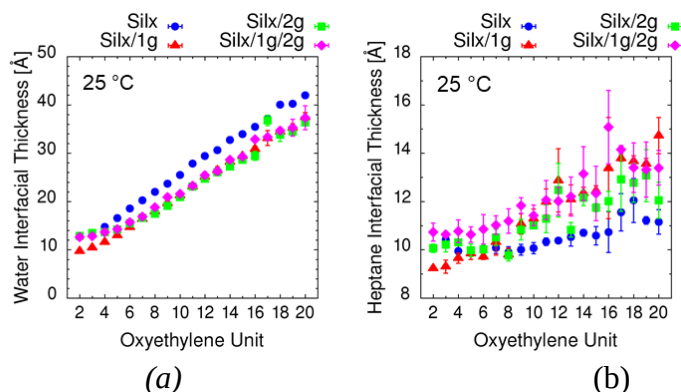


Figure 61. The interfacial thickness of (a) water (b) heptane of pure trisiloxane, trisiloxane/1g9, trisiloxane/2g9, and trisiloxane/1g9/2g9 at 25 °C as function of trisiloxane oxyethylene length.

5.7.2.3. Heptane to Surfactant Ratio (hsr) and Heptane Surface Number Density ($hsnd$)

The region between 10% and 90 % of the bulk heptane density is used to calculate heptane to the surfactant ratio (hsr) [36]. The hsr is the ratio of number of heptane molecule to number of surfactant molecule (72 for all systems in this report) in the interface, i.e. it is the number of heptane molecule per surfactant molecule. The heptane surface number density ($hsnd$) is the number of heptane molecule per unit area (Angstrom²), and it is calculated by $hsnd = hsr/A$, where A is the surface area per surfactant molecule.

As shown in Figure 62a, generally, the hsr increases as n increase for all systems. The hsr of pure trisiloxane is greater than two- and three-component mixtures. The hsr of pure trisiloxane at 60 °C is significantly greater than the value of 25 °C, which suggests strong temperature

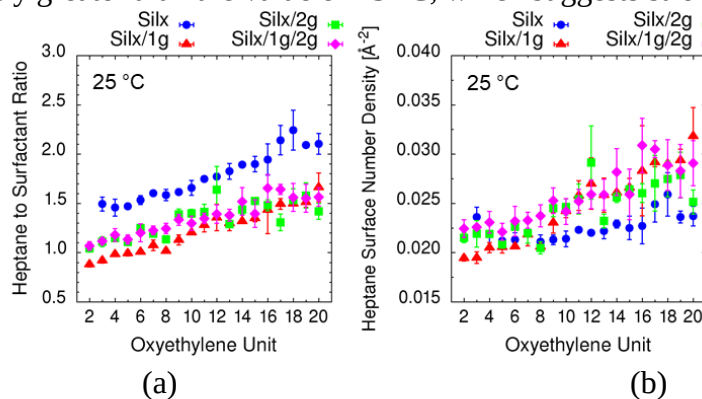


Figure 62. (a) Heptane to surfactant ratio of pure trisiloxane, trisiloxane/1g9, trisiloxane/2g9, and trisiloxane/1g9/2g9 at the interface and (b) the heptane surface number density at 25 °C as function of trisiloxane oxyethylene length [36].

dependence of hsr . The $hsnd$ values of trisiloxane/1g9 and trisiloxane/2g9 are slightly higher when $n \geq 9$ at 25 °C (Figure 62b), while the $hsnd$ of pure trisiloxane are nearly n independent, and trisiloxane/1g9/2g9 are slightly increases when $n \geq 4$ at 60 °C,

5.7.2.4. MD Predictions for Volumetric Number Densities ($msnd^{-1}$ and $hvnd$)

Atomic number density profile of each component (type of molecule) can also be calculated based on atomic number density of each individual atoms [36]. Then the maximum surfactant volumetric number density ($msnd$) and the heptane volumetric number density ($hvnd$) at $msnd$ are calculated based on molecular/group number density. The $msnd$ is the atomic number density of surfactant is at its maximum, and the $hvnd$ is the atomic number density of heptane where the atomic number density of surfactant is at its maximum, as shown in Figure 63. The $msnd$ and $hvnd$ are calculated because they can be used to describe the smallest channel size and the minimum (limit) heptane concentration that can pass through the surfactant monolayer. In this report, the inverse of $msnd$, i.e. $msnd^{-1}$ is used instead of $msnd$ in order to correlate it to $hvnd$ trend directly. The $msnd^{-1}$ is the channel size of the narrowest region in the surfactant monolayer. Generally we expect high $hvnd$ when $msnd^{-1}$ is high.

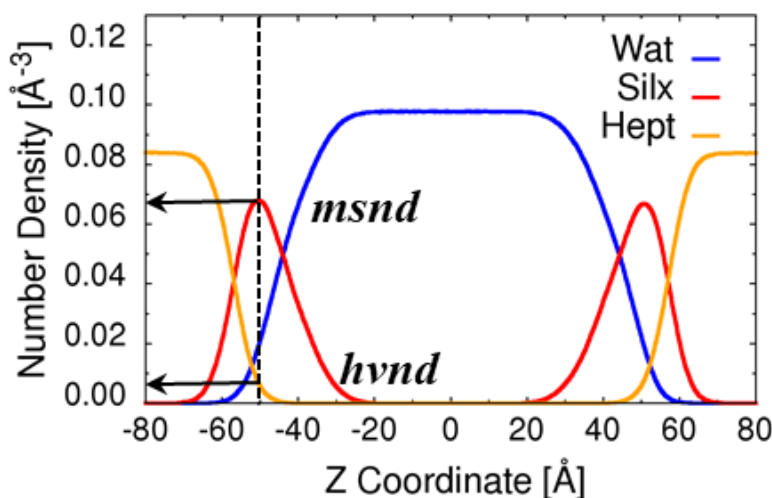


Figure 63. Atomic number density profile of each component in trisiloxane H8 system. The lines indicate the definition of the maximum surfactant volumetric number density ($msnd$) and the heptane volumetric number density ($hvnd$) at the $msnd$ [36].

As shown in Figure 64a, the $msnd$ of pure trisiloxane at 25 °C is slightly greater than the values at 60 °C. The $msnd^{-1}$ of trisiloxane/1g9 and trisiloxane/2g9 are smaller than pure trisiloxane, and the trisiloxane/1g9/2g9 have the smallest $msnd^{-1}$ values. As n increase, $msnd^{-1}$ of trisiloxane/1g9, trisiloxane/2g9 and trisiloxane/1g9/2g9 do not show n dependence. As n increase, the $hvnd$ of pure trisiloxane increases slightly, while the $hvnd$ of all mixtures increases more significantly. The $hvnd$ of pure trisiloxane are greater than trisiloxane/1g9 and trisiloxane/2g9 when n is small ($n \leq 11$). However, the $hvnd$ of trisiloxane/1g9 increases so fast that the values get very close to pure trisiloxane at 25 °C (Figure 64b), similar trend is also observed in the $hvnd$ of trisiloxane/1g9/2g9 which is likely due to the presence of 1g9.

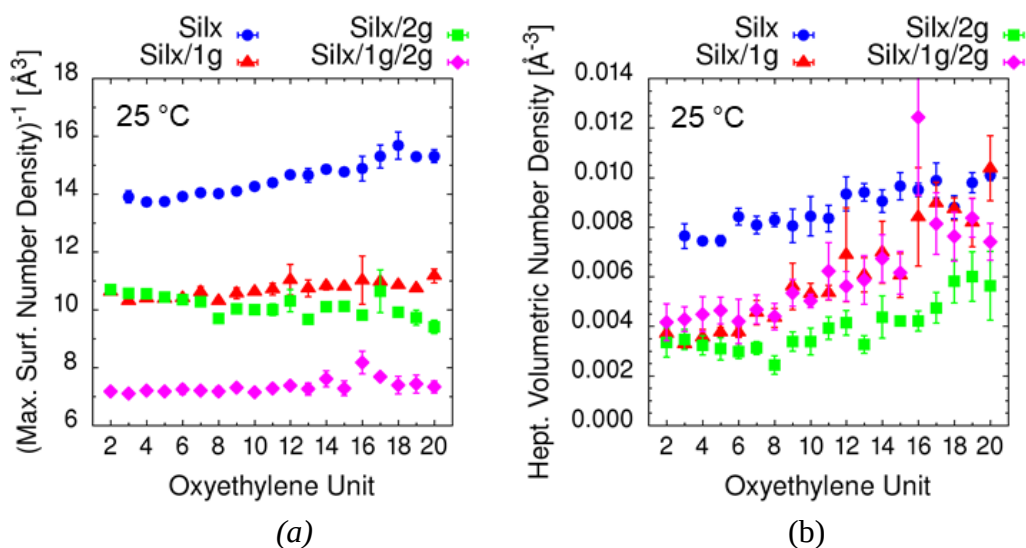


Figure 64. (a) Inverse of the maximum surfactant volumetric number density ($msnd^{-1}$) and (b) the heptane volumetric number density ($hvnd$) at $msnd$ at 25 °C as function of trisiloxane oxyethylene length [36].

5.7.2.5. MD Predictions of Intermolecular Hydrogen Bonds

The number of hydrogen bond is calculated based on the condition that the distance of proton-donor and proton-acceptor pair is less than 2.4 Å, and the angle between them is greater than 150° [36]. The intermolecular hydrogen bond is the hydrogen bond formed between different surfactant molecules, while the intramolecular hydrogen bond is the hydrogen bond formed within the same molecule, which involves bending of proton-donor and proton-acceptor group. The more the intermolecular hydrogen bond, and the less intramolecular hydrogen bond, the more stable the surfactant monolayer head group region. The intramolecular hydrogen bond numbers are generally very small, therefore, the data are not presented in this report. However, it is considered in the intermolecular hydrogen bond calculation for higher accuracy. The number of the intermolecular hydrogen bond is calculated by subtracting the number of intramolecular hydrogen bond from the total number of hydrogen bond, i.e. $N_{inter} = N_{tot} - N_{intra}$.

The (intermolecular) hydrogen bond number per molecule ($hbnm$) of pure trisiloxane at 60 °C are slightly smaller than the ones at 25 °C (Figure 65a), which agree with the slightly greater surface area at 60 °C. As n increases, the $hbna$ of pure trisiloxane decreases (Figure 65b) while the $hbnm$ of mixture decrease and level off (and may have a minimum between $9 \leq n \leq 12$) (Figure 65d). The opposite trend of $hbnm$ and $hbna$ indicate that besides the stability of the monolayer, the $hbna$ as a cross-sectional unit area properties, may be related to the heptane transport rate. The $hbnm$ of trisiloxane/2g9 are much greater trisiloxane/1g9, and the pure trisiloxane have the least $hbnm$ and $hbna$ due to the number of glucoside in the system (Figure 65c, 65d). As n increases, the $hbnm$ of trisiloxane/1g9 increases when $n \leq 11$, and then level off. The $hbnm$ of trisiloxane/2g9 when $n \geq 13$ are generally greater than smaller n . However, both the $hbnm$ and $hbna$ of trisiloxane/2g9 data are quite scattered at 25 °C.

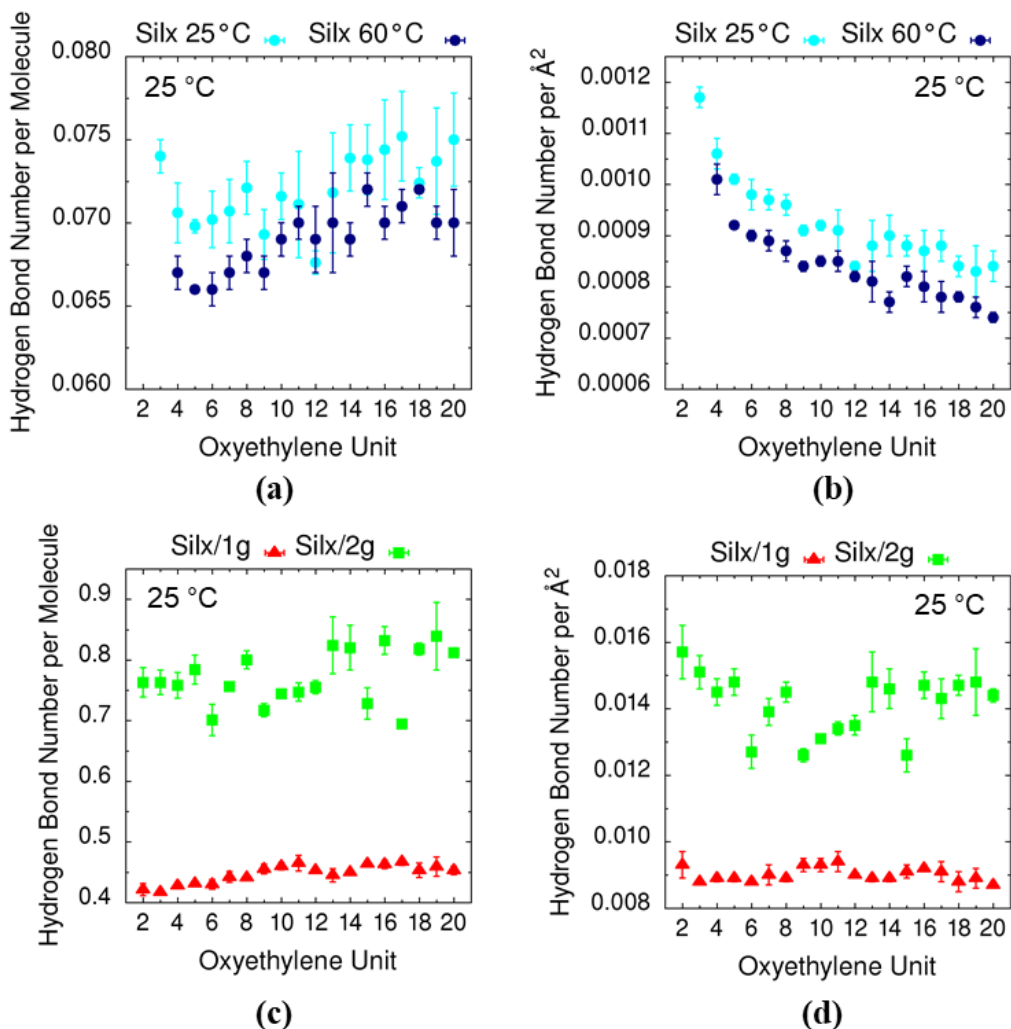


Figure 65. Intermolecular hydrogen bond number per molecule and intermolecular hydrogen bond number per Å² of (a-b) pure trisiloxane at 25 °C and 60 °C, and (c-d) mixed trisiloxane/1g9, and trisiloxane/2g9 at 25 °C as function of trisiloxane oxyethylene length [36].

5.7.2.6. Comparison of Surfactants Packing at an Interface

As shown in Figure 66, the packing of pure capstone is tightest and most ordered, and the 1g9 is packed tighter and more ordered than 2g9, while pure trisiloxane H10 has the loosest packing and it is much less ordered, which agree with the surface area per molecule A that the A of capstone is smallest, followed by 1g9 and 2g9, and trisiloxane H10 has the highest A [36]. The pure capstone has the least penetration of heptane into the monolayer, followed by 1g9 and 2g9, while pure trisiloxane H10 has the most heptane penetration, which agree with hsr values. By mixing capstone with 1g9 with ratio 3:2, the Ca/1g9 and Ca/2g9 pack tighter and also have less heptane penetration than both pure capstone and 1g9. The packing of H10/1g9 and H10/2g9 and the heptane penetration is between pure H10 and 1g9, however, the heptane penetration is closer to 1g9 and 2g9, which agree with hsr values.

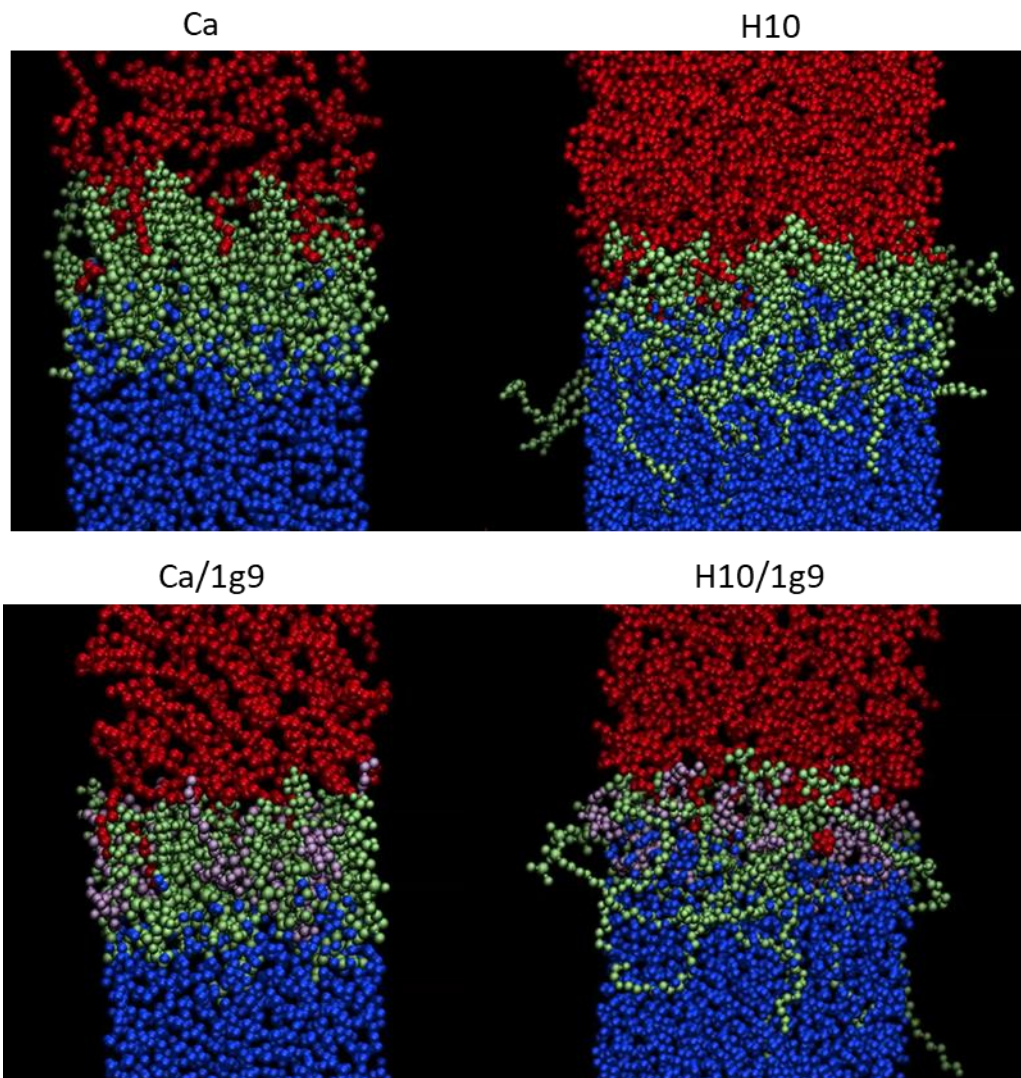


Figure 66. The pure capstone, polyoxyethylenated trisiloxane H10 ($X=OH$, $n=10$), and two-component capstone/1g9 (with ratio 3:2), and H10/1g9 (with ratio 2:3) surfactant monolayer at the heptane/water interface system at the end of the MD simulations at 25 °C, respectively. (Water is shown in blue spheres, heptane is shown in red, capstone and trisiloxane surfactant are shown in green, and 1g9 is shown in pink spheres.) Only the top half in the z direction of the simulation setup are shown, the bottom half is a mirror image of top one [36].

5.7.3. Findings from the MD Simulations

For trisiloxane/1g9, trisiloxane/2g9, and trisiloxane/1g9/2g9, as trisiloxane oxyethylene length n increases, the surface area per molecule A increase and then level off when $n \geq 8$ [36]. The h_{sr} of the mixtures at $n \leq 8$ are smaller than the ones at $n \geq 9$. The h_{vnd} of the mixtures increases dramatically when $n \geq 8$. Therefore, to minimize fuel transport rate, the good trisiloxane candidate is to use $n \leq 8$. However, the h_{bnm} of trisiloxane/2g9 are mostly higher when $n \geq 13$, which suggest that the monolayer may be more stable. Therefore, when using trisiloxane with single oxyethylene unit length, fuel transport rate and stability are trade off, and the optimization based on n is limited. One possible solution to mix the short and long oxyethylene length ($n \leq 8$ and $n \geq 13$).

By comparing the hydroxyl-capped (H) and methoxyl-capped (M) trisiloxane, the results show that the hydroxyl-capped trisiloxane has smaller heptane interfacial thickness (d_h), heptane to surfactant ratio (hsr), and $msnd^{-1}$ than the methoxyl-capped trisiloxane. Therefore, the hydroxyl-capped trisiloxane would be a better choice.

For trisiloxane/alkylglucoside H11/1g and H11/2g, as alkyl glucoside hydrocarbon length n increases, the heptane surface number density $hsnd$ for $n \leq 6$ is greater than the values for $n \geq 7$ and it shows a possible minimum at n around 8 for 25 °C. As the alkyl glucoside hydrocarbon length n increases, the maximum surfactant number density $msnd$ increases first and then level off at $n=9$, and the heptane volumetric number density ($hvnd$) decreases and level off as expected. The alkyl glucoside with hydrocarbon length $n \geq 8$ has high $hbnm$ and $hbna$, thus high monolayer stability. Therefore, the alkyl glucoside with hydrocarbon length $n \geq 8$ would be a better choice.

With the same hydrocarbon length, the β - and (α, β -1 $\rightarrow$ 4)alkyl glucoside (represented by mkn) have significantly smaller surface area per molecule A , heptane to surfactant ratio hsr , $hvnd$ than the α - and (α, α -1 $\rightarrow$ 6)-alkylglucoside (represented by mgn). Moreover, for mkn , the smaller hydrocarbon length has slightly lower hsr , but also higher $msnd^{-1}$ and $hvnd$. Therefore, intermediate value $n=10$ may be the best option.

Siloxane with 1g or cn head group with 3u or 6s tail has the smallest A . 1k3u has the smallest hsr and 2g3t has the smallest $hsnd$ at 60 °C. 2k6s has the greatest $msnd$, followed by 2k3s and 2k3t at both 25 °C and 60 °C. 2k6s, 2k3s and 2k3t also have the smallest $hvnd$, which make these three surfactants good candidates to minimize heptane transport rate. The siloxane 2k6s has the greatest hydrogen bond number per molecule ($hbnm$) and the hydrogen bond number per angstrom ($hbna$), followed by 2k3s and 2k3t, which make them form more stable surfactant monolayers, and better surfactant candidates for fire suppression. (Or maybe we can try $cn6s$, $cn3u$ if it is feasible to prepare them experimentally).

The surfactants 1k10 and dm9 have a smaller hsr , smaller $hsnd$ than the rest of the surfactants modeled in this work. The 2k10 and 2k12 have much greater $msnd$, and much smaller $hvnd$ than the charged hydrocarbon surfactants s310, lau, s312, sds, and dtab, which may suggest that neutral charged hydrocarbon surfactants have lower heptane transport rate than the charged ones.

By comparing the interfacial properties with varied capstone or trisiloxane H10 to alkylglucoside (1g9, 2g9) fraction, we conclude that capstone/alkylglucoside has minimum d_h and minimum $msnd^{-1}$ when capstone fraction $f=0.5$, and capstone/1g9 has maximum $hbnm$ when $f=0.2$. The H10/alkylglucoside has minimum $msnd^{-1}$ when trisiloxane H10 fraction $f=0.2$.

By studying the commercial surfactants, we conclude that two Glucocon-based hydrocarbon surfactants (g215 and g225) have very similar interface properties. Among the commercial surfactant, capstone and capstone/g215e have the minimum $hvnd$ which agree with the experimental heptane diffusion rate of AFFF. Among the pure trisiloxane and trisiloxane/alkylglucoside studied, the H8 and H8/g225 have the minimum d_h , hsr and also $msnd^{-1}$.

¹ and *hvnd*, which agree with the experimental results that pure H8 has the minimum heptane diffusion coefficient.

5.8. Fuel-Surfactant Interaction Effects

We conducted large scale pool fire testing of NRL's drop-in siloxane502W formulation, which is the 2:3 Siloxane-Gluc225 composition listed in Table 19. Tables 53a and 53b compare 28 ft² pool fire extinction performance for heptane and gasoline fuels. They show that the siloxane formulations are much more effective on heptane than on a gasoline fire.

Table 53. (a) Large scale heptane fire extinction, (b) Large scale gasoline fire extinction.

(a)				(b)		
	Drop-in Requirement	28 ft ² Heptane Pool Fire		28 ft ² Gasoline Pool Fire		
	3% concentrate viscosity cP	Extinction Time (s)	Burnback Time (s)		Extinction Time (s)	Burnback Time (s)
Ref AFFF	4.7	30	981			
NRL's Drop-In Siloxane Formulation	7.4	51	338	MilSpec Criteria	< 30	> 360
Commercial Fluorine-Free Foam	16,120	42	778	Ref AFFF	24	759
				Drop-in 502W Formulation	> 60, no extinction	N/A

*28 ft² heptane pool fire at 2 gpm foam solution application rate

To understand the causes for this difference among fuels, we studied the composition of gasoline that differentiates it from heptane, and conducted a series of bench scale experiments with siloxane formulation as well as other commercial fluorine-free formulations [70]. We found that the AFFF formulations are relative insensitive to the identity of the fuel, but the fluorine-free formulations display a significant divergence in extinction capability between these two fuels with the gasoline fire being the more difficult to extinguish. Using the NRL's siloxane formulation, twelve major components of gasoline from the *n*-alkane, *iso*-alkane, *cyclo*-alkane, aromatic and olefin categories were examined to determine a source for this difference in extinction capability. We found that it is the aromatic components category that caused the divergence in performance. Within the aromatic components this effect substantially increased with the number of methyl substituents (trimethylbenzene > xylenes > toluene > benzene). The mechanism involved was investigated by an experiment monitoring the aqueous surfactant solution – fuel interface for the crossing of surfactants and fuel with the finding that the surfactant was extracted by the fuel. The degree of extraction of surfactant into the fuel correlated with the effect of the fuel component on extinction, particularly within the aromatic components (trimethylbenzene > xylenes > toluene > benzene). As a simple two-component simulant for gasoline, a trimethylbenzene/heptane mixture is proposed and supported by foam degradation and fuel vapor transport through the foam characterization [70].

We digress a little in the next figure to remind 502W formulation's heptane-fire suppression before getting back to the discussion of fuel-surfactant effects. The 19 cm diameter heptane pool fire extinction times as a function of foam flow rate are plotted in Figure 67 for the RefAFFF and siloxane-glycoside formulations. The RefAFFF extinction time – foam flow rate profile represents a performance goal which is derived from this formulation's passing the MilSpec pool fire extinction time requirement. As indicated above, the screening of many commercial siloxane and hydrocarbon surfactants by substituting them for the Capstone 1157 surfactant in the RefAFFF formulation produced only one candidate that displayed an extinction profile remotely comparable to that of RefAFFF. The 502W substitution for Capstone at the 3:2 ratio with

Glucopon® 215UP is plotted in Figure 67 (Siloxane #1). The surfactant ratio was then systematically varied from 3:1 to 1:3 with the finding that the best improvement occurred at the 2:3 ratio (Siloxane #2). Next, a series of four alkyl polyglycoside surfactants were tested with the finding that the 2:3 502W:Glucopon® 225DK (Siloxane #3) with its larger glycoside head group closely approached the RefAFFF profile on the heptane pool fire.

To further evaluate this Siloxane #3 formulation, the MilSpec extinction test on the 28 ft² gasoline pool at NRL Chesapeake Bay Detachment (CBD) showed neither an extinction nor a fire knockdown. As a control experiment, the RefAFFF formulation was retested, and it again extinguished the pool fire in less than the 30 sec MilSpec requirement. Sources suspected for this divergent behavior included fuel identity (heptane vs ethanol-free gasoline), foam generation method (near ambient pressure bubbling through a glass frit vs 100 psi passage through an aspirating nozzle, and pool size (correlation with heat intensity).

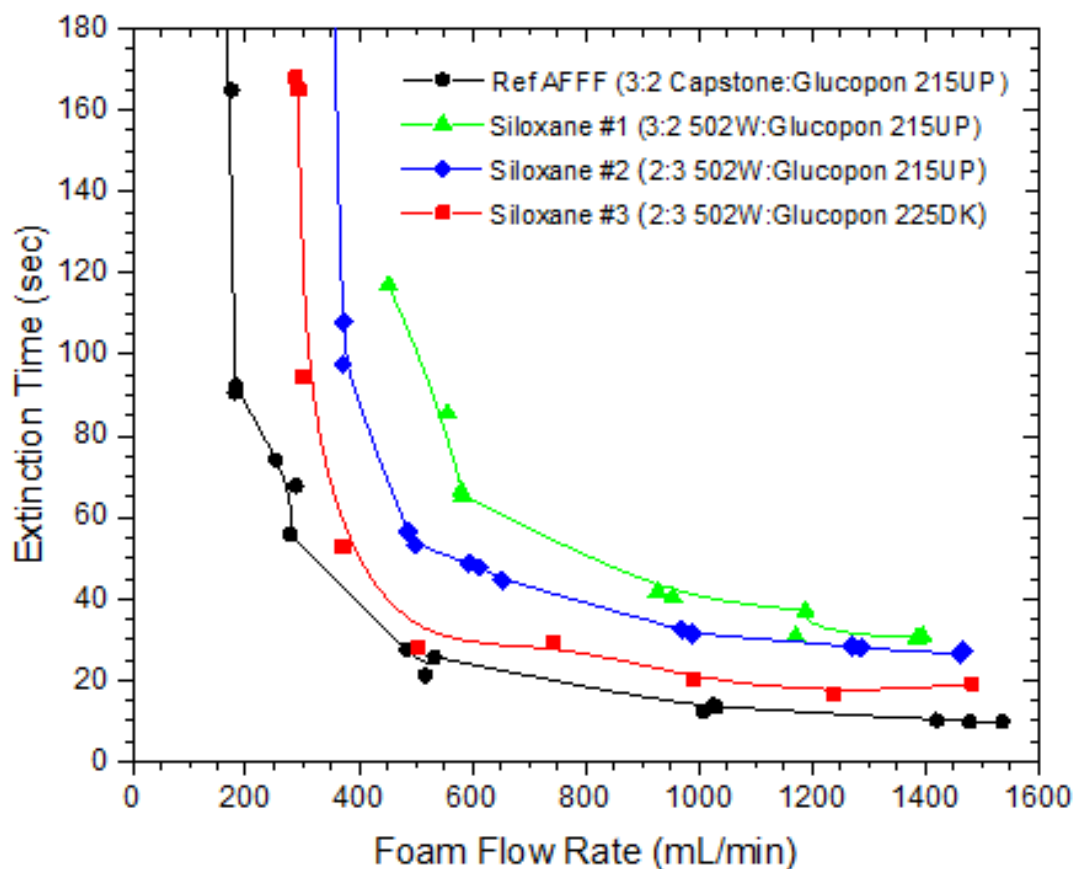


Figure 67. 19 cm diameter heptane pool fire extinction time vs foam flow rate for the RefAFFF formulation and an evolution of siloxane-glycoside formulations based on 502W siloxane surfactant and the alkyl polyglycoside surfactants Glucopon 215UP and Glucopon 225DK. Foams applied at the center of the pool.

The alcohol-free gasoline used for the CBD MilSpec pool-fire testing was first item to be investigated. It was used as the fuel in the 19 cm pool fire, and gasoline vs heptane comparative data were obtained (Figure 68). For the Ref AFFF the difference between extinction profiles is

small with the gasoline pool-fire being slightly more difficult to suppress although both fuels could be extinguished in less than 20 sec at the 1200 mL/min foam flow rate. However, for the NRL's Siloxane502W formulation the gasoline-heptane extinction profile difference is quite large with no extinction being observed at and below the 1200 mL/min foam flow rate. This remarkable difference is clearly attributable to the identity of the fuel and more particularly to the interaction of gasoline with components of the Siloxane formulation.

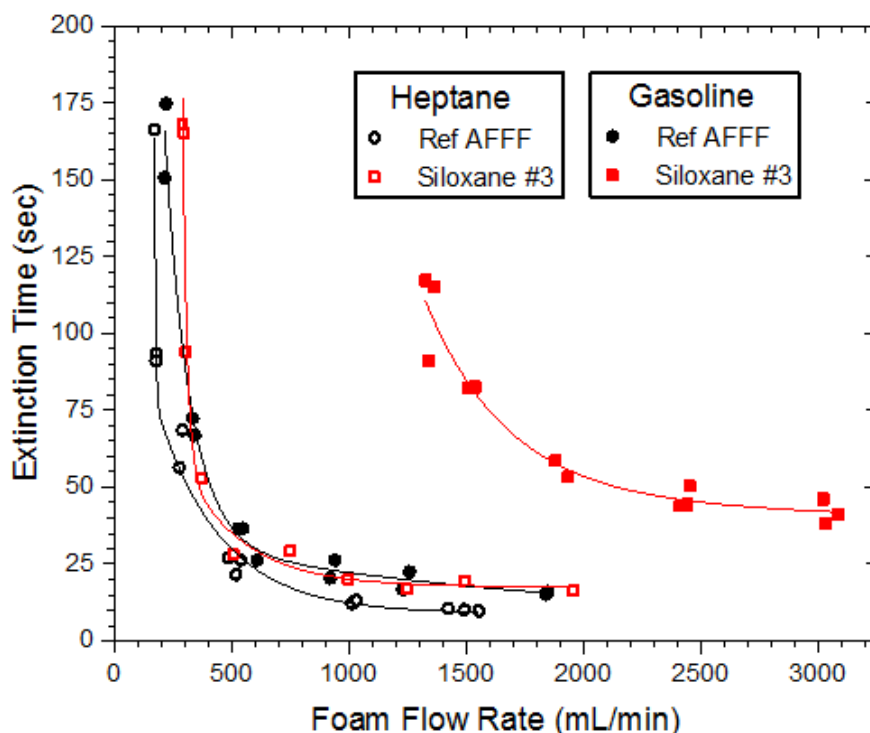


Figure 68. Comparative gasoline vs heptane pool-fire extinction profiles of RefAFFF and Siloxane #3 (502W:Glucopon225DK 2:3) formulations on a 19 cm diameter pool. Foams applied at the center of the pool.

Gasoline is a complex mixture of hydrocarbon components, and its composition varies depending on petroleum source, refining process and formulation for season of intended use. A simple ^1H NMR analysis was conducted on the gasoline used in the CBD testing and compared with the heptane fuel used in the benchtop testing and with *n*-heptane as well. Spectra of each fuel are presented in Figure 69. In the gasoline spectrum there are two groups of resonances: one in the 0.5-2.3 ppm range associated with protons bonded to aliphatic carbon structures and the other in the 6.8-7.2 ppm range associated with protons bonded to unsaturated carbon structures. Integration of these two groupings of resonances indicate that a significant quantity of aromatic and olefinic components reside in the gasoline. Within the aliphatic group, the resonances within the 2.0-2.3 ppm range correlate with methyl groups bonded to aromatic or olefinic structures. Examination of the heptane and *n*-heptane spectra provides further insight. Neither of these spectra display resonances corresponding to unsaturation in hydrocarbon structures. The heptane (or “heptanes” as commercial heptane is frequently termed) is a mixture of C7 alkane isomers and closely related cyclic hydrocarbons. The inset in the Figure 69 heptane spectrum is a typical

composition of commercial heptane [70] and identifies the numbers of methyl, methylene and methane groups in each major component. The branched chain isomers accentuate the number of $-CH_3$ groups per molecule and result in an integration ratio of methyl to methylene/methane that approaches 1. In the single component *n*-heptane this ratio is 6:10 which is reasonably well approached by the experimental 1.00:1.58. The extra methyl groups in heptane cause a small depression of its surface tension (19.8 mN/m at 19 °C) compared with that for *n*-heptane (20.0 mN/m at 19 °C) which can make a difference with respect to film formation on the fuel surface as calculated by spreading coefficient. With respect to gasoline, the non-aliphatic components appear to cause an increase in the surface tension (22.7 mN/m at 19 °C). However, as to be presented in a later section, the prevalent identified aromatic components in gasoline can cause a significant and negative effect in pool fire suppression by F3 formulations.

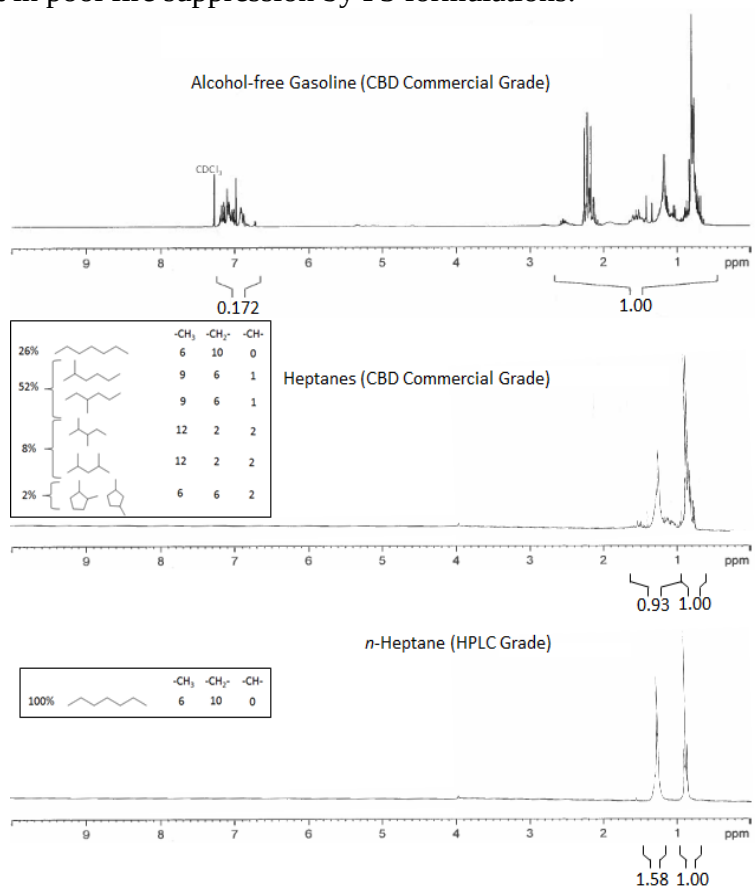


Figure 69. ^1H NMR spectra of alcohol-free gasoline, heptanes and *n*-heptane used in 28 ft² and benchtop pool-fire extinction testing. Integrations are discussed in the text. The inserts on the heptanes and *n*-heptane spectra identify quantities of major components [70] and the number of methyl, methylene and methane structural units in each component.

Two diagnostics that relate valuable information about foam-fuel interaction are a foam degradation test and a fuel-vapor transport test. Foam degradation was evaluated by monitoring the disappearance of a 4 cm thick layer of laboratory generated foam deposited over 60 ml of 35°C heptane or gasoline in a 100 ml beaker (Figure 70). There is an increase in bubble size followed by a shrinking of the foam volume. A plot of foam height vs time depicts significant foam degradation differences between the heptane and gasoline fuels for the RefAFFF and Siloxane #3

formulations (Figure 71(a)). This plot indicates the stronger degrading character of the gasoline on the stability of the RefAFFF and siloxane #3 foams. Fuel vapor transport through a foam layer is measured by a similar but closed apparatus where the headspace air above the foam is transported through an FTIR gas cell and monitored for fuel vapor content. These data are plotted in Figure 71(b). This vapor permeation occurs on a shorter time scale than that of the foam degradation experiment. The results indicate that the Siloxane #3 foam is more susceptible to hydrocarbon vapor permeation and that gasoline is the more permeable vapor through both foams. These diagnostics are conducted under conditions significantly different from fire suppression.

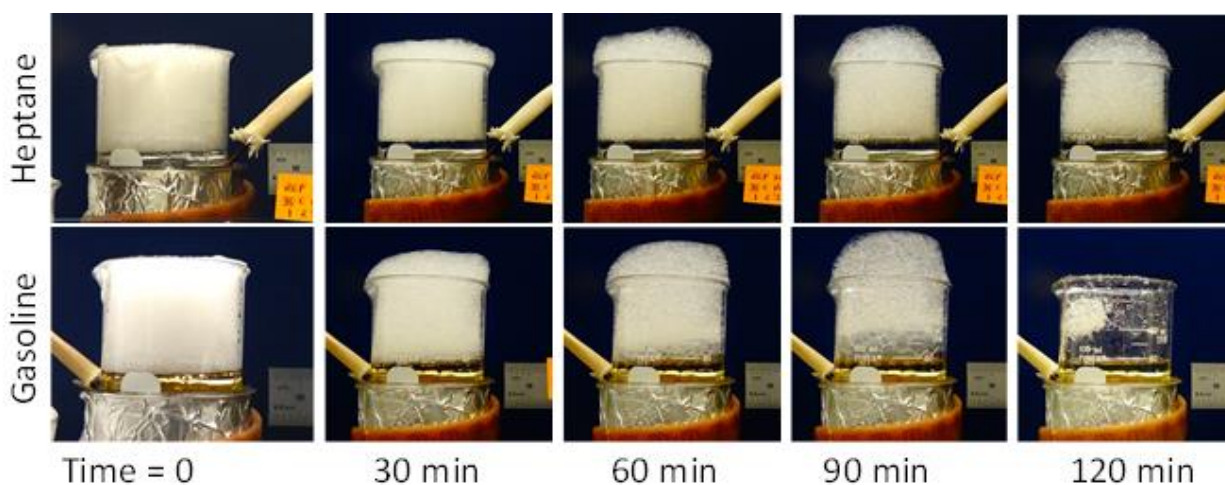


Figure 70. Photographic images of RefAFFF foam degradation over heptane and gasoline at 35°C.

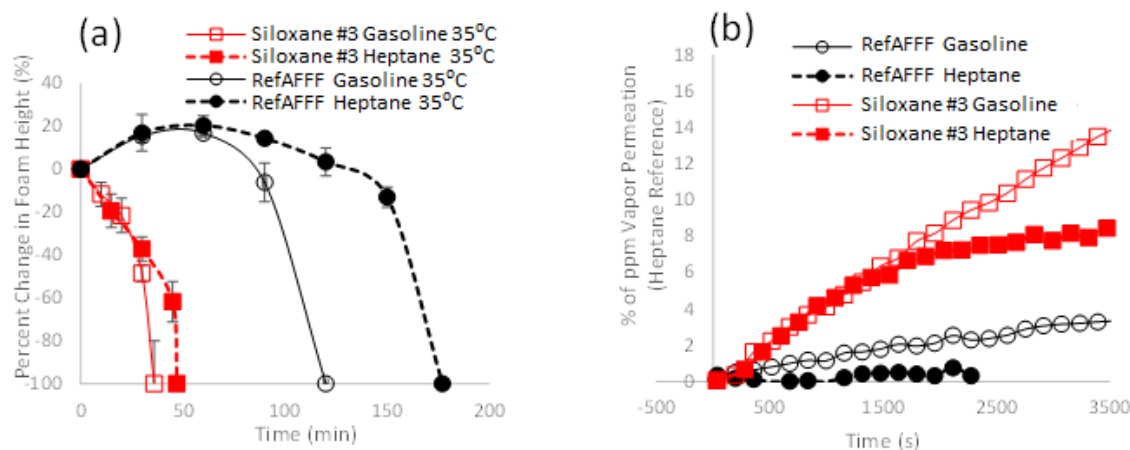


Figure 71. (a) Plot of RefAFFF and siloxane #3 foam degradations over heptane and gasoline at 35°C; (b) Plot of heptane and gasoline vapor concentration increase in the purged headspace following deposition of a 4 cm layer of foam over a pool of fuel.

5.8.1. Fuel Effect on Fire Suppression

As described above and depicted in Figure 68, the use of gasoline or heptane as a pool fire fuel causes a large divergence in fire suppression behavior for an experimental F3 formulation based on a siloxane-glycoside surfactant formulation. This observation raises the question as to whether this may be a general characteristic of F3 formulations and whether there may even be a significant difference in AFFF extinction performance on pool fires of gasoline vs heptane. In the

introduction, we cited literature references, which indicate that this is unresolved. In this section this issue is addressed for both AFFF and F3 formulations by conducting comparative extinction profile experiments with a benchtop 19 cm diameter pool fire apparatus under controlled conditions using gasoline and heptane as fuels.

Three AFFF formulation concentrates were evaluated, the first being the RefAFFF [70] described above and the second and third being commercial formulations, Buckeye 3% MIL SPEC AFFF and FireStopper PFE-FR(FFC) Green. These concentrates are characterized by non-volatiles component content determined by evaporation under stepped application of vacuum and by fluorine content determined by ^{19}F NMR.[70] The RefAFFF concentrate has a non-volatiles content of 7.3 wt% and a fluorine content of 1.7 wt%. The Buckeye and FireStopper commercial concentrates have respective non-volatiles contents of 15 and 67 wt% and fluorine contents of 0.77 and 1.2 wt%. These concentrates were diluted at a proportionating rate of 3% and fire extinction profile data obtained using benchtop apparatus. The gasoline vs heptane pool fire extinction profile data are presented in Figure 72. The extinction time correlates with foam flow rates being rapid at rates >500 mL/min progressing to a non-extinction at rates <200 mL/min. The fire extinction dependence on the fuel identity is small. All three of these formulations extinguished the MilSpec 28 ft² gasoline pool fire in less than the required 30 sec.

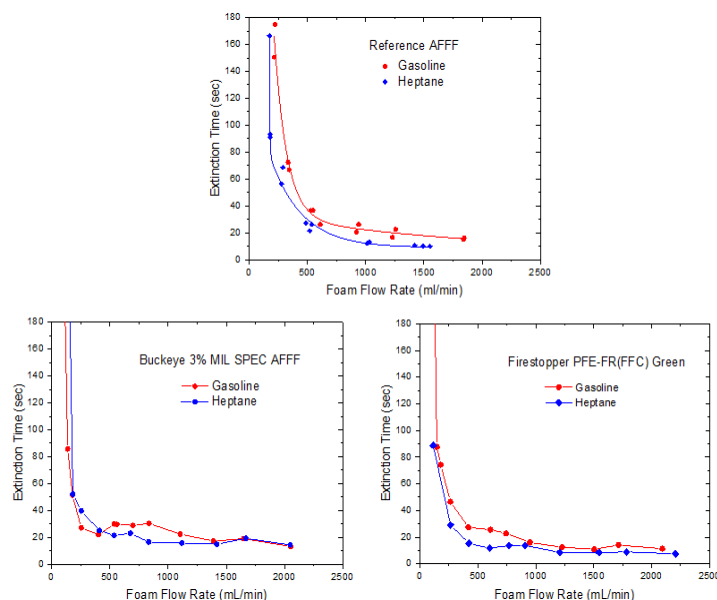


Figure 72. Comparative extinction time profiles of AFFF formulations for gasoline and heptane 19 cm diameter pool fires. Foams applied at the center of the pool.

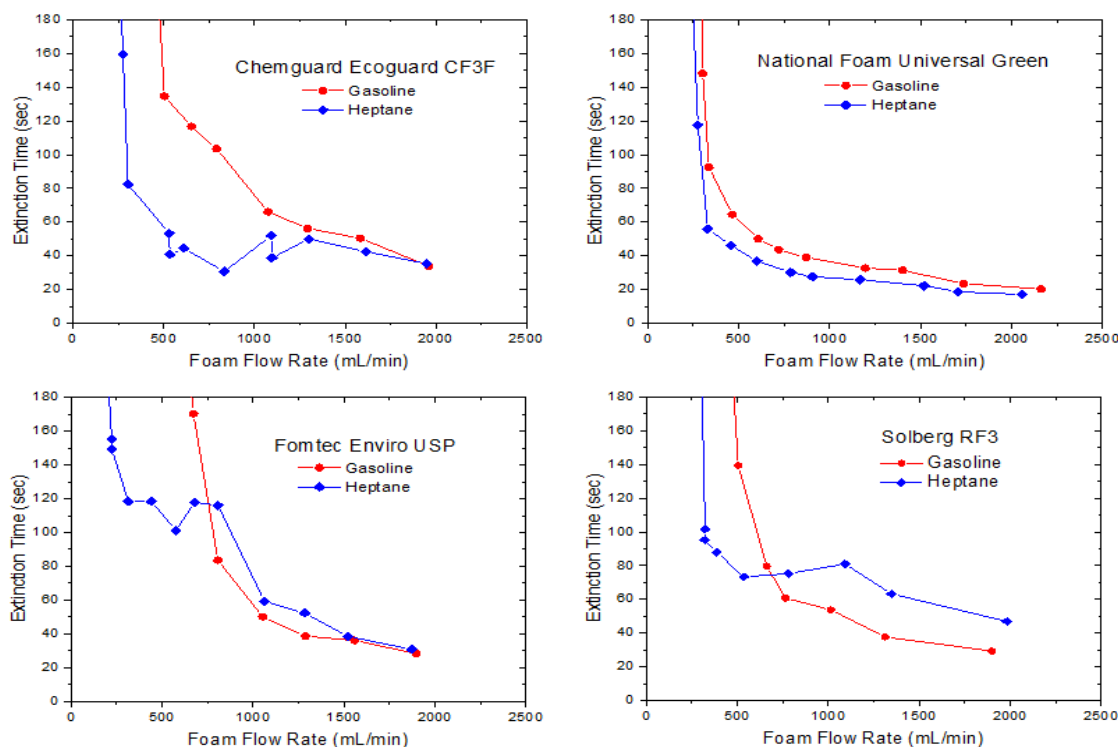


Figure 73. Comparative time extinction profiles of four commercial Fluorine-free (F3) formulations for gasoline and heptane 19 cm diameter pool fires. Foams were applied at the center of the pool.

The issue of specific interest here is to determine whether the of gasoline vs heptane as the pool fire fuel causes a significant difference in fire extinction when using commercial F3 formulations as was the case with the experimental Siloxane #3 formulation. Four commercial F3 formulation concentrates were evaluated. These were purchased from the manufacturer/distributor and include: Chemguard (Ecoguard 3%F3); Fomtec (Enviro ARC 3x6); National Foam (Universal Green 3-3%); and Solberg (Re-Healing Foam RF3). General composition information from SDS is in their material data sheet, but specific compositions are proprietary. The gasoline vs heptane pool fire extinction profile data are plotted in Figure 73.

The extinction profile results for these F3 products display considerable variation in effectiveness on both the gasoline and heptane pool fires and are considerably different from the profile of the Siloxane #3 (502W:Glucopon225DK 2:3) experimental formulation presented in Figure 68. Unlike the AFFF formulations, none of the F3 formulations have an extinction time of less than 20 seconds at the high foam flow rate limit. The region of practical importance is the <1000 mL/min flow rate, and only the National Foam product shows an attractive performance in this region. With respect to the gasoline vs heptane issue, the extinction behavior is quite varied with two products displaying a crossover in effectiveness. In the <1000 mL/min flow region gasoline is the predominantly more difficult fuel fire to extinguish with the differences becoming quite large at the 500 mL/min.

Figures 74a and b compare extinction time versus foam flow rate profiles for different formulations for gasoline and heptane respectively. In practice, only a limited quantities of

surfactant concentrate can be carried or available for firefighting. Therefore, solution flow rate is important rather than the foam flow rate. Figures 74 c and d compare the profiles as functions of solution flow rate rather than the foam flow rate. There is a significant variation in the measured

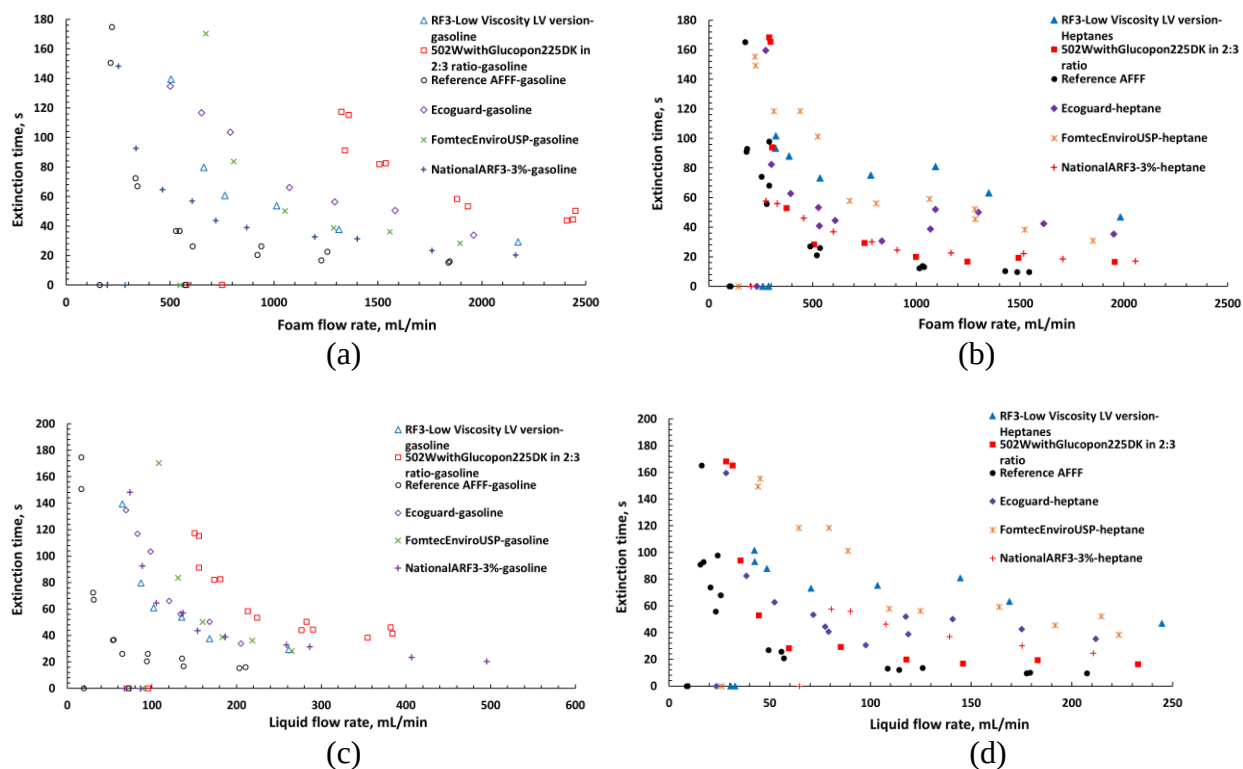


Figure 74. Comparison of extinction time versus foam flow rate for four commercial F3 formulations along with NRL's siloxane 3 formulation and RefAFFF for 19-cm diameter pool fires of (a) gasoline, (b) heptane. Similar comparisons are made for extinction time versus solution flow rate for gasoline and heptane fires in (c) and (d) respectively. Foams deposited at the center of the pool.

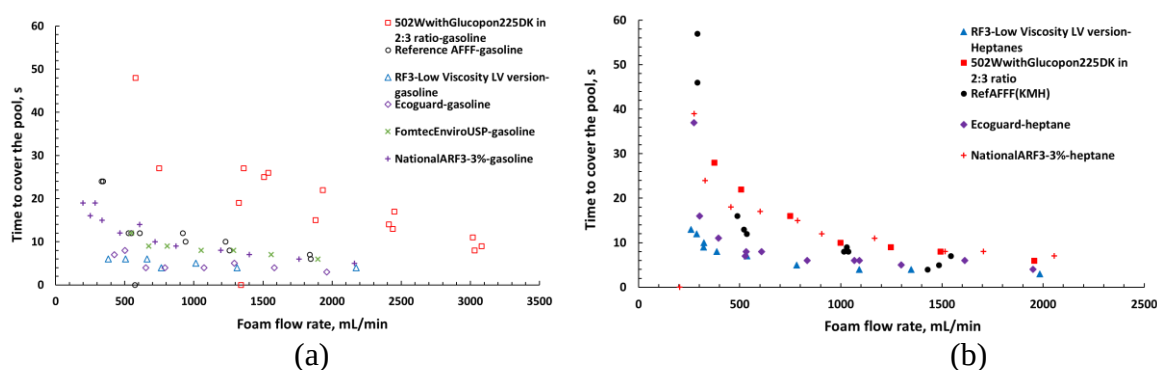


Figure 75. Comparison of coverage time versus foam flow rate for four commercial F3 formulations along with NRL's Siloxane 3 formulation and RefAFFF for 19-cm diameter pool fires of (a) gasoline, (b) heptane. Foams deposited at the center of the pool.

initial foam expansion ratio among different foams that affects the extinction profiles when plotted against solution flow rate, which is calculated by dividing the foam flow rate with the measured

expansion ratio. Figures 75 a and b show pool-coverage times versus foam application rate for gasoline and heptane fuels, respectively.

While the intent here is not to analyze failures and limitations of the F3 formulations, there are some other properties of these formulations that are readily measured and have importance with respect to MilSpec requirements. These include non-volatiles and viscosity of the concentrate, surface and fuel-interface tensions of the premix and expansion ratio of the foam, and they are reported for the AFFF and F3 formulations in Table 54. The variation in concentrate non-volatile component quantities and viscosity cover a substantial range. The AFFF formulations appear to reflect extremes with the three-component RefAFFF being composed of what is minimally necessary to generate foams and suppress pool fires without addressing other requirements and the FireStopper being heavily loaded with components for maximum versatility. The four commercial F3 formulations have variations in non-volatile content consistent with proprietary compositions, and the NRL experimental Siloxane #3 formulation has a relatively low non-volatiles content reflecting a minimal composition to investigation extinction similar to that for the RefAFFF formulation. The viscosity of the concentrate is typically low for AFFF formulations and can be quite high for F3 formulations approaching that of a gel. Its importance is in compatibility with the equipment needed to rapidly dilute the concentrate (3 or 6%) to the premix concentration immediately prior to foam generation. In this regard MilSpec requires a concentrate viscosity range of 2-20 cP. High viscosity can enhance slow drainage of water from foam which many F3 formulations rely upon for fire extinction. Surface and fuel interface tensions of the AFFF and F3 formulations at their premix concentrations is an important difference between these groups. The higher surface tension of the F3 solutions cause a negative spreading coefficient condition, and a continuous aqueous-surfactant film is not formed by drainage from a foam applied to the fuel surface. The lower surface tension AFFF solution drained from its foam can form a continuous film barrier and, along with the oleophobic character of the fluorinated surfactant foam above, can more effectively retard fuel vapor transport to the fire above the foam. Finally, the expansion ratio parameter should pass the MilSpec threshold of >5 such that the foam's dryness results in an efficient consumption of the concentrate. F3 formulations that utilize very wet foams (expansion ratio <5) and slow drainage can increase fire suppression effectiveness but at a high rate of consumption of the concentrate supply.

In addition to pool fire suppression, the AFFF and F3 formulations have differing concentrate, premix and foam properties and can be thought of as separate groups having related but different capabilities due to the uniqueness of the fluorocarbon surfactant in AFFF compared with the hydrocarbon surfactants in F3. F3 formulations have different mechanisms of fire suppression and different foam, concentrate, and premix solution properties than AFFF. The main issue of interest is the divergent behavior of the F3 formulation in extinguishing of gasoline and heptane pool fires. What may be the underlying cause for divergence is undertaken in the following section.

Table 54. AFFF and fluorine-free (F3) formulation concentrate, premix and foam properties.

F3 Manufacturer (Product)	Non-Volatiles Content (wt%)	Viscosity (cP)	Surface Tension (mN/N)	Gasoline Interfacial Tension (mN/N)	Heptane Interfacial Tension (mN/N)	Expansion Ratio
AFFF						
NRL (RefAFFF)	7.3	3.19	15.2	1.05	1.00	9.4
Buckeye Buckeye BFC-3MS	15.0	6.97	16.4	1.63	1.50	6.7
FireStopper (FireStopper PFE-FR)	67.4	9.84	14.1	2.74	3.36	6.0
F3						
Chemguard (Ecoguard 3%F3)	36.2	22	27.0	0.64	1.98	9.0
Fomtec (Enviro ARC 3x6)	21.2	150	24.0	1.00	2.74	6.5
National Foam (Universal Green 3-3%)	14.6	????	23.1	3.61	5.11	4.4
Solberg (Re-Healing Foam RF3)	30.1	4900	26.1	0.56	2.40	7.7
NRL (Siloxane #3)	13.6	5.3	22.4	2.20	2.29	8.2

5.8.2. Surfactant Extraction by Aromatic Fuels

A comparison of the extinction profiles shows that the Siloxane #3 formulation exhibits greatest divergence in gasoline vs heptane pool fires. For the heptane pool fire, its extinction profile approaches that of an AFFF formulation, while for the gasoline pool fire its profile is far less effective than the other F3 formulations. The underlying cause for this divergence has been correlated with the content of gasoline having non-aliphatic components. To uncover a reason why F3 formulations exhibit this divergence in varying degrees, the Siloxane #3 formulation is examined for a deeper analysis of this phenomenon. In this section the isolated effects these gasoline and surfactant formulation components will be examined to learn how these components interact causing a degradation of extinction performance.

The composition of gasoline is variable depending on the season of the year and its source. Its content consists of over a hundred components, and analyses of gasoline composition is usually divided into various classes of compounds. The results of a recent analysis of four commercial gasolines is depicted in Table 55 [70]. These individual compounds along with their content in each gasoline were selected as the predominant members of a particular class and are inserted into the columns of Table 55 in indented format. With respect to quantity, the main compound classes and content ranges are: paraffins (10-22%); isoparaffins (20-40%); cycloparaffins (3-4%); aromatics (20-40%); and alkenes (5-7%). It was hypothesized that the observed gasoline-heptane difference in pool fire suppression would correlate with the presence of the non-alkane compound groups in gasoline, particularly the aromatics. A pool fire suppression experiment was designed where representative compounds from the main classes cited above were selected for 19 cm pool fire extinction evaluation. With the exceptions of *n*-butane and *iso*-pentane the individual compounds

in Table 55 were tested as individual fuels and as mixtures ranging from 0 to 40 vol% in heptane for fire suppression with the 19 cm pool fire apparatus using the Siloxane #3 formulation.

Table 55. Compositions of four gasoline fuels based on chemical groups.

Component Class	Fuel A (%)	Fuel B (%)	Fuel C (%)	Fuel D (%)
Parafins	11.084	14.638	15.568	12.765
<i>n</i> -butane	1.175	1.220	0.887	0.996
<i>n</i> -pentane	0.958	5.173	6.223	6.346
<i>n</i> -hexane	6.557	6.271	6.375	4.646
<i>n</i> -heptane	0.265	0.296	0.220	0.227
<i>n</i> -octane	0.351	0.393	0.249	0.228
<i>n</i> -nonane	0.833	0.668	0.747	0.183
<i>n</i> -decane	0.648	0.319	0.343	0.088
Isoparafins	44.317	28.497	18.535	23.343
<i>i</i> -pentane	5.758	1.892	3.150	2.885
<i>i</i> -octane	13.499	7.108	2.174	9.038
Cycloparafins	4.329	4.527	5.285	3.311
methylcyclopentane	3.226	3.087	3.125	2.291
methylcyclohexane	0.103	0.114	0.085	0.089
Mono-aromatics	18.436	31.428	41.375	41.376
benzene	0.879	0.768	0.804	0.828
toluene	4.362	7.240	10.539	9.366
xylenes	3.762	5.990	7.651	9.516
1,2,4-trimethylbenzene	1.786	4.199	6.355	6.097
Naphthalenes	0.225	0.295	0.225	0.230
Naphthaleon/olefin-benzene	0.319	0.503	0.396	0.402
Indenes	0.538	0.785	0.806	0.697
Mono-naphthalenes	5.231	5.087	5.325	3.310
<i>n</i> -Olefins	6.354	6.214	5.273	6.583
1-hexene	5.548	5.348	4.611	5.930
Isoolefins	0.793	0.761	0.747	0.521
Naphthaleno-olefins	0.099	0.134	0.131	0.089
Oxygenates	11.032	10.504	10.276	10.422

The fire extinction – flow rate profile results are plotted in Figure 76a and b. The results for the aromatic set of compounds (benzene, toluene, xylenes, trimethylbenzene) are remarkable in that 3 of the 4 compounds were not extinguishable as 100% fuels by the Siloxane #3 foam. It had further been hypothesized that that the vapor pressure of these aromatic compounds would correlate with the time and with foam flow rate needed for extinction (i.e. benzene with its higher vapor pressure would have a larger degrading effect on the foam and a greater permeation through the foam to feed the fire). Just the opposite trend was observed: the difficulty to extinguish is in the order trimethylbenzene > xylenes > toluene > benzene.

This unexpected result is further probed by experiments described below. A less pronounced but similarly unexpected trend for difficulty in extinction was observed

for the *n*-alkane series: *n*-decane, *n*-nonane > *n*-octane > *n*-heptane > *n*-pentane. It is further noteworthy that within the pair of octanes (*iso*-octane and *n*-octane), *n*-octane was the more difficult fuel fire to extinguish. Finally, the cycloalkanes (methyl cyclopentane and methyl cyclohexane) and alkene (1-hexene) pool fires proved to be not significantly more difficult to extinguish than that of heptane. The remarkable features in this series of gasoline-component experiments are the large effects and systematic trend of the aromatic compounds and the effects of *n*-alkane chain length as fuel composition approaches 100%.

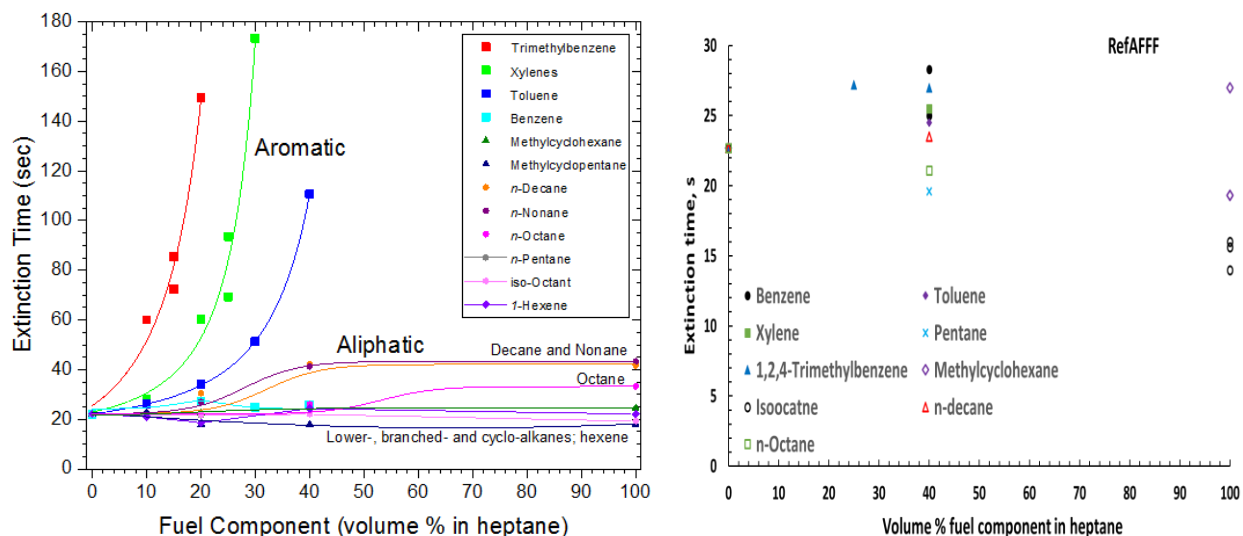


Figure 76. Effect of varying amounts of aromatic and aliphatic gasoline components added to heptane in 19 cm diameter pool fire extinction time testing of (a) Siloxane #3 (502W:Glucopon225DK 2:3) formulation and (b) for RefAFFF at a constant foam flow rate of 1000 ml/min, applied at the center of the pool.

As to causes of this aromatic component induced behavior and to the order of its effectiveness being opposite to vapor pressure, a hypothesis was directed at the interface between the aqueous surfactant solution and the hydrocarbon fuel with speculation that the fuel component might be crossing the interface to reside in aqueous micelles and thereby reduce the foam stability, or that perhaps one of the surfactants is transporting across the interface to dissolve in the fuel leaving the other surfactant unable to stabilize the foam at this interface. A relatively simple experiment was designed to diagnose such behavior and is illustrated in the Figure 77. It involves ^1H NMR spectra to detect transport across the interface between an aqueous solution of the Siloxane #3 surfactants and a hydrocarbon fuel component before and after a short time of contact. A stock solution of 0.5 wt% surfactant(s) in D_2O with a comparable small quantity of DMSO reference was prepared. A 2.0 ml quantity of the stock solution was placed in the vial; a 670-700 mg sample is withdrawn for a control spectrum; a gasoline component is gently added for a 1-2 mm upper phase thickness with minimum perturbation of the interface; the aqueous phase is slowly stirred (no vortex formation) for 5.0 min; and a second 670-700 mg sample of the aqueous phase is collected via syringe from the bottom of the vial for NMR analysis. The experiments include stock solutions of 502W, Glucopon 225DK and a 1:1 502W:Glucopon 225DK surfactant mixture and gasoline components of 1,2,4-trimethylbenzene (TMB), xylenes (Xyls), toluene (Tol), benzene (Bz), *n*-decane ($\text{C}_{10}\text{H}_{22}$), *n*-heptane (C_7H_{16}) and *n*-pentane (C_5H_{12}). Some spectral

features are unique to a surfactant (e.g. Si-CH₃) or to a gasoline component (e.g. Ar-H) and other features have two or more contributors (e.g. -O-CH₂- from both surfactants). In the spectrum these features or resonances are integrated and normalized to the DMSO resonance. In the Table 56 below is a correlation of spectral features with the chemical shift range, general structural assignment and the corresponding components. Spectra of the individual surfactants and gasoline components and the resonance assignments used are presented in reference [70] along with a table of integrated values.

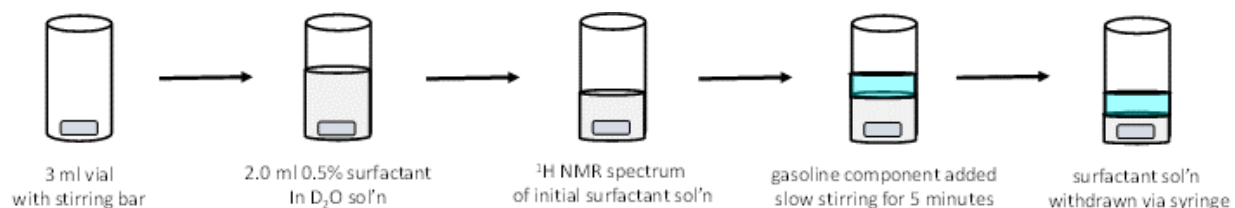


Figure 77. Depiction of simple NMR experiment to probe transport across the aqueous surfactant solution – hydrocarbon interface.

Table 56. NMR Resonance chemical shift – structure correlation.

Chem Shift	Assignment	Corresponding Component
0.0 – 0.2 ppm	Si-CH ₃	502W
3.2 – 4.0 ppm	-O-CH ₂ -	502W, Glucopon
1.5 – 1.7 ppm	-O-CH ₂ -CH ₂ -	502W, Glucopon
1.2 – 1.4 ppm	C-CH ₂ -CH ₂ -C	Glucopon, Aliphatic Gas Component
0.8 – 1.0 ppm	Aliph-CH ₃	Glucopon, Aliphatic Gas Component
0.4 – 0.5 ppm	Si-CH ₂ -	502W
1.8 – 2.1 ppm	Ar-CH ₃	Aromatic Gas Component
6.5 – 6.8 ppm	Ar-H	Aromatic Gas Component

In Table 56, there is a color and pattern code which is used in a bar graph depiction (Figure 78) of surfactants and gasoline components transporting across the aqueous-organic interface. The solid colors without pattern denote surfactant only resonances; the parallel line pattern denotes overlapping resonances from a surfactant and a gasoline component; and the cross-hatched pattern denotes gasoline component resonances only. All of the transport experiments are summarized in the form of bar graphs in Figure 78. There are six bar graphs arranged in two columns and three rows. For comparative purposes the column on the left represents the aromatic gasoline component experiments, and that on the right represents the aliphatic gasoline component experiments. The three rows correspond to different surfactant solutions; the top row is 502W only, the middle row is Glucopon 225DK only and the bottom row is the 1:1 502W:Glucopon 225DK surfactant combination. Within an individual series of bar graphs, the control experiment is on the left representing the surfactant solution prior to interface contact with the gasoline component, and the subsequent groupings to the right progress from least volatile to most volatile gasoline component. The intent in this design is to identify systematic trends for surfactant and gasoline component interface crossing.

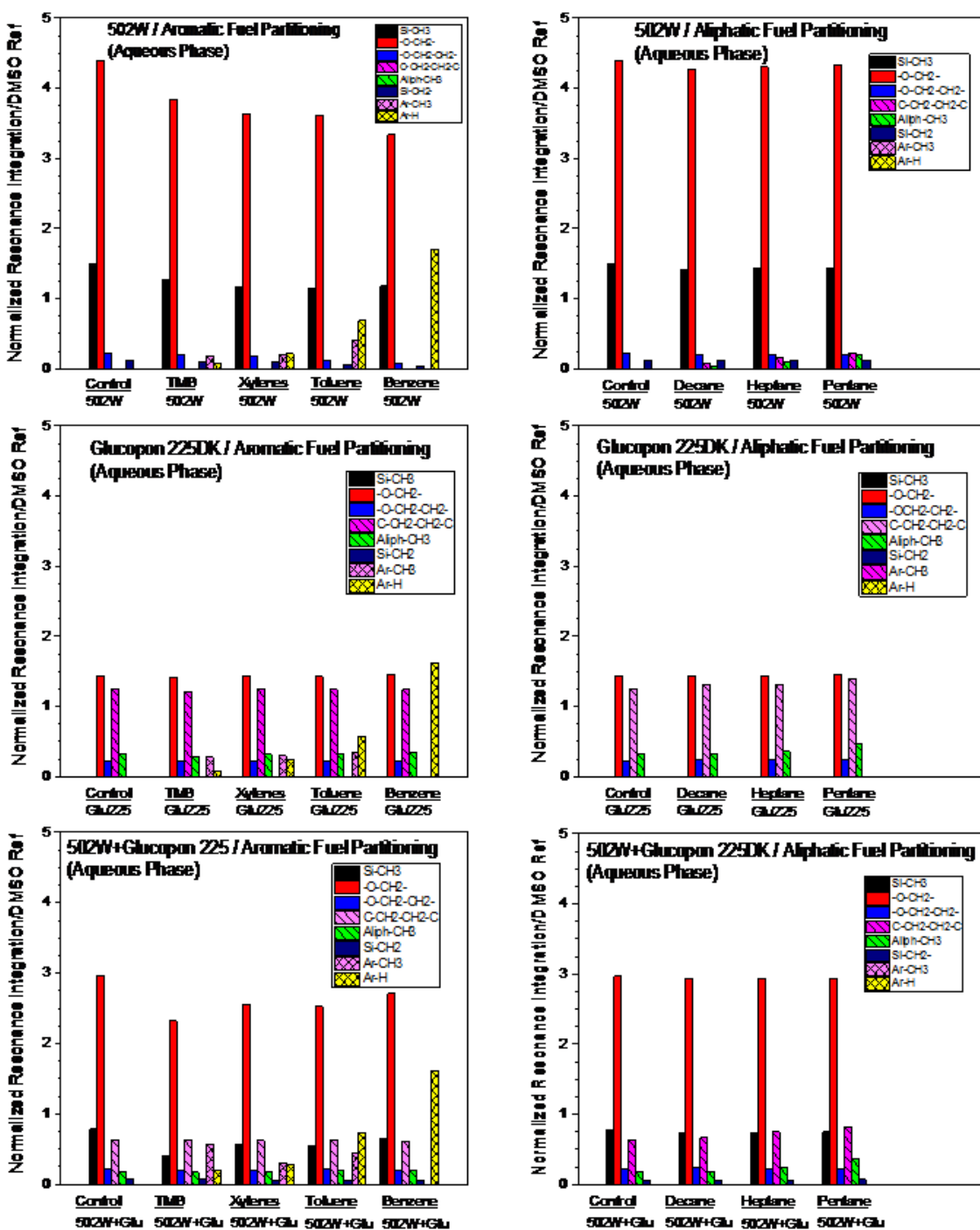


Figure 78. Synopsis of ^1H NMR results of surfactant and gasoline component diffusion across the aqueous-organic interface.

One way to interpret the data in Figure 78 is to start with the relatively simple aromatic and aliphatic gasoline components. In the left column of bar graphs there is a progression of yellow (Ar-H) and pink (Ar-CH₃) that increase in height as one proceeds from TMB to Bz indicating an

increasing quantity of aromatic component crossing the interface into the aqueous phase. There is a parallel with these components' solubility in water: Bz (0.178%) > Tol (0.0515%) > Xyls (0.0187%) > TMB (0.0057%). By comparison in the right column of bar graphs, the aliphatic components (purple parallel line pattern (C-CH₂CH₂-C) and green parallel line pattern (Aliph-CH₃)) display a low transport into the aqueous phase. This is particularly visible in the top right bar graph where there is no Glucopon to contribute to these aliphatic component column heights. The relative amounts of aliphatic component in the aqueous phase also parallels these components' solubility in water: C₅H₁₂ (0.0038%) > C₇H₁₆ (0.00029%) > C₁₀H₂₂ (0.0000052%). While the amount of aromatic components transferring to the aqueous phase is substantially greater than that for the aliphatic components and the aromatic component also has a pronounced increasing effect on extinction time compared to the aliphatic component, the order of this increased extinction time (TMB > Xyls > Tol > Bz) is opposite to that for aqueous transfer (Bz > Tol > Xyls > TMB). This appears to indicate that diffusion of aromatic components into the aqueous phase does not have a retarding effect on the 502W-Glucopon 225DK formulation's pool fire extinguishing activity.

The data in Figure 78 provide an interesting insight into diffusion of the surfactant from the aqueous into the organic phase. Comparing the 502W data (particularly black and red bars relative to the controls) in the first row, the amount of diffusion into an aromatic phase is much higher than into an aliphatic phase. Within the aromatic components, 502W displays more interface diffusion for Bz than for TMB. In the second row the interface diffusion behavior for Glucopon 225DK is noteworthy for its lack of diffusion as indicated by the constant height of its red bar. However for the 1:1 502W:Glucopon 225DK in the third row, the aromatic phase diffusion activity of the 502 surfactant is altered with the amount now for TMB greater than that for Bz as is evident from comparison of the 502W exclusive black bar data. Surfactant diffusion toward the aliphatic phase is nominal as is the case for the individual surfactants in the upper rows.

The result of significance from these interface transfer experiments is that diffusion of the 502W surfactant from the aqueous to the aromatic organic phase is substantial. When 502W is combined with Glucopon 225DK in a 1:1 formulation, its diffusion out of the aqueous phase is the greatest for TMB in the aromatic component series. This result correlates with the pool fire extinction results in Figure 73. A speculated scenario is that 502W when combined with Glucopon 225DK at the aqueous-organic interface is more prone to cross this interface into the receptive aromatic environment. Its departure from the 502W-Glucopon aqueous foam structure at the foam-fuel interface destabilizes the foam and thus diminishes the ability of this formulation to extinguish pool fires. This speculation can lead to hypothesizing about doing something to 502W that would make it less prone to cross an aqueous interface into an aromatic-hydrocarbon medium. This speculation may also be applied to the hydrocarbon surfactants in the other F3 formulations although their proprietary identities impede experimental verifications.

5.8.3. A Two-Component Aromatic Simulant for Gasoline

From the foregoing results, it is clear that the aromatic components in gasoline are responsible for a pool fire suppression behavior that diverges from that of heptane when foams generated from F3 formulations are used. Of the aromatic components investigated, 1,2,4-trimethyl-benzene is the most effective. In this section data are presented to support the possibility of designating a two-component simulant for commercial alcohol-free unleaded gasoline. As indicated in the previous section, gasoline is a very complex mixture of over 100 hydrocarbon components with seasonal and source variations. If it is possible to formulate a two

component mixture from heptane and an aromatic counterpart that will effectively simulate a general F3 formulation's extinction performance with the gasoline pool fire, it could be a very useful and simple reference fuel for a testing protocol. A substantial body of data is needed to validate the concept of a gasoline simulate. Presented below are foam degradation and extinction data for the fluorine-free Siloxane #3 formulation and for the RefAFFF formulation to represent this concept's initial viability.

Foam degradation data were obtained by monitoring the time-dependent reduction of a 4 cm layer of foam deposited onto a 60 mL volume of 60°C preheated fuel in a 150 mL beaker. For the Siloxane #3 foam, its degradation over heptane, gasoline and the comparative effects of adding 15 and 25% TMB to heptane are depicted in Figure 79. The 15% TMB data represent intermediate behavior in the foam height vs time plot for the 4 cm layer of foam to disappear. Increasing the TMB content to 25% results in a foam degradation time coincident with that for gasoline. The degradation effect of this 25% TMB/heptane fuel on RefAFFF foam is presented in Figure 80. The rapid decrease in foam height occurs at an intermediate time (130-140 sec) compared with that for the heptane (160-180 sec) and the gasoline (100-120 sec). In this case the foam degradation is accelerated by the 25% TMB but does not match that produced by the gasoline.

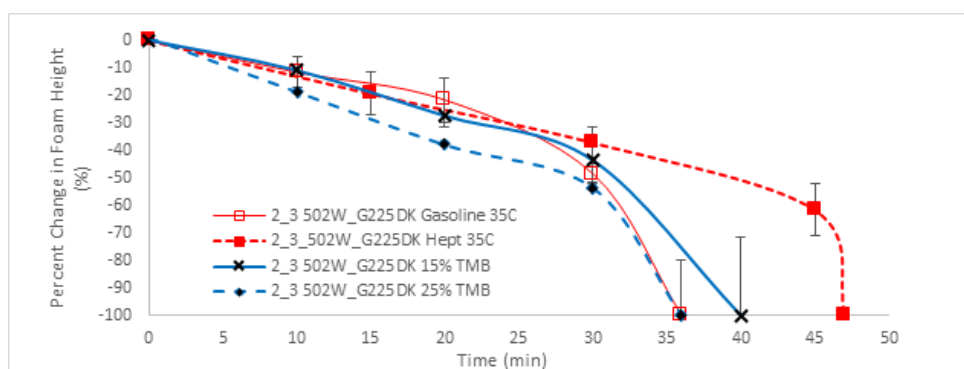


Figure 79. Degradation of a 4 cm thick Siloxane #3 foam layer over gasoline, heptane and combinations of 15 and 25% TMB/heptane at 35°C.

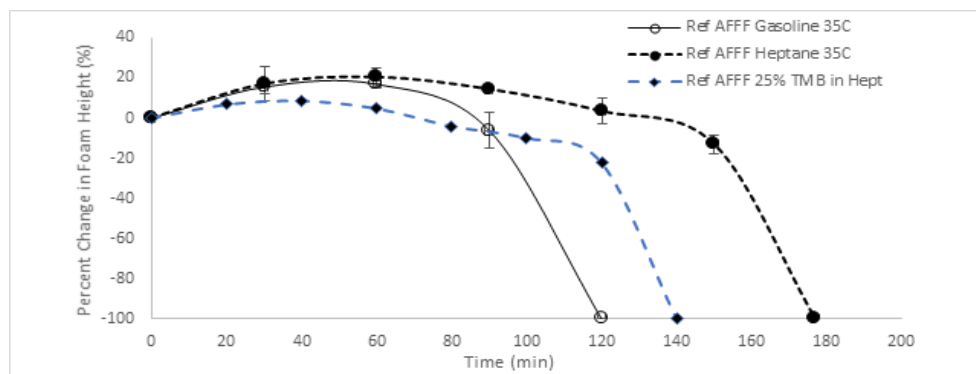


Figure 80. Degradation of a 4 cm thick RefAFFF foam layer over gasoline, heptane and a 25% TMB/heptane fuels at 35°C.

The 25% TMB/heptane fuel composition's effect on the Siloxane #3 formulation's pool fire extinction time for gasoline and heptane fuels is presented in Figure 81. As previously

indicated, this F3 silicone formulation's ability to extinguish gasoline fires is much diminished compared with heptane fires. The 25% TMB/heptane fuel fire extinction by the Siloxane #3 formulation is in reasonably close proximity (about 90 sec) to that for gasoline (average 110 sec) and significantly removed from that for heptane (17 sec). As a two-component simulant for gasoline, these data indicate the 25% TMB/heptane is a good candidate for further benchtop and large scale testing.

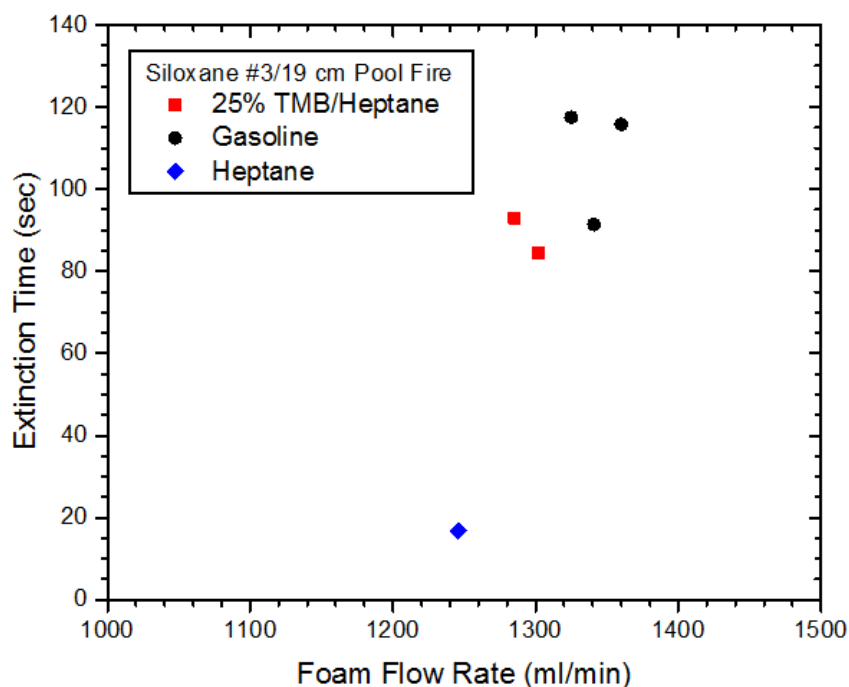


Figure 81. Comparison of extinction times for 25% trimethylbenzene/heptane fuel vs gasoline and heptane fuels using the Siloxane #3 formulation for foams applied at the center of the benchtop 19 cm diameter pool.

Figure 82a to d show a comparison for Jet fuel for RefAFFF and Siloxane 3 (502W:Glucopon225DK 2:3) formulations with foams deposited at the edge of the pool. Jet fuels have high boiling point and are easier to extinguish. For high boiling point fuels, surface cooling by foams play a significant role. Within seconds after foam is applied, the pool surface temperature decreases to an arithmetic average between the fuel boiling point and the room temperature of the foam [33]. The rapid drop in pool surface temperature reduced the fuel vapor pressure dramatically because the vapor pressure is related to surface temperature exponentially by Clausius-Clapeyron equation [33]. This makes it easier to extinguish. The rapid drop in temperature is followed by a slow decrease as the heat is extracted from the pool surface by the foam layer [33].

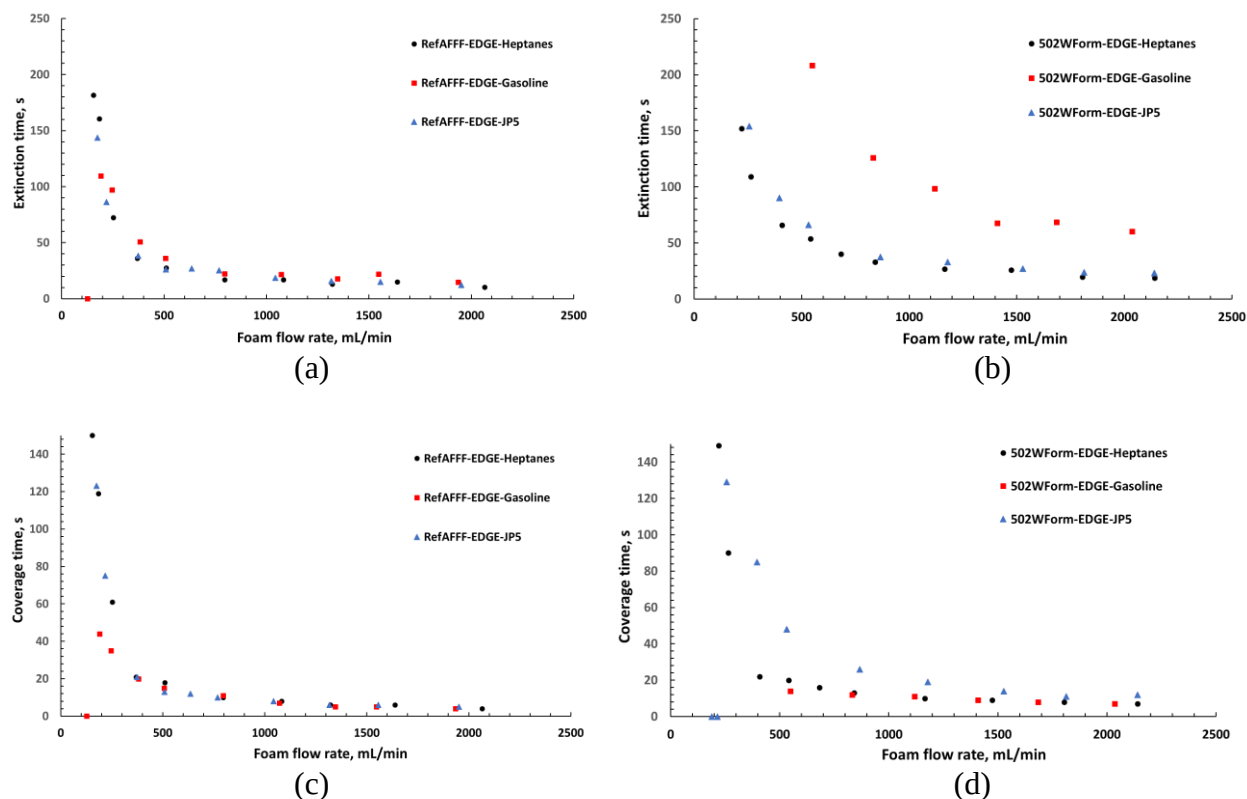


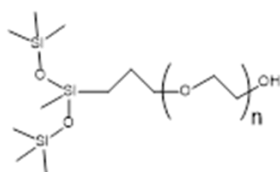
Figure 82. Comparative extinction time profiles for gasoline, heptane, and Jet fuel for (a) RefAFFF and (b) 502WForm (502W:Glucopon225DK 2:3 ratio) for 19 cm diameter pool fires. Similar comparison for coverage time for (c) RefAFFF and (d) 502WForm. Foams applied at the edge of the pool.

5.9. Effects of Varying Head Size of Siloxane Surfactant

We focused on increasing the synergistic foam stability and heptane-fire extinction that we discovered between commercial siloxane-polyether copolymer and alkyl polyglycoside surfactants (Figure 17) in the NRL's siloxane formulation; synergistic surfactants in combination exhibit performance above that of the individual surfactants. Even though the exact mechanisms of synergism are not well understood, the interactions between the oxyethylene and glycoside head groups shown in Figure 17 are crucial for the synergism in decreasing the foam degradation by heptane. The commercial siloxane surfactant in Dowsil 502W (Dow Silicones Inc.) has general structure of siloxane-polyoxyethylene at 100% concentration [38]. The siloxane surfactant has a hydroxyl functional group ($R=OH$) and a distribution of polyoxyethylene (OCH_2CH_2) chain lengths represented by the parameters m and y as shown in Figure 17. The distributions and the average values of m , y , and z are proprietary according to Dow Corning Co.'s literature [38]. We varied the glycoside head size to a limited extent possible by using commercial materials and increased synergism and fire suppression effectiveness up to 60% of AFFF at bench scale as shown in Figures 51.

In this section, we discuss the results from varying the oxyethylene head size using siloxane surfactant synthesis. To improve fire suppression performance, we synthesized siloxanes with a distribution of m and $y=1$, $z=1$ as shown in Figure 83. We prepared 12 synthesized siloxanes with an average value of m varying from 0 to 50 characterized by the precursor sources, NMR, and Gel

Permeation Chromatography (GPC). These are substituted for Dowsil 502W in the formulation listed in the first column of Table 19 (NRL's siloxane formulation) and evaluated. The results show that the extinction performance exhibited a maximum with increasing oxyethylene head size and is consistent with the molecular dynamics models, which predicted a maximum in interface stability. However, the maximum extinction effectiveness obtained by varying the siloxane head size still remained at 60% of AFFF like the NRL's siloxane502W formulation as described in detail below.



Average $n = 0$ to 50

Figure 83. Synthesized branched heptamethyl-trisiloxane poly(oxyethylene) (BHMTS-OEn) where n is the number of oxyethylene units.

5.9.1. Homologous Siloxane Surfactants Synthesis and Characterizations

We synthesized half a gram to multi-gram, synthesis of a homologous series of trisiloxane-poly(oxyethylene) surfactants with known and analytically defined chain lengths. A single step hydrosilylation reaction between bis(trimethylsiloxy)methylsilane and the allyloxy-poly(oxyethylene) reagent catalyzed by chloroplatinic acid in isopropanol as depicted in Figure 84. The catalyst reactivity is sensitive to the oxyethylene chain length. Initial reactions were conducted on a 0.5g scale to establish conditions (catalyst quantity, ratio of reagents and reaction temperature and time prior to scaling up to a 15-20g quantity needed for further characterization and benchtop fire extinction testing. Reaction conversion was monitored by ^1H NMR.

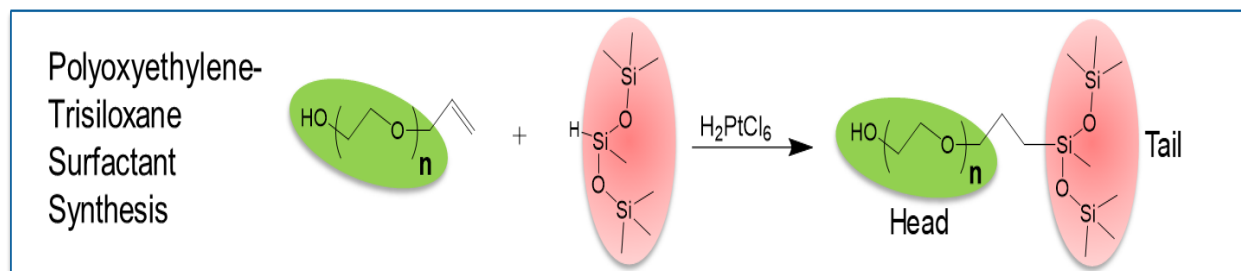


Figure 84. Single-step synthesis of trisiloxane poly(oxyethylene) (BHMTS-OEn) surfactants with homologous head lengths, average n .

The synthesized surfactant products were evaluated for their foamability and fire extinction. The results are summarized in Table 57. The NMR, surface tension, and the critical micelle concentration (CMC) are reported for the siloxane surfactant solution in water, not formulation containing glycoside surfactant. The fire extinction times (at 1000 mL/min foam application rate) and foam expansion ratios listed are for the siloxane formulation containing the glycoside surfactant and DGBE solvent in distilled water.

There are two general issues that complicate the synthesis: (1) reactivity/specificity of the catalyst and (2) purification of the surfactant product. Several platinum hydrosilylation catalysts

are known and their degree of reactivity and product specificity is much dependent on identities of the reagents. The catalyst is used in 1-100 ppm amounts, and the reaction is frequently characterized by an induction period followed by a rapid exotherm. Side reactions can also occur. These involve the coupling of the Si-H group to the –OH to generate a Si-O-C linkage which is hydrolytically unstable, the isomerization of the C=C bond from the terminal to an internal position in the allyl group and condensation of the trisiloxane structure to a higher polysiloxane. Use of an excess allyloxy reagent helps to lower the amount of side reaction products. Volatile surfactant products ($n \leq 3$) may be purified by distillation but the excess allyloxy reagent complicates the distillation. If the excess allyloxy poly(ethylene) reagent does not affect the application, commercial surfactant concentrates frequently contain such components. In other cases solvent extraction procedures are developed for purification. Also, for $n > 3$ the oxyethylene chain length is usually polydisperse. Having purified monodisperse series of trisiloxane-poly(oxyethylene) surfactants is a very useful analytical tool to interpret important differences in fire suppression properties between seemingly similar commercial surfactants.

Synthesis of the trisiloxane-poly(oxyethylene) or BHMTS-OEn was performed by adding a 20% excess allyloxy reagent to a solution of 100 ppm H₂PtCl₆ in heptamethyl-trisiloxane and gradually stepping the temperature from 30 to 125°C over an 8 hour period while monitoring by NMR. The 1,1,1,3,5,5,5-heptamethyl-trisiloxane tail group has a characteristic signature in the ¹H, ¹³C and ²⁹Si NMR spectra that is useful for identifying the category of siloxane surfactant. Further, the oxyethylene tail has a relatively simple ¹H NMR spectral feature where in most of these proton resonances are closely grouped or overlap as the oxyethylene chain becomes longer. The NMR spectra for some of the synthesized and commercial surfactants used for fire extinction are presented in Figure 85 and 86.

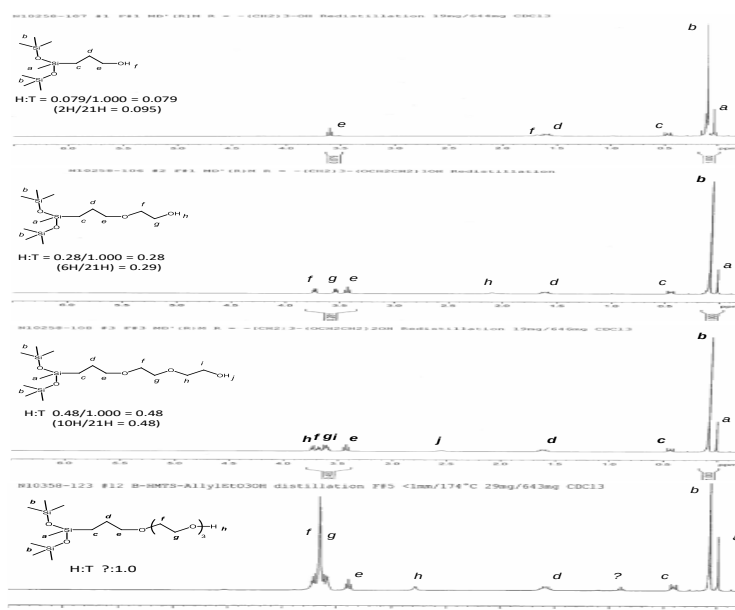


Figure 85. ¹H NMR spectra of (Si(CH₃)₃)₂Si(CH₃)(CH₂)₃(OCH₂CH₂)_nOH or BHMTS-OEn illustrating assignments and integration for head:tail (H:T) ratio.

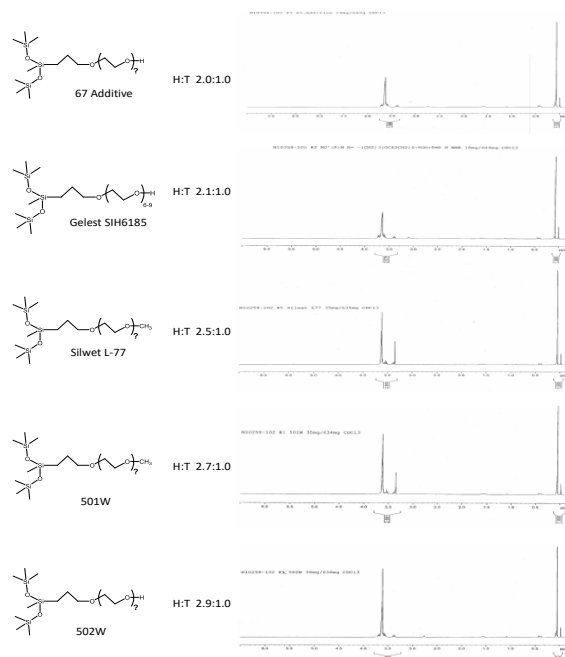


Figure 86. ^1H NMR spectra of commercial trisiloxane-poly(oxyethylene) surfactants depicting the H:T integration ratio comparable to the synthesized surfactants.

The ^1H NMR spectra of Figure 85 are comparable to spectra of the commercial trisiloxane-poly(oxyethylene) surfactants (67A, Gelest SIH6185, Silwet L-77, 501W and 502W) which were evaluated for fire suppression properties. These spectra are depicted in Figure 86 along with their corresponding H:T integration ratio. Figure 87 shows integrated NMR analyses of the ratio of head to tail protons as a function of chain length for the synthesized trisiloxane surfactants. The dashed red line corresponds to theoretical calibration derived from chemical structure with head and tail proton counts. The 502W near the ordinate are the experimental results assuming 100% surfactant purity.

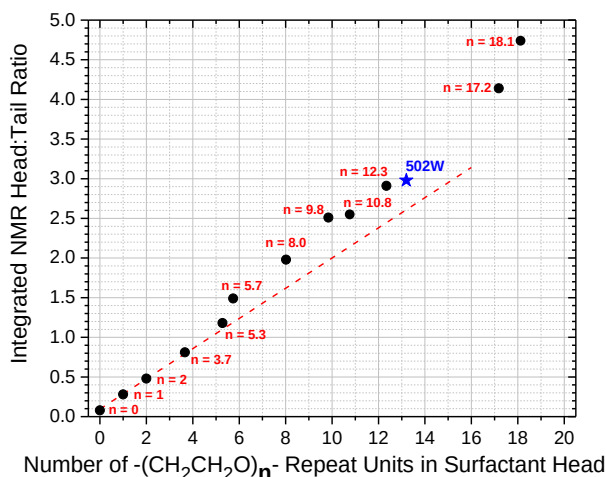


Figure 87. Calibration plot of ^1H NMR measurement of integrated H:T proton ratio as a function of oxyethylene chain length (n) in synthesized and commercial trisiloxane surfactants (BHMTS-OEn).

5.9.2. Synthesized Siloxanes – Interface and Solution Properties

Figure 88 shows the surface tension measurements for the synthesized trisiloxane BHMTS-OEn surfactants for different values of n . The surface tension of aqueous surfactant solutions were measured using DuNoy ring apparatus at different dilutions of a stock solution containing 2 volume % surfactant. Above the critical micelle concentration, the surface tension becomes independent of the surfactant concentration. CMC is determined by a standard method of fitting two lines to the data as shown in Figure 88(a). Figures 88(b) shows that the equilibrium surface tension reaches a minimum between $n=6$ to 10 as the oxyethylene length n increases. It shows $n=12-20$ has slightly higher equilibrium surface tension than BHMTS-OEn with $n=9-12$ (24 mN/m versus 20 mN/m). For comparison 502W solution has a surface tension of 20.5 mN/m. The CMC also decreases and then increases with n before reaching a constant value as shown in Figure 88 (c). Figures 89 (a) and (b) show that the solubility in water and cloud point increase rapidly above $n=10$. Figures 89(c) and (d) show that the excess surfactant concentration and area per molecule change rapidly up to $n=10$ and then change only slightly at larger values of n . These data suggest oxyethylene units of 10 appear to be a transition point in head length for many physical and interfacial properties.

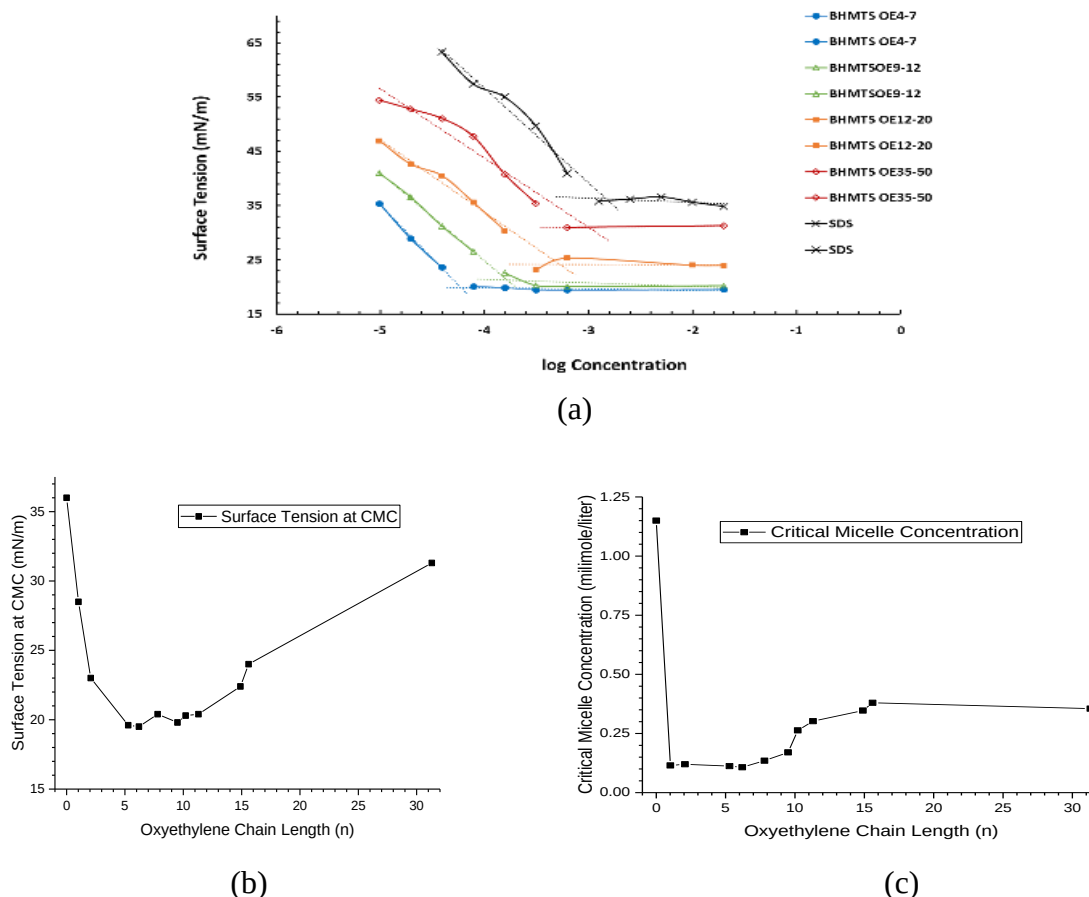


Figure 88. (a) Surface tension versus surfactant concentration, (b) surface tension at CMC, (c) CMC versus oxyethylene length n of the synthesized trisiloxane poly(oxyethylene) (BHMTS-OEn) as the only component in water.

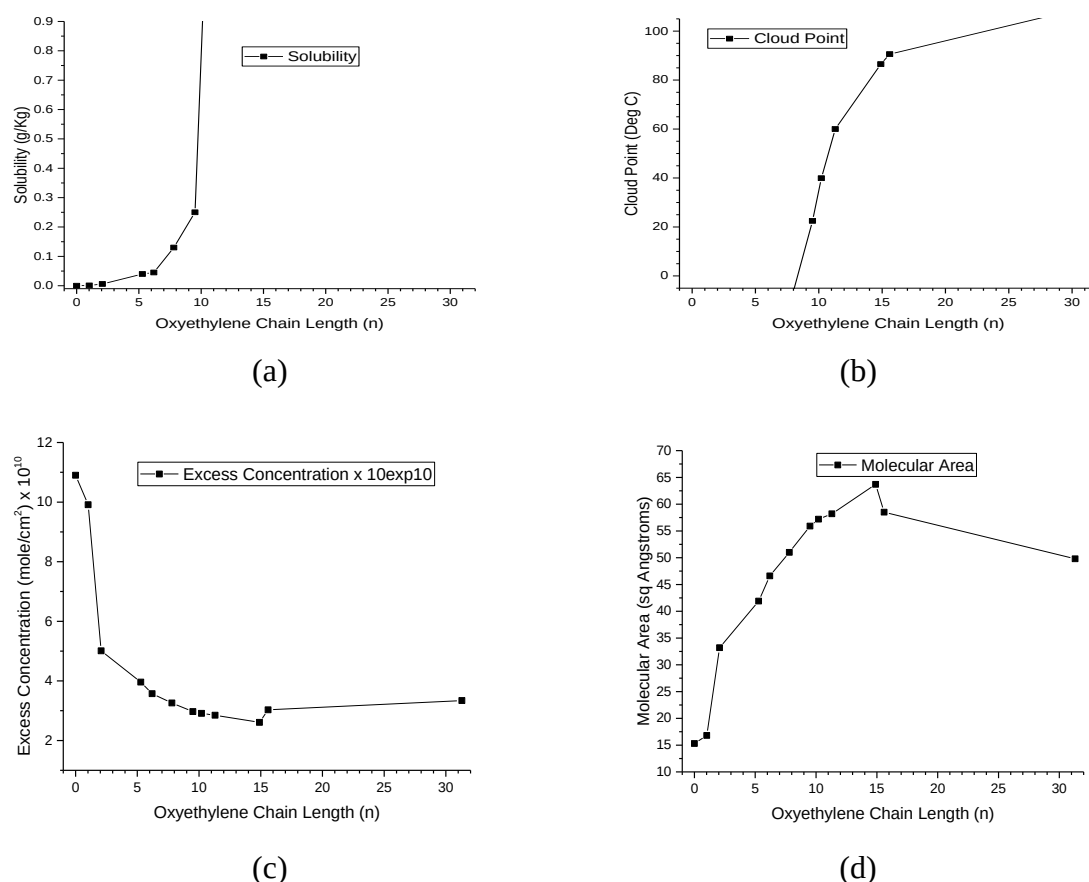
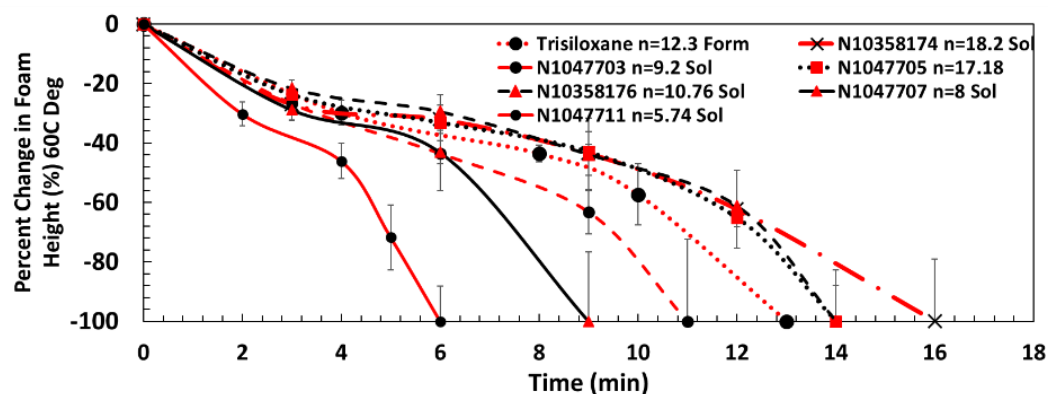


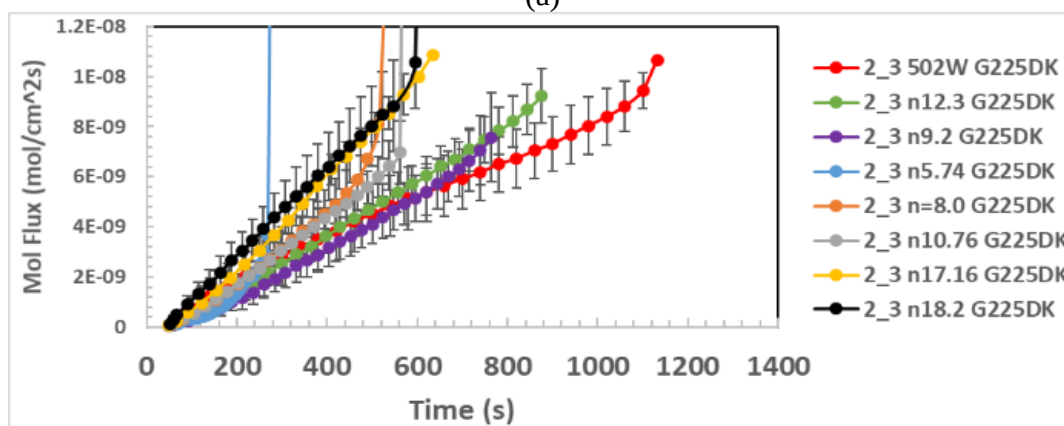
Figure 89. (a) Solubility in water, (b) cloud point, (c) excess concentration, and (d) area per molecule at air/water interface versus oxyethylene length n of the synthesized trisiloxane poly(oxyethylene) (BHMTS-OEn) as the only component in water.

5.9.3. Synthesized Siloxanes – Foam/Fuel Interaction Dynamics

Figure 90 shows the foam-fuel interaction effects. Figure 90(a) shows a decrease in foam layer thickness (initially 4-cm thick) on a hot (60 °C) heptane pool with time, measured in an open beaker, for the synthesized siloxane surfactants with varying oxyethylene length, n. As the fuel vapors diffuse through the foam the lamellae between the bubbles rupture and the bubbles coalesce to form larger bubbles near the pool surface. As the time progresses, the large bubbles move up the foam driven by buoyancy force and rupture to release the fuel vapor from the top of the foam layer. That decreases the foam layer thickness. The coalescence most rapid within the first layer of bubbles at the pool surface and decreases progressively in the bubble layers above the first layer. The foam lifetime (100% degradation) is significantly affected by n. The lifetimes increase with increasing n. Assuming fuel diffusion through foams, the time is expected to be proportional to the square of the foam thickness. So, 1400 s lifetime for a 4-cm thick foam will be reduced to 22 s for a 0.5 cm thick foam layer, which is more typical in a fire extinction scenario; although extinction occurs under very dynamic conditions unlike the degradation measurements.



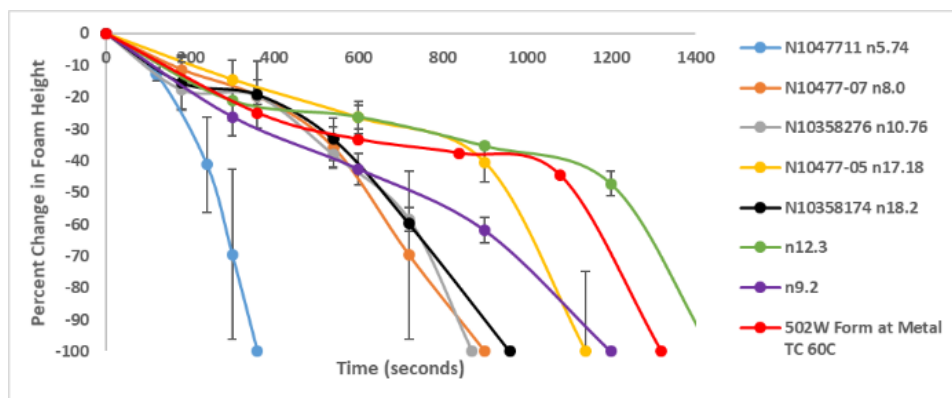
(a)



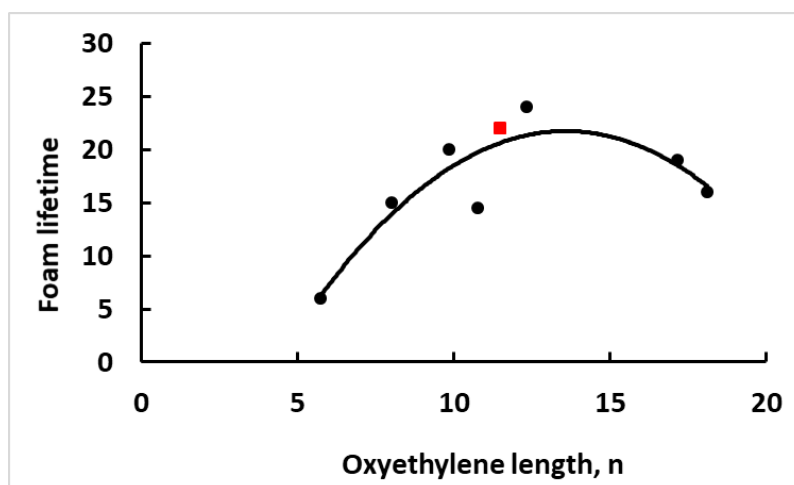
(b)

Figure 90. (a) Foam degradation in an open beaker, (b) Fuel vapor transport through an initially 4-cm thick foam layer covering a hot heptane pool (60 °C) for formulations containing 0.2% synthesized trisiloxane poly(oxyethylene) (BHMTS-OEn), 0.3 % Glucopon 225DK, and 0.5 % DGBE by weight.

Figure 90(b) shows the rate of fuel vapors permeating through a foam layer (initially 4-cm thick) on top of a hot (60 °C) heptane pool in a closed chamber. It is measured by sweeping the vapors emerging from the foam surface with nitrogen flow into FTIR, which measures the fuel concentration with time. The foams degrade in the closed chamber also during the fuel transport measurements, but more slowly than in the open beaker measurements shown in Figure 90(a). The fuel mass must balance between rate fuel emerging from the foam surface and the rate of fuel passing through FTIR cell; fuel flux is calculated by multiplying the molar concentration with gas flow rate and dividing with pool surface area. Figure 90(b) shows that the fuel flux is affected significantly by the oxyethylene length, n . The measured concentration of 6150 ppm or 1.4×10^{-7} mole/cm²s by FTIR corresponds to 29 mole% vapor concentration (0.29 atm vapor pressure) above a bare heptane pool at 60 °C. The lower flammability limit of 1.1 mole% corresponds to 5.3×10^{-9} mole/cm²s that can support spontaneous combustion in air at ambient conditions. Figure 91(a) shows the foam degradation measured inside the fuel flux chamber and are different from those shown in Figure 90 (a) which are open beaker measurements. Figure 91(b) shows a maximum in foam lifetime versus n unlike that exhibited in Figure 90(a), which shows monotonically increasing lifetimes with the increasing n .



(a)



(b)

Figure 91. (a) Foam degradation measured inside the closed fuel flux chamber versus time, (b) Foam life time versus oxyethylene length, n.

5.9.4. Synthesized Siloxanes - Fire Extinction Evaluation

Figure 92 shows fire suppression by foams generated from the formulations containing the synthesized siloxanes that replaced the 502W in column 1 of Table 19. Figure 92(a) shows the time taken for the foam to fully cover the 19-cm diameter burning heptane pool and Figure 92(b) shows the fire extinction time versus foam application rate in the same experiment where the foams are applied at a fixed position at the center of the pool at a constant rate. Figure 92(a) clearly shows that the foams spread faster as the oxyethylene length n is increased. At n greater than 12, the foams spread faster than 502W and RefAFFF. Figure 92 (b) shows that the extinction time is affected significantly by n and the effect depends on the foam application rate. At high foam application rates and n greater than 12, the extinction times are higher than 502W. We noticed, that the foams cover the pool quickly and the vapors rapidly escape from the pool edges and burn vigorously. The edge flames subside slowly and prolong the fire extinction. At low foam application rates and n greater than 12, the extinction times are lower than that for 502W formulation despite fast degradation and fuel transport shown in Figure 90(a) and (b) respectively.

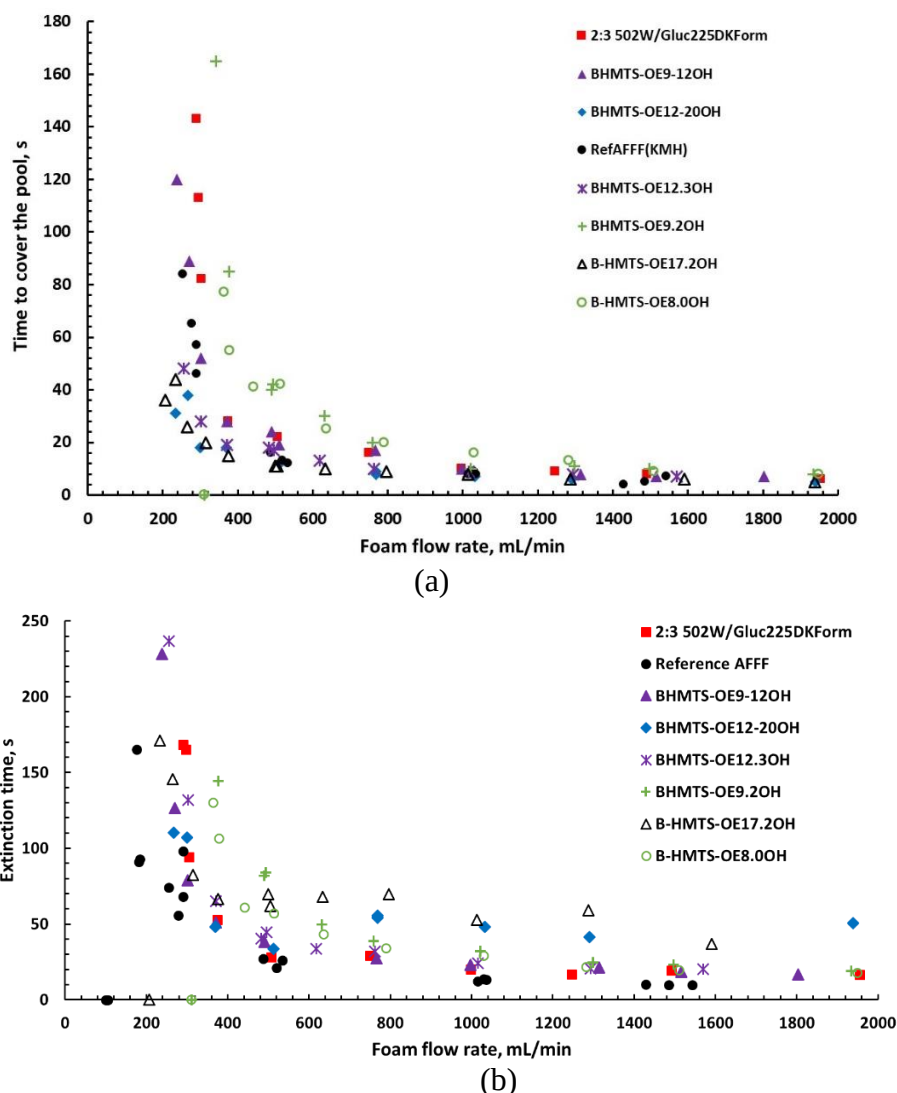


Figure 92. (a) time for foam to cover the burning pool surface, (b) fire extinction time for a 19-cm diameter heptane pool versus foam application rate for foams generated from formulations containing 0.2% synthesized trisiloxane surfactant (BHMTS-OEn), 0.3 % Glucopon225DK, and 0.5 % DGBE by weight. Foams applied at the center of the pool.

5.9.5. Effects of Oxyethylene Length

Figure 93 shows foam expansion ratio, foam lifetime, fuel transport time at 5.3×10^{-9} mole/cm²s, and fire extinction time at 1000 mL/min foam application rate as functions of the oxyethylene length, n . While the change in expansion ratio is relatively small, the lifetime, transport time, and extinction times are very much affected by n . While the lifetime increases monotonically with increasing n , the transport and extinction times exhibit maximum and a minimum near $n = 10$ to 12 , respectively. At small oxyethylene chain lengths, foams seem to degrade and unable to block the fuel vapors quickly. Clearly, $n=10$ to 12 are close to the optimum oxyethylene lengths. However, it is the edge effects that prolonged extinction in Figure 92 (b) may also play a role in causing the parabolic behavior in Figure 93 (d). It is unclear to what extent the edge effects transfer to the large scale Milspec pool firefighting, where an active firefighter moves around the edges of the pool applying the foam. The synthesized trisiloxane fire performance for

n=9-12 and 12.3 are comparable to that of 502W fire performance. Unlike the commercial 502W surfactant, the synthesized surfactant structure is characterized by known reagents, chemical history and spectroscopic analysis. These synthesized surfactants can be modified with additional synthesis in a systematic way to improve the performance further.

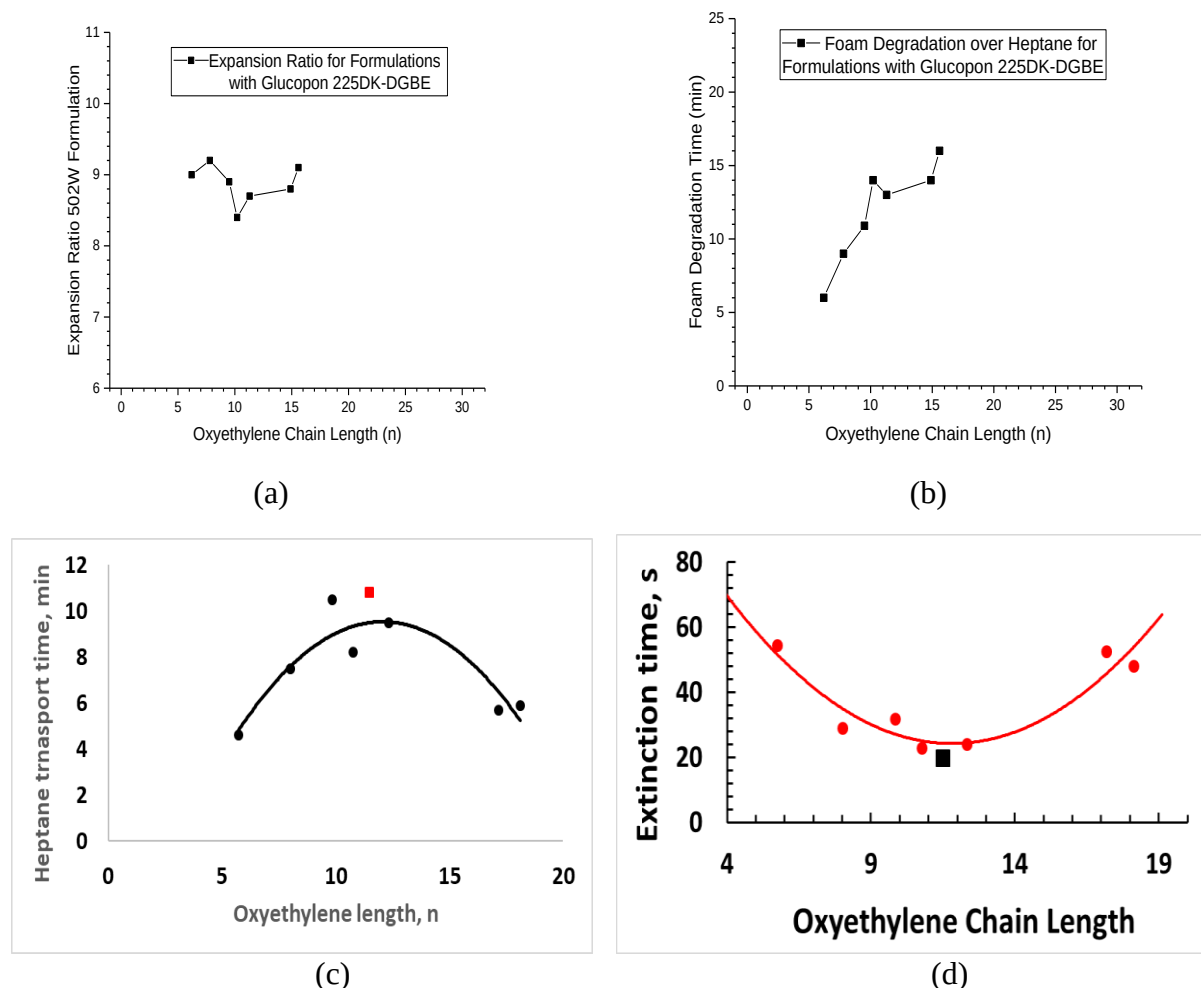
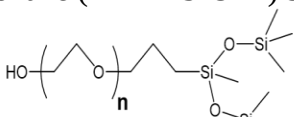


Figure 93. Foam-fuel interaction dynamics. (a) expansion ratio, (b) foam degradation lifetime, (c) fuel transport time, (d) heptane fire extinction time versus oxyethylene length, n. The transport time is obtained from Figure 90 (b) at a fixed fuel flux of 5.3×10^{-9} mole/cm²s corresponding to the lower flammability limit (1.1 mole%). Square symbol is the data for 502W formulation shown in column 1, Table 19.

Table 57 lists the foam properties and fire extinction properties at different oxyethylene lengths along with the analytical characterizations and specific identities of the precursor materials. The Ross-Miles tests shows initial and after 5 min foam heights in the absence of any fuel effects. Table 57 shows that n=10.8, based on NMR of the precursor material, is the optimum length for properties of interest for firefighting.

Table 57. Synthesized trisiloxane (BHMTS-OEn) surfactants and their properties.

B-HMTS(OE)n-OH



NRL Notebook Ref	N10358-107	N10358-106	N10358-108		N10358-135	N10477-12	N10477-07	N10477-03	N10358-176	N10477-01	N10477-05	N10358-174	N10358-169
n (precursor NMR)	0	1.02	2.07	3.56	5.28	5.74	8.02	9.84	10.76	12.34	17.18	18.12	45.13
n (precursor source)	0(Acos)	1(Acos)	2(Glst)	3.2(NOF)	3.0(Glst)	4-7(Glst)	7.8(NOF)	8-9(NOF)	9-12(Glst)	11.9(NOF)	15.7(NOF)	12-20(Glst)	35-50(Glst)
n (precursor GPC)	—	—	—	—	—	6.2	7.8	9.5	10.2	11.3	14.9	15.6	31.3
MWprecursor (g/mole)	58.08	103.0	149.3	—	290.7	331	402	477	507	556	714	745	1437
MWsurfactant (g/mole)	280.6	325.5	372	—	513	554	624	699	730	778	937	968	1659
Solubility (g/Kg)	<0.001	0.001	0.006	—	0.040	0.045	0.13	0.25	miscible	miscible	miscible	miscible	miscible
Cloud Point (°C)	—	—	—	—	—	—	<0	22.5	39.9	60.0	86.5	90.6	>100
CMC (%)	0.2	0.0062	0.004	—	0.005	0.0059	0.0085	0.010	0.017	0.025	0.035	0.053	0.099
CMC (g/Kg)	0.309	0.0398	0.0457	—	0.0676	0.0617	0.0912	0.115	0.191	0.240	0.316	0.372	0.575
CMC (mM)	1.15	0.115	0.120	—	0.112	0.107	0.135	0.170	0.263	0.302	0.347	0.380	0.355
Y _{CMC} (mN/m)	36.0	28.5	23.0	—	19.6	19.5	20.4	19.8	20.3	20.4	22.4	24.0	31.3
Excess, Γ (mol./cm ² x10 ¹⁰)	10.9	9.91	0/0	—	3.96	3.57	3.26	2.97	2.91	2.85	2.61	3.03	151/121
Area/molecule A (Å ²)	15.3	16.8	5.01	—	41.9	46.6	51.0	55.9	57.2	58.2	63.7	54.8	3.34
Ros Miles (H ₂ mm/H ₃ mm)	—	—	33.2	—	—	8/1	64/45	78/64	151/140	188/137	200/163	219/150	49.8
19cm Pool (hepts/1000)	—	—	—	—	—	√	√	√	√	√	√	√	—
ext time (sec)	—	—	—	—	—	55	31	32	23	24	60	65	—
exp ratio	—	—	—	—	—	9.0	9.2	8.9	8.4	8.7	8.8	9.1	—
Degradation (min)	—	—	—	—	—	6.0	9.0	10.9	14.0	13.0	14.0	16.0	—
Transport	—	—	—	—	—	4.6	7.5	10.5	8.2	9.5	5.7	5.9	—

5.10. Varying Head and Tail Sizes of Glycoside Surfactant

We quantified the effect of variations to alkylpolyglycoside (APG) co-surfactant's head and tail sizes shown in Figure 17 on heptane pool fire suppression performance, foam dynamic and physical properties, and solution properties. As mentioned earlier, our approach is to focus on the roles of surfactants in a multi-component formulation to increase oleophobicity and synergisms between siloxane and glycoside surfactants in the NRL siloxane formulation. The glycoside co-surfactant is one of the two surfactants in NRL's siloxane formulation, which contains polydispersed commercial glycoside (Glucopon225DK) with a head size of $x=0.7$ and tail size $n=8$ to 10 as shown in Figure 17, polydispersed commercial siloxane surfactant (502W), and diethyleneglycol butylether (DGBE) as shown in column 1, Table 19. To vary the glycoside surfactant's head size with the tail size fixed and vary the tail size with the head size fixed, we used two approaches: (1) fractionation of polydispersed commercial Glucopon225DK to enrich the fraction with average glycoside head size greater than 0.7, (2) used commercially available monodispersed alkyl glycosides with head size ranging up to 2 and tail sizes ranging from carbon backbone lengths of C6 to C12. We evaluated foams generated by these glycosides, which replaced the Glucopon225DK in the formulation containing Dowsil 502W, as listed in column 1, Table 19. We measured the effects of varying the glycoside head and tail sizes on solution and foam properties, and heptane fire suppression. The results showed a minima in extinction time and foam degradation lifetimes as the head size and tail sizes are varied one at a time. The extinction time changed by a factor of 2 due to the head or tail variation. Thus, both tail size and head size have significant effect on the degree of fire suppression. Even though, the minimum extinction time did not fall below that of Dowsil 502W siloxane formulation, the results suggest that the head and tail sizes need to be increased simultaneously, rather than one at a time, to maintain amphiphilicity of the surfactant mixture while increasing the synergism. Also, instead of using monodispersed alkylglycosides in NRL's siloxane formulation, polydispersed glycosides with an average head size greater than 0.7 need to be used to increase synergism with the polydispersed siloxane 502W; the polydispersed glycosides may be created from mixing commercially available monodispersed alkylglycosides.

5.10.1. Compositions of Siloxane-Glycoside Formulations

We prepared formulations listed in Table 58 for generating foams, where the enriched fractions of Glucopon225DK as well as the monodispersed glycosides with different head and tail sizes are substituted for Glucopon225DK in a formulation containing 502W siloxane surfactant.

Table 58. Siloxane (502W-Glycoside) surfactant formulations and fluorinated RefAFFF formulation. The values shown under each column are weight percentages of the individual components (or concentrates) in distilled water. The formulations were used for foam generation, property and fire performance measurements.

2:3 Siloxane-Gluc225 (NRL Siloxane Formulation)	2:3 Siloxane- Fractionated Gluc225DK	2:3 Siloxane- Glycosides	3:2 Cap-Gluc215 (RefAFFF [37])
0.2 % 502W, polydispersed	0.2 % 502W, polydispersed	0.2% 502W, polydispersed	0.3% Capstone
0.3% Glucopon 225 DK, polydispersed	0.3% Fractions of Glucopon 225DK, polydispersed	0.3% Glycosides of different head/tail sizes, monodispersed	0.2% Glucopon 215 CS UP, polydispersed
0.5% DGBE	0.5% DGBE	0.5% DGBE	0.5% DGBE

5.10.2. Fractionation of Polydispersed Glucopon225DK

Glucopon 225DK is a BASF alkyl polyglycoside surfactant product is polydispersed [39] and is a very important component of the NRL siloxane (502w-Glucopon 225DK-DGBE) formulation [44,71]. It out-performed other glycoside surfactants (Glucopon 215UP, Glucopon 600UP, Triton CG425) in combination with 502W as a foam formulation for fire suppression. Commercial APG surfactant preparation is usually done via Fischer synthesis from glucose and fatty alcohols. The reaction yields products which are complex mixtures of mono-, di-, and higher glycosides with a variation in geometric and stereo isomer structures along with a range in alkyl chain length of 8-10. APG surfactants are schematically represented by the structure shown in Figure 17 accompanied by numerical averages and ranges for the polyglycoside and alkyl chain lengths [39]. The structure, however, over simplifies the complexity in that glycosides moieties bond to each other at variable positions and with different stereochemistry in addition to that illustrated by the structure.

We found a correlation of higher degree of fire suppression with the higher polyglycoside content of Glucopons and with TritonCG-425 ($x=0-2$ and $n=8-14$). The correlation appears to indicate that improvement may be obtained by increasing the glycoside content. Unable to obtain commercial APGs with higher glycoside content, the approaches of fraction of Glucopon 224DK, purchasing analytical APG compounds and of synthesis of a monodispersed triglycoside were adopted as hypotheses for fire suppression improvement over that for the NRL's 502W-Glucopon 225DK-DGBE formulation shown in Column 1 of Table 58.

The solubility of APG compounds is dependent on the quantities of glycoside head and alkane tail in the surfactant. Solubility testing of Glucopon 225DK in a range of solvents produced an interesting pattern of degree of solubility (Table 59).

Table 59. Solubilities of Glucopon225DK in different solvents

<u>Glucopon 225DK Solubilities</u>		
Solvent	% PPT Fraction	% Sol Fraction
DMSO	0%	100%
CHCl ₃	0%	100%
MeOH	3.0%	97.0%
EtOH	13.3%	86.7%
iPrOH	22.7%	77.3%
THF	29.8%	70.2%
Acetone	38.4%	61.6%
EtOAc	53.6%	46.4%
CH ₃ CN	60.8%	39.2%
Toluene	97.4%	2.6%

With the exception of chloroform, there appears to be a correlation of solubility with solvent polarity. Chemical intuition would expect the glycoside structure with its multi-hydroxyl functionality to favor water, DMSO and alcohol solubility with molecules having higher hydroxyl contents requiring higher degrees solvent polarity for solubility. This behavior is the basis of Glucopon 225DK fractionation based on solubility. Solubility based fractionation is a practical technique as it can be readily adapted to 100g quantities of surfactant. The fractionation approach developed involved starting with the acetone solvent, and collecting acetone-soluble and acetone-precipitated fractions. The acetone-soluble fraction is then subjected to acetonitrile dissolution and results in acetonitrile-soluble and acetonitrile-precipitated fractions. Finally, noting that ethanol dissolves almost 90% of the Glucopon 225DK, an ethanol-precipitated fraction was collected by dropwise addition of the Glucopon 225DK concentrate into stirred ethanol. Figure 94 illustrates this overall fractionation scheme below.

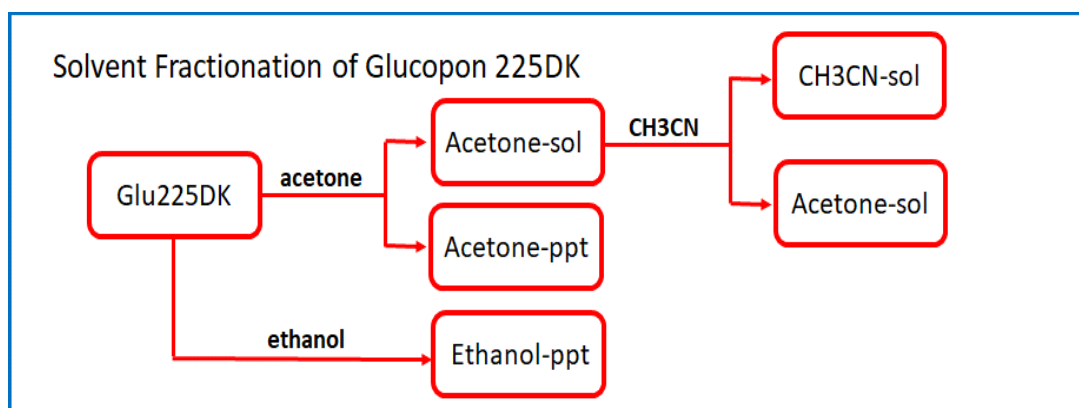


Figure 94. Fractionation scheme for Glucopon225DK with acetone, ethanol, and acetonitrile.

5.10.2.1. Fractionation Procedure

The commercial BASF surfactant concentrate Glucopon 225DK was analyzed by thin-layered chromatography on silica gel plates. Although there were no UV-active components of the product, the plates could be visualized by staining with 10 wt% phosphomolybdic acid in ethanol. The best solvent system for elution was 20 vol% methanol in chloroform. By this method, the 225DK was separated and was found to be mostly a single spot of $R_f = 0.6$, along with a streaking material from the origin and a strong spot at the origin. A 5 g sample of 225DK was then separated by silica gel chromatography, and a sample of the upper spot at $R_f = 0.6$ was obtained pure. Proton and carbon-13 NMR showed that the purified material was the C8/C10 mono-glucoside.

Next, 225DK was separated into various fractions with organic solvents. First, it was found that 225DK (6.5 g) would yield a precipitate when dissolved in both ethanol and acetone (100 mL of either solvent). For expediency, all later further separation employed acetone as the starting point. The granular solid that precipitated from acetone could be collected on a medium porosity glass filter frit and then dried under vacuum. In one such run, 6.5 g 225DK yielded 1.89 g of a light tan precipitate (~29%). The acetone filtrate could then be evaporated down to a gummy residue. TLC analysis of the two fraction showed that the mono-glucoside spot at $R_f = 0.6$ was nearly completely gone from the acetone-insoluble fraction, while the acetone-soluble fraction appeared to be enriched with it, the latter also having less of the lower running components. The acetone-soluble fraction was further fractionated by dissolving into warm acetonitrile. Allowing the acetonitrile solution to cool to room temperature resulted in a precipitate. The precipitate from the acetonitrile was not a well-behaved solid but stuck well to the sides of the flask. Thus, the acetonitrile solution could be decanted away from the precipitate. However, there was not a great amount of acetonitrile-insoluble material, most of the material was soluble in acetonitrile. In fact, after repeating the acetonitrile fractionation a second time, the resulting acetonitrile-soluble material was almost completely clean mono-glucosides by TLC analysis. Three samples from this fractionation process were available for pool fire extinction testing: 1) ~60 g of acetone-insoluble 225DK; 2) ~40 g of acetone-soluble 225DK; and 3) ~20 g of acetonitrile-soluble 225DK.

The EtOH-ppt fraction of Glucopon 225DK was prepared as described in NRL Notebook N10477-77 and is described as follows. BASF Glucopon 225DK is a concentrate with a non-volatiles content of 70wt%. It was prepared in two batches by dropwise addition of 50.0 g 225DK concentrate into 2000 ml absolute ethanol and 40.0 g 225DK concentrate into 1600 ml absolute ethanol while stirred (vortex of 2/3) over a 1 hr period. These suspensions were stirred for an additional hr. The finely divided precipitate was collected by slow filtration through a 15cm Whatman #41 filter paper supported by a large conical funnel. The soft paste filtrate was transferred by spatula to a large petri dish and placed in a vacuum desiccator and covered by a large watch glass. Vacuum was gradually increased at a rate where spattering of ethanol was avoided. After six hours a maximum mechanical pump vacuum (<1mm) was obtained. The <1mm vacuum was maintained for 3 days. Product yield was 7.395g (90.3% based on 70% 225DK non-volatiles and 225DK solubility in ethanol of 13.3%). ^1H NMR showed trace of residual EtOH which 3 additional days <1mm vacuum treatment could not remove.

5.10.2.2. Analytical Characterization of Glucopon Fractions

The four fractions (CH₃CN-sol; Acetone-sol; Acetone-ppt and EtOH-ppt) were collected in 8-20g quantities and were characterized by ¹H NMR spectroscopy and gel permeation chromatography. The NMR spectra is somewhat complicated by the mixed-isomer structure of the polyglycoside moiety. An oversimplified APG structural representation is provided in Figure 95 with ppm chemical shift assignments for various proton resonances indicated. The spectra of the unfractionated Glucopon 225DK and its series of fractions are presented in Figure 96. In viewing the APG structural representation it should be kept in mind that, in addition to the 6 position illustrated, polyglycoside linkages can occur at the 2, 3 and 4 positions and that stereochemistry can vary at the 1 position.

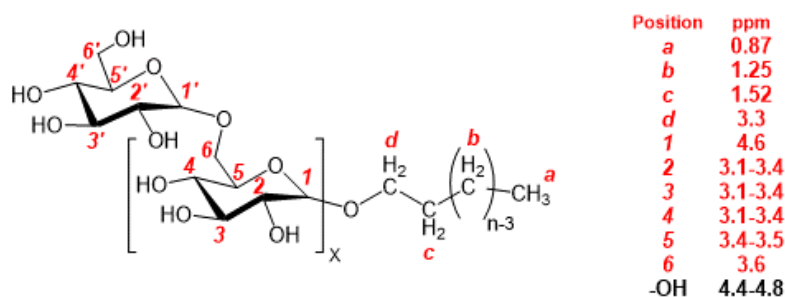


Figure 95. Structural representation of a glycoside surfactant with identification of chemical shift assignments.

In the spectra shown in Figure 96, the a, b and c resonances attributed to the alkyl group are readily identified, and the d resonance overlaps with glycoside resonances. In the glycoside part of the structure for $X > 0$, the polydispersity of the glycoside chain length and its isomeric variability complicate and broaden the structure. However, as X increases the spectral broadening of its resonances becomes greater and their intensity ratio to the alkyl resonances becomes larger. The spectra in Figure 96 have been arranged such that those corresponding to fractions soluble in the less polar solvent are placed immediately below the spectrum of the unfractionated Glucopon 225DK, and spectra of those fractions precipitated from the more polar solvents are at the bottom. The trend of higher glycoside signal resolution and higher alkyl resonance intensity correlates with the shorter chain lengths (lower value of X) of the organic solvent soluble fractions.

Another diagnostic for the polyglycoside chain length is gel permeation chromatography. This method separates molecules according to size by using a gel that has a pore size that retards the passage of small molecules through the column. Most GPC columns use organic solvents, most often THF as is the case at NRL. As indicated above Glucopon 225DK is 70% soluble in THF. While the insoluble fraction may include the longer chain polyglycosides, such an analysis of this APG and its fractions can provide useful characterization information. The chromatograms of the THF soluble portions of the unfractionated Glucopon and its CH₃CN-sol, Acetone-sol and Acetone-ppt fractions (the EtOH-ppt fraction was insoluble in THF) are depicted in Figure 97. The distribution of mono-, di- and triglycoside contents is clearly indicated by the intensities of the chromatographic peaks. It clearly shows that the content CH₃CN-sol fraction relative to that of the unfractionated Glucopon 225DK is significantly enriched in monoglycoside, strongly diminished in diglycoside and depleted of triglycoside. The Acetone-sol fraction is also enriched in monoglycoside, slightly enhanced

In diglycoside and slightly diminished in triglycoside content. The Acetone-ppt fraction is strongly diminished in monoglycoside, has a near equivalent quantity of diglycoside and a greater quantity of triglycoside. This correlates well with the glycoside composition variation indicated by the NMR characterization. By extrapolation, the EtOH-ppt fraction is to be more enriched in the triglycoside content.

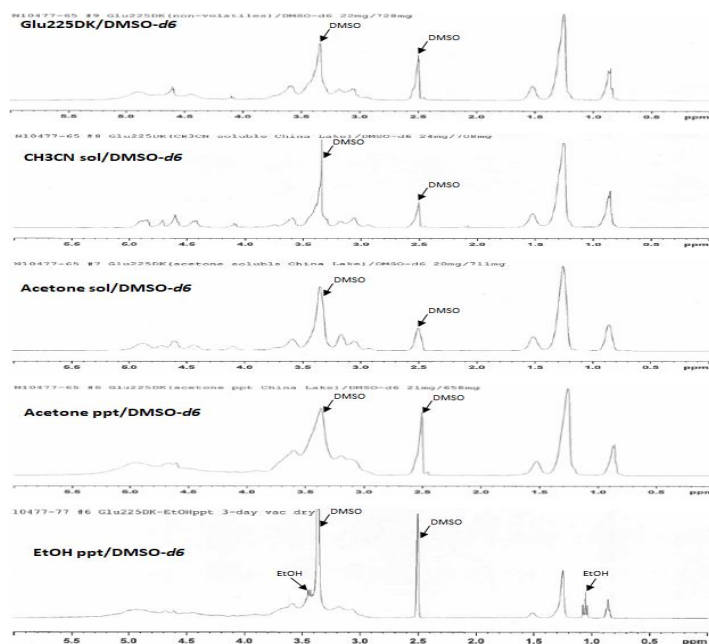


Figure 96. NMR spectra of the unfractionated Glucopon 225DK and CH₃CN-sol; Acetone-sol; Acetone-ppt and EtOH-ppt fractions depicted in order of increasing fractioning solvent polarity.

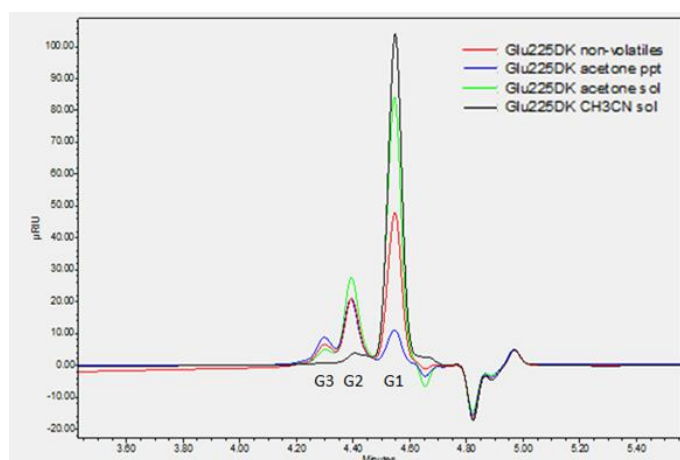


Figure 97. GPC chromatogram of the unfractionated Glucopon 225DK and CH₃CN-sol; Acetone-sol; Acetone-ppt fractions. The G1, G2 and G3 indicate retention times that correspond to mono-, di- and triglycoside size molecules as calibrated by the analytical glycoside compounds (ANATRACE Inc.).

5.10.3. Monodispersed Glycosides

A number of analytical grade monodispersed alkylglycoside surfactants with well-defined chemical structures were purchased from ANATRACE Co., Maumee, OH [72]. They are used to replace Glucopon225DK in formulations shown in column 1 of Table 58. Their chemical structures are shown in Figure 98.

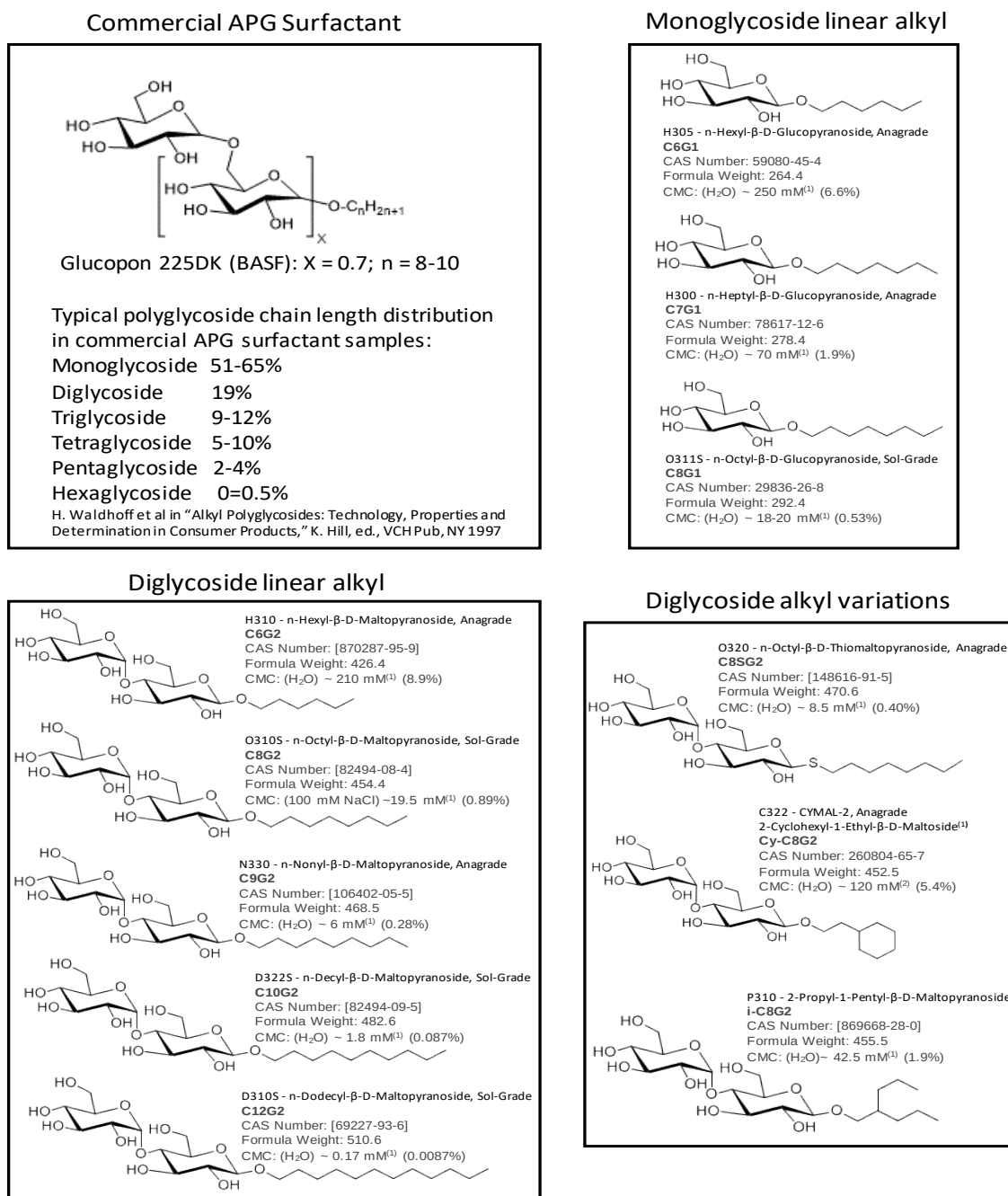


Figure 98. Chemical structures [72] of monodispersed alkyl glycosides used to replace Glucopon225DK as shown in column 1 of Table 58.

While the fractionation of GlucoPON225DK yielded polydispersed fractions, monodispersed glycosides can be used both as references for analytical characterizations but also can enable well-defined, systematic, variations of the glycoside structure to provide insights into how they affect fire extinction. They enable variation of alkyl tail length with head size fixed and variation of glycoside head with the alkyl tail length fixed. Their effects on solution and foam properties, and fire extinction can also be quantified. In addition to the commercial glycosides, Dr. Matthew Davis kindly provided us with monodispersed alkyltriglycosides, which he synthesized at NAWC, China Lake, CA for foam and fire suppression evaluations.

5.10.4. Surface tension and CMC

Table 60 shows the measurements of surface and interfacial tensions for formulations containing the commercial glycosides (ANATRACE Co., Maumee, OH) as shown in column 3 of Table 58. Increased alkyl length of the alkylglycoside appears to increase the surface tension slightly. Figure 99 shows the surface tension of siloxane formulation with hexyldiglycoside C6G2 as a function of total surfactant concentration in water. The critical micelle concentration (cmc) is 0.009 wt% as determined from the plot.

Table 60. Interfacial properties of siloxane-glycoside formulations shown in column 3 of Table 58.

Formulation	Surface Tension mN/m (± 0.5 mN/m)	Int Tension Hept mN/m (± 0.5 mN/m)	Int Tension Gasoline mN/m (± 0.5 mN/m)
502W+C8G1	21.5	3.0	2.7
502W+C8G2	21.6	4.0	4.3
502W+C10G2	23.8	3.9	2.1
502W+C12G2	24.1	3.3	1.5

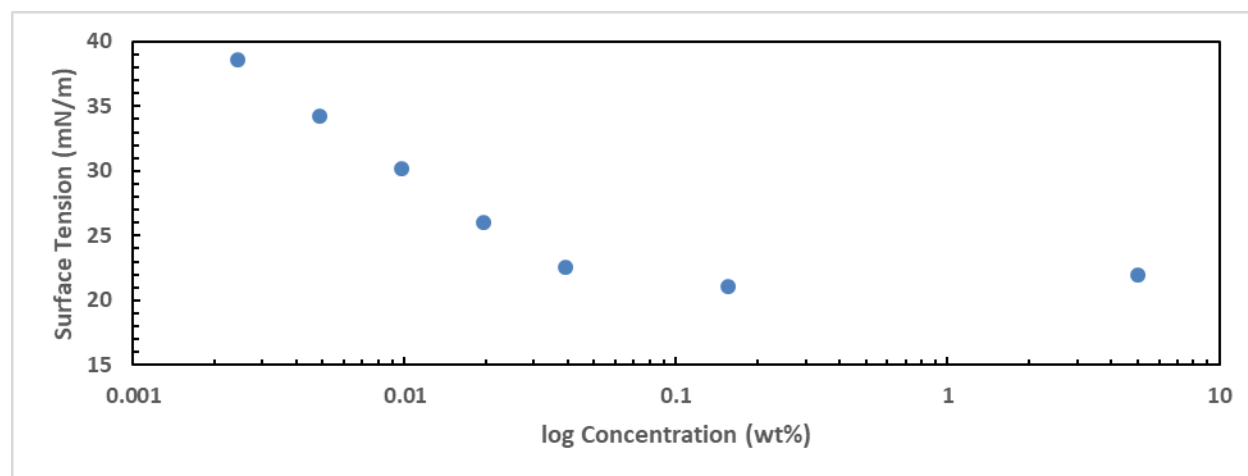


Figure 99. Critical micelle concentration (cmc) for siloxane formulation with C6G2 replacing GlucoPON225DK as shown in column 3 of Table 58.

Figure 100 shows cmc as a function of alkyl tail length for solutions of alkylglycoside surfactants. These are aqueous solutions of individual surfactants rather than formulations

containing surfactant mixtures. Log of cmc decreases linearly with increasing tail length, number of carbon atoms n , for both mono and di- glycosides. Thioglycoside has lower cmc than iso and cyclic glycosides.

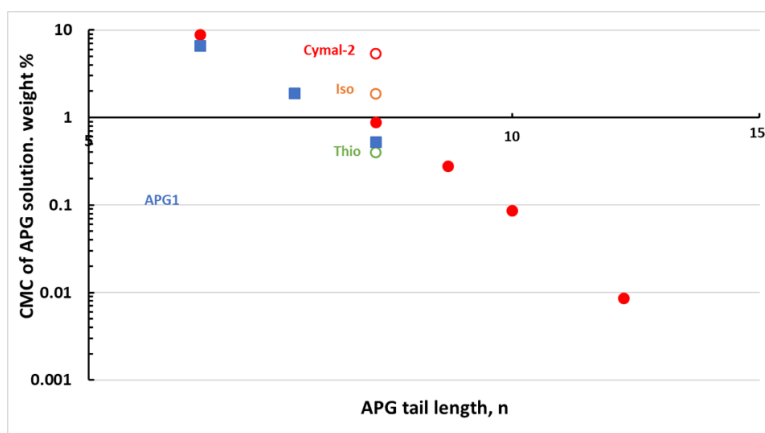


Figure 100. Critical Micelle Concentration (CMC) as a function of alkyl tail length for individual monodispersed alkyl glycoside solutions in water.

5.10.5. Foam generation and Expansion ratio

Foams were generated using sparging method. The expansion ratio (volume of foam/volume of liquid) was calculated by measuring the weight and volume of the foam and it represents water content of the foam. Figure 101 shows the expansion ratio versus foam generation rate using formulations containing different fractions of Gluco225DK replacing Guco225DK as shown in column 2 of Table 58.

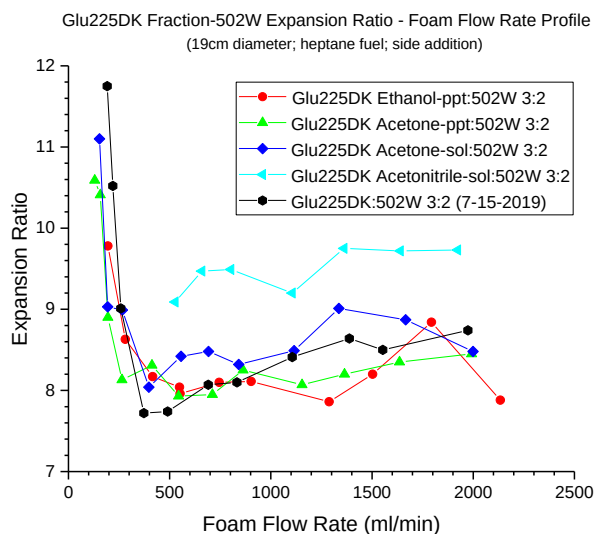


Figure 101. Foam expansion ratio with foam generation rate through the sparger disc for the formulations shown in column 2 of Table 58; different glycoside fractions varying in monoglycoside content (shown in Figure 97).

Figure 101 shows relatively constant expansion ratio at foam flow rates higher than 500 mL/min and an increase in expansion ratio when foam flow rate is below 500 mL/min. This is due

to increased liquid drainage from the foam before it exits the generator outlet at low foam flow rates; liquid drains from foam collected above the solution in foam generation cup for longer times at low foam flow rates. Among different fractions, acetonitrile fraction that is enriched in monoglycoside content has higher expansion ratio than other fractions.

Figure 102 is similar to Figure 101 but for the monodispersed alkylglycosides shown in Figure 98. Figure 102 shows that the expansion ratio is relatively independent of foam generation rate with the exception RefAFFF, which exhibits a decrease in expansion ratio with increased generation rate. Figure 103 shows that expansion ratio relatively independent of alkyl tail length of alkyl diglycosides shown in Figure 98.

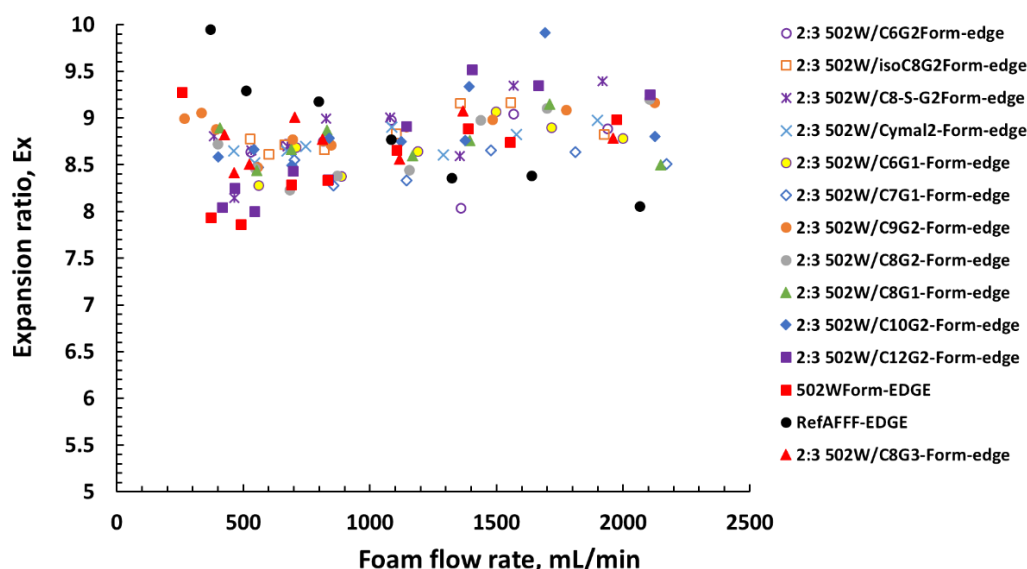


Figure 102. Foam expansion ratio with foam generation rate through the sparger disc for formulations shown in column 3 of Table 58.

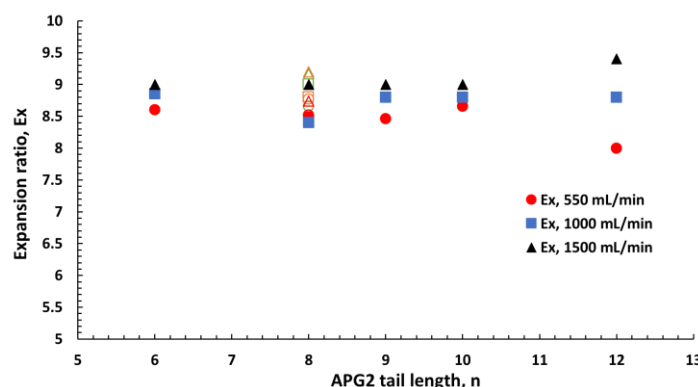


Figure 103. Foam expansion ratio versus alkyl tail length for formulations shown in column 3 of Table 58 generated at different foam flow rates, 550 mL/min to 1500 mL/min.

5.10.6. Foam-Fuel Interaction Dynamics

The foams derived from formulations containing each of the three Glucopon 225DK fractions substituted into the 502W shown in column 2 of Table 58 were characterized by

degradation measurements and compared with analogous data for the unfractionated Glucopon 225DK formulation. This characterization involves monitoring the time-dependent reduction of a 4cm layer of foam deposited onto a 60 mL volume of 60°C preheated fuel in a 150 mL beaker and results are depicted in Figure 104.

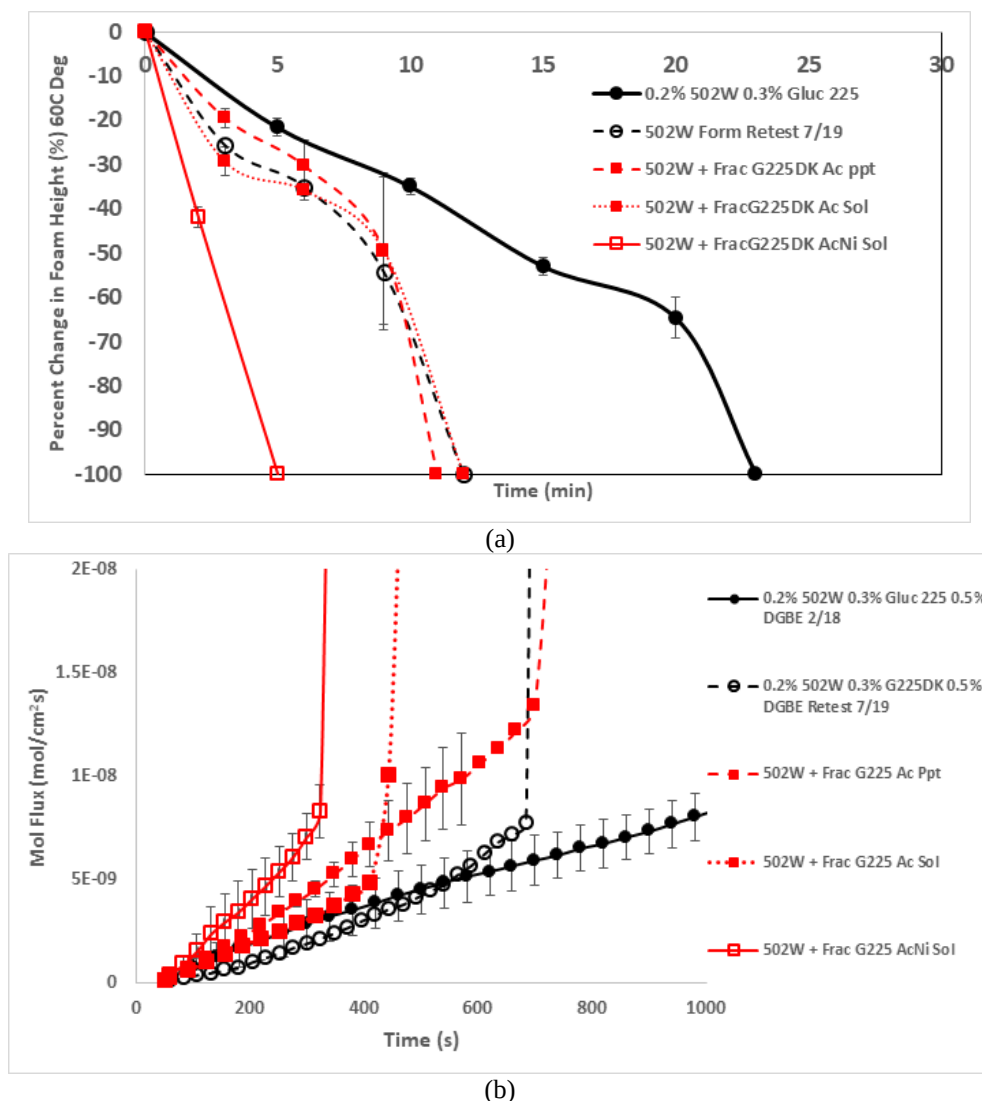


Figure 104. (a) Foam degradation measurements, (b) fuel vapor flux from the foam covered heptane pool at 60 °C for foams generated from formulations in column 2 of Table 58; the solvent-separated 225DK fractions (Acetone-ppt; Acetone-sol; CH₃CN-sol).

This result displayed in Figure 104(a) shows that substitution of the CH₃CN-sol fraction in the formulation results in the most rapidly degraded foam. This correlates with the extinction data in that the associated monoglycoside content of this fraction is associated with both the lesser extinction performance and the more rapid foam degradation. The degradation data for the foams associated with the Acetone-sol and Acetone-ppt fractions' formulations shows little difference between the foams. Comparison with degradation of the foam derived from the unfractionated Glucopon 225DK will require more testing as results in one run indicate little difference and another run indicate the unfractionated 225DK derived foam to be more degradation resistant.

These foams were also characterized by heptane fuel vapor transport measurements where the heptane content in the headspace above an initial 4 cm foam layer laid over a 60°C heptane pool is monitored as a function of time via an infrared gas cell and slow moving carrier gas. Results are presented in Figure 104(b). The foam derived from CH₃CN-sol fraction exhibited the highest permeability which would also correlate with the lowest extinction activity. The foams derived from the Acetone-sol and Acetone-ppt fractions' formulations show moderately divergent behavior with the former being less permeable but both being slight more permeable to heptane vapors than foam derived from the formulation with the unfractionated Glucopon 225DK.

Fuel transport and foam degradation data was also collected for a set of monoglucoside materials that were fire tested in a formulation containing 502W siloxane as shown in column 3 of Table 58. The set included 11 monoglucosides with variation in glucoside value (G1 or G2), tail length (C6, 7, 8, 9, 10, 12) and additional variation on the C8G2 (cymal, i-C8G2, C8SG2).

Figure 105 plots fuel transport rates for all 11 in comparison to 0.5% 502W alone and 502W in a 2:3 formulation with Glucopon 225DK and 0.5% DGBE. Little difference in transport rates were seen for all of the monoglucosides tested. Most had worse transport performance than the 502W surfactant individually, and none compared to the performance of the formulation containing 502W and Glucopon 225DK (column1, Table 58). Figures 106 to 108 are monoglucosides separated to identify potential trends in glucoside size, tail length, or variations on C8G2. Differences in transport are very minor, but the best two performers from the group for transport were C6G1, C8G2, and C12G2.

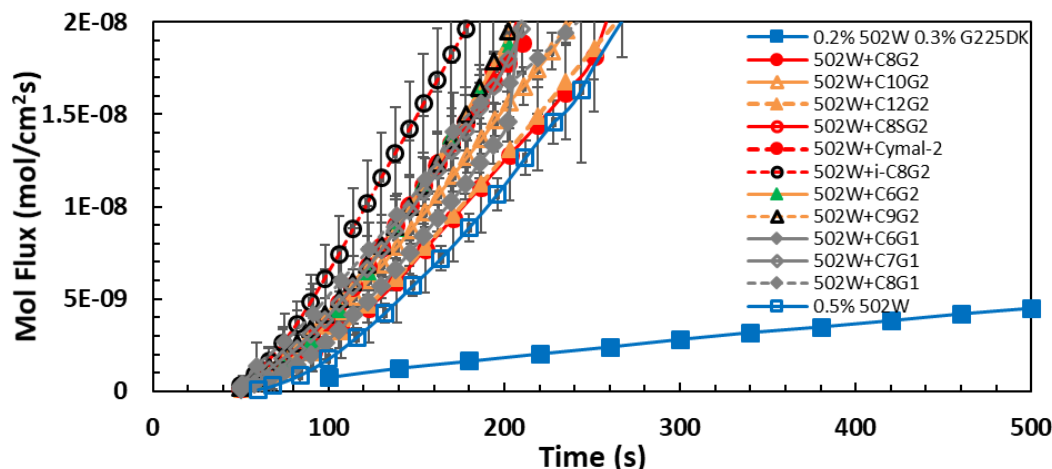


Figure 105. Heptane fuel transport rate through a 4-cm thick foam layer covering hot (60 °C) heptane pool with time. All foams are generated by sparging method with formulations shown in column 3, Table 58.

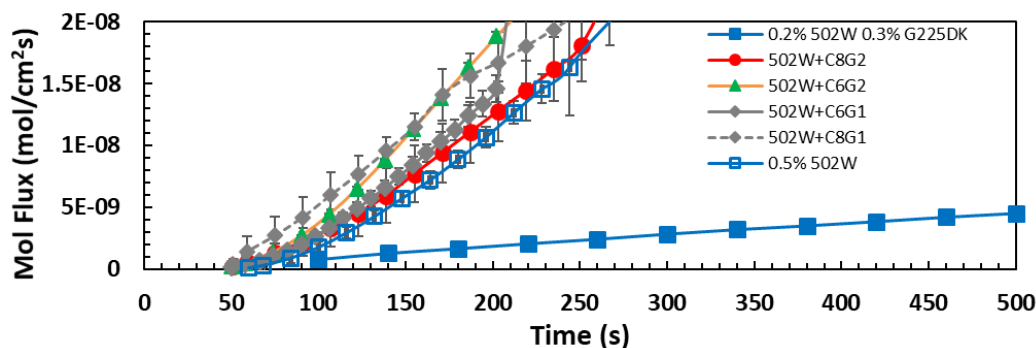


Figure 106. Trends in G1 vs G2: No clear trend, C8G2 has better transport than C8G1, however, C6G1 has better transport than C6G2 and might be due to different degrees of amphiphilicity.

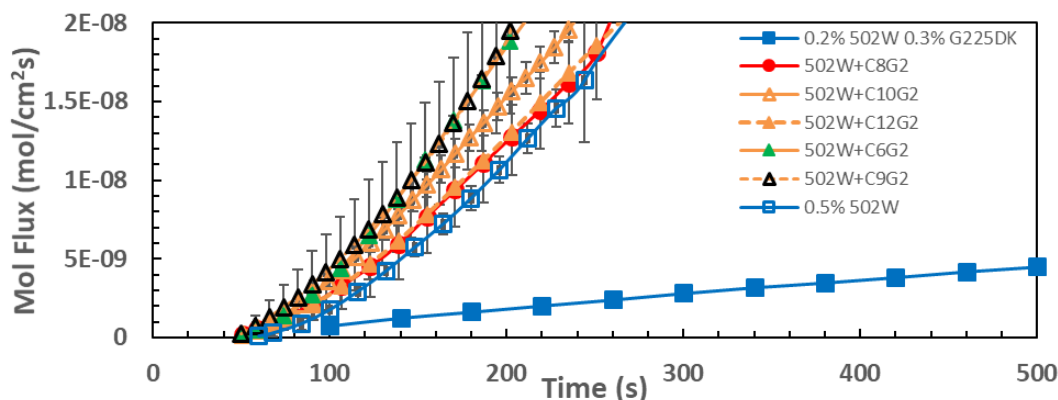


Figure 107. Trend in length: No clear trend, transport rate order from fast to slow C9G2=C6G2 > C10G2 > C8G2=C12G2.

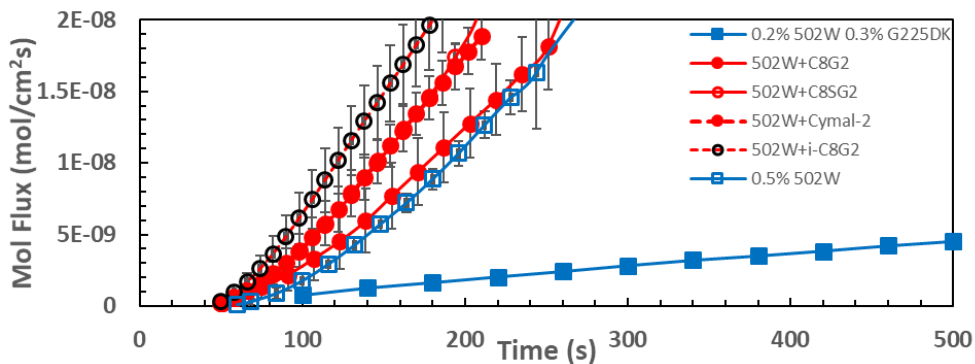


Figure 108. Variations in C8G2 showed some differentiation. C8G2 performed better than the other 3. Cymal and C8SG2 performed similarly, and i-C8G2 performed the worse. C8G2 containing 502W and DGBE performed as well as 502W alone with the other formulations showing faster (worse) transport despite 502W being in the formulation with the monoglucoside.

Degradation data in an open beaker was also collected for this series and the data is plotted in Figure 109. Little variation seen in degradation performance. Foam lifetimes are slightly longer than the 3 minutes of the 0.5% 502W surfactant alone, but do not match the 23 minute performance of the 502W formulation with Glucopon 225DK and DGBE. Figure 109 plots the 11 variations together. Figures 110 to 112 separate degradation profiles based on glucoside value, tail length,

and variations in C8G2. Foams with the longest lifetimes were 502W+Cymal-2 and 502W+C9G2, this does not trend with transport performance which showed these two foams having marginal transport performance: not the worst or the best.

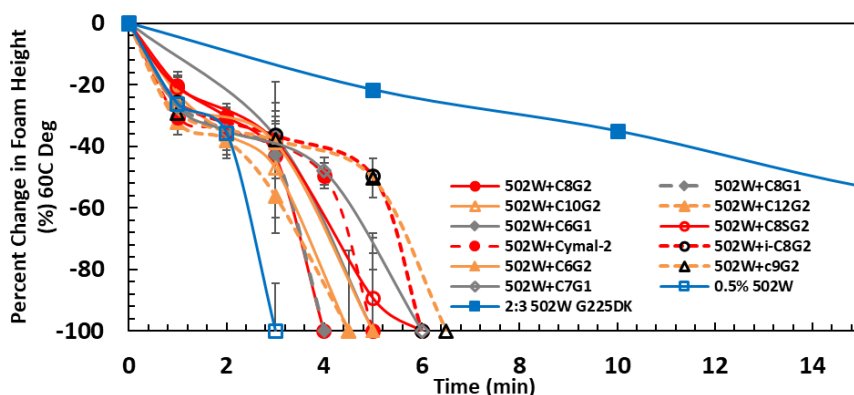


Figure 109. Change in foam layer thickness with time due to degradation by hot heptane (60 °C)

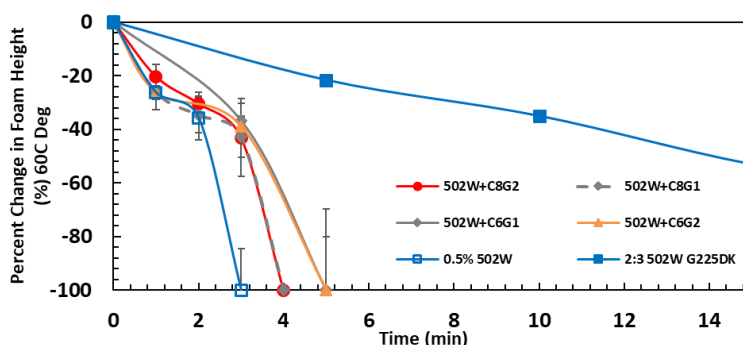


Figure 110. Trends in G1 vs. G2: change from G1 to G2 does not appear to effect degradation performance for tail lengths of C6 and C8 significantly. C6G1 and C6G2 have the same foam lifetime with small differences in degradation profile. Similarly, C8G1 and C8G2 have the same foam lifetime and small differences in degradation profile.

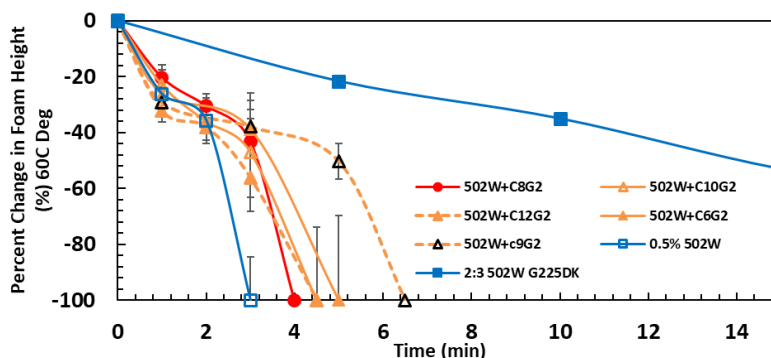


Figure 111. No clear trend in degradation performance due to tail length. Foam lifetimes are in the order C8G2 < C10G2 = C12G2 < C6G2 < C9G2. All are an improvement in lifetime over 502W alone, but do not compare to the performance of 502W with Glucopon 225DK.

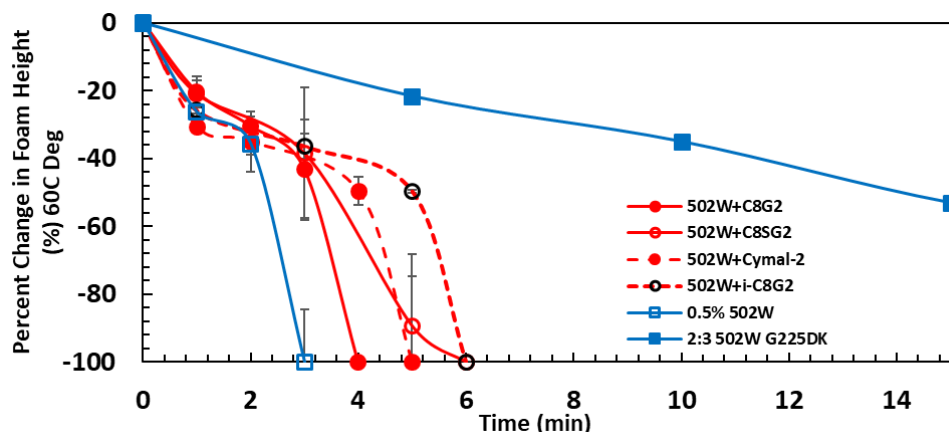


Figure 112. Trends in C8G2 variation: exhibit similar foam lifetimes and profiles. Slight variations, foam lifetime in the order of C8G2 < Cymal-2 $\approx$ C8SG2 $\approx$ i-C8G2.

5.10.7. Bench Scale Fire Extinction

Benchtop fire extinction testing of the four fractionated compositions of Glucopon 225DK in a formulation shown in column 2 of Table 58 (502W: fractions of Glucopon225DK:DGBE) was conducted 19 cm heptane pool using the edge deposition of foam. The extinction time versus foam flow rate and time for full coverage of the pool surface versus foam flow rate profiles data are illustrated in Figures 113 and 114. Using the unfractionated Glucopon 225DK in the 502W formulation as a reference, the formulations using the Acetone-sol and Acetone-ppt fractions as the APG component very closely track this reference. The CH₃CN-sol fraction containing formulation has a profile displaced to longer extinction times and faster foam flow rates making it significantly less effective compared to the unfractionated Glucopon225DK. Use of the EtOH-ppt fraction in place of Glucopon 225DK in the formulation results in a profile moderately displaced to longer extinction times and faster flow rates. These results indicate that the monoglucoside component in Glucopon 225DK does not contribute as much as the di- and triglucoside surfactant components to the fire extinction. However, substitution of the acetone-sol and acetone-ppt fractions with their diminished monoglycoside and enhanced di- and triglycoside contents did not improve extinction performance beyond that of the formulation with the unfractionated Glucopon 225DK. The presumably triglycoside rich EtOH-ppt fraction containing formulation also did not improve but diminished fire suppression effectiveness. This result appears to indicate that simply increasing the glycoside chain length beyond a certain threshold does not result in an enhanced fire suppression capability. One of the reason is that tail length can have significant effect on fire suppression; the GPC shown in Figure 97 could only resolve glycoside head size but not the tail sizes. Second reason has to do with the polydispersity. One must also keep in mind that there are a multitude of glycoside isomers and other components in the complex Glucopon 225DK. Also, 502W siloxane is a polydispersed mixture leading to a geometrical fit among different sized molecules in NRL's siloxane formulation (column 1, Table 58) mixture resulting in synergism to increase fire suppression. The siloxane has wide tail and skinny head of different sizes and vice versa for the Glucopon that could fit geometrically, and increase surfactant packing density at the interface. The fractions from Glucopon225DK would have shifted that polydispersity one way or another from Glucopon225DK that could have a deteriorating effect on the synergisms and the degree of fire suppression.

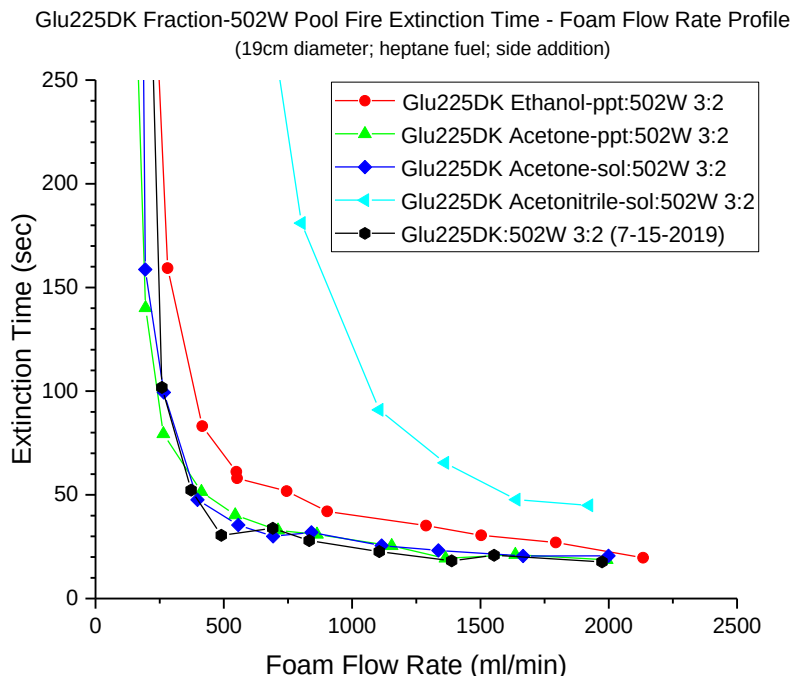


Figure 113. Heptane pool fire extinction time at different foam application rates for different fractions of Glucocon225DK as shown in column 2 of Table 58, replacing the unfractionated Glucocon225DK in NRL formulation. Foam was deposited at the edge of the pool and was allowed to spread to cover the pool.

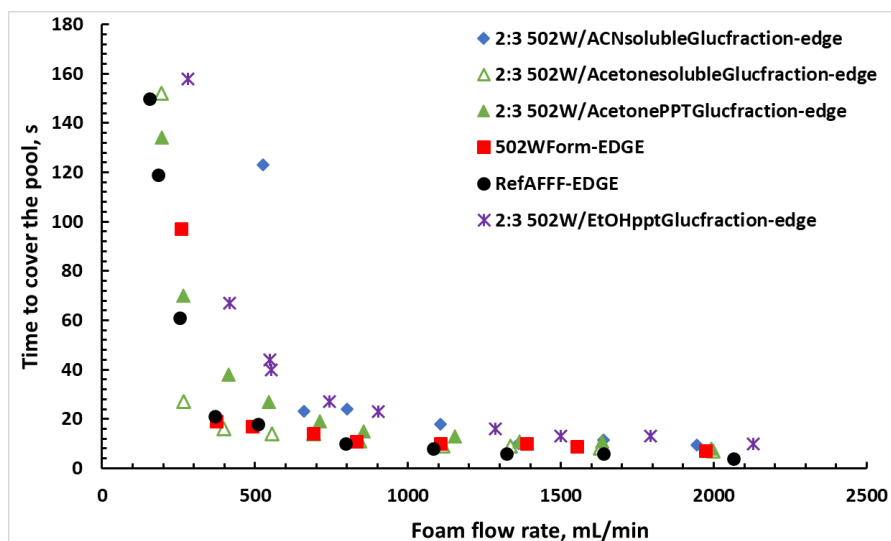


Figure 114. Time for foam to completely cover the pool surface measured at different foam application or generation rates for different fractions of Glucocon225DK as shown in column 2, Table 58. All foams are generated using sparging method and deposited at the edge of the pool.

The time for full coverage of the pool surface was also measured during the fire extinction experiment and are shown in Figure 114. The coverage time data appear to follow the extinction time data especially at low foam flow rates. It is interesting that the expansion ratio data shown in

Figure 101 indicate that only the CH₃CN-sol fraction (value of 9.5) is consistently outside of the 7.5-8.5 range of the other fractions and unfractionated Glucopon 225DK.

A 19 cm benchtop extinction test is also conducted on a burning heptane pool fire by foam formulations shown in column 3 of Table 58. These are based on the 502W polyoxyethylene-trisiloxane and Glucopon 225DK APG surfactants wherein the ANATRACE analytical APG compounds are substituted for the Glucopon 225DK surfactant. Fire extinction times are measured as a function of foam flow rate to correlate with the analytical APG compound chemical structure.

An initial experiment involved extinction testing the series of alkyl diglycoside analytical compounds to determine the effect of the carbon chain length in the alkyl group. The extinction profile plot is presented in the left side in Figure 115. While none of the substitutions outperformed the 502W-Glucopon 225DK formulation, it appears that there is an optimum in extinction effectiveness near the C8 alkyl chain length with a very large drop in effectiveness as the alkyl chain length increased to 10 and 12 carbon atoms.

We varied the position where the foam is delivered onto the pool surface from center to the edge of the pool to examine how it affected fire extinction time and its sensitivity to glycoside structure as shown in Figure 116. The foam, generated by air sparging, has to travel through a relatively long glass tube to a point above the center of the burning pool where it exits the tube, drops to the center of the burning pool surface and spreads to the edges. The glass tube is positioned over the burning pool and becomes quite hot especially at low foam flow rates where extinction times are long. As the foam travels through the hot tube, the foam can undergo thermal degradation before it exits the delivery tube. That can reduce the delivery rate and change properties of the foam that is actually delivered to the pool center be different from the foam that is generated. The adjustment in protocol involved positioning the end of the foam delivery tube just over the edge of the burning pool instead of the center of the pool. Very little heating of the foam delivery tube occurs at the edge position. But, after being deposited on the edge of the burning pool, the foam must spread to the opposite side of the pool before extinction can occur. This is referred to an “edge deposition,” and its results are presented in Figure 116. The disparity between extinction time versus foam flow rate profiles becomes much smaller with the C10 and C12 members becoming much more effective. This may indicate that C10 and C12 members may actually be more effective in a MilSpec tests where the nozzle and foam do not get hot because the foam travels through the fire very quickly in time significantly less than the extinction time. This may also indicate that foams derived from these longer chain APG compounds have a greater susceptibility to thermal degradation. With respect to the C6 to C8 chain length data, the performance is much less effected by the center vs edge foam deposition. With respect to higher performance formulations such as 502W-Glucopon 225DK and the RefAFFF (Capstone 1157-Glucopon215UP), the difference in profiles derived from the center vs edge foam depositions is very small as shown in Figure 116.

A result of particular importance in Figure 117 is the very significant effect of alkyl tail length on fire extinction profile. At a fixed foam flow rate, the extinction time decreases as the tail length is increased from C6G2 to C9G2 and increases slightly with further increase in the tail length to C12G2. C9 tail length appears to have the optimum fire extinction profile among the different tail lengths examined. This appears to be consistent with Figure 111, which also

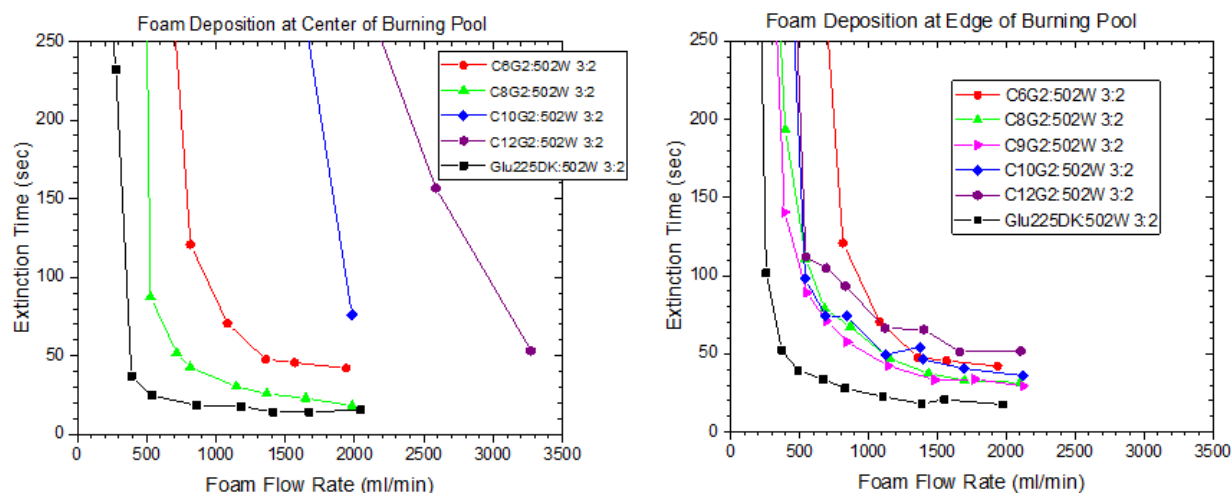


Figure 115. Fire extinction testing of foams from solutions where the CnG2 analytical APG compounds have been substituted for Glucopon 225DK as shown in column 3, Table 58. The effect of a foam deposited at center (left) and at the edge (right) of a burning heptane 19 cm pool.

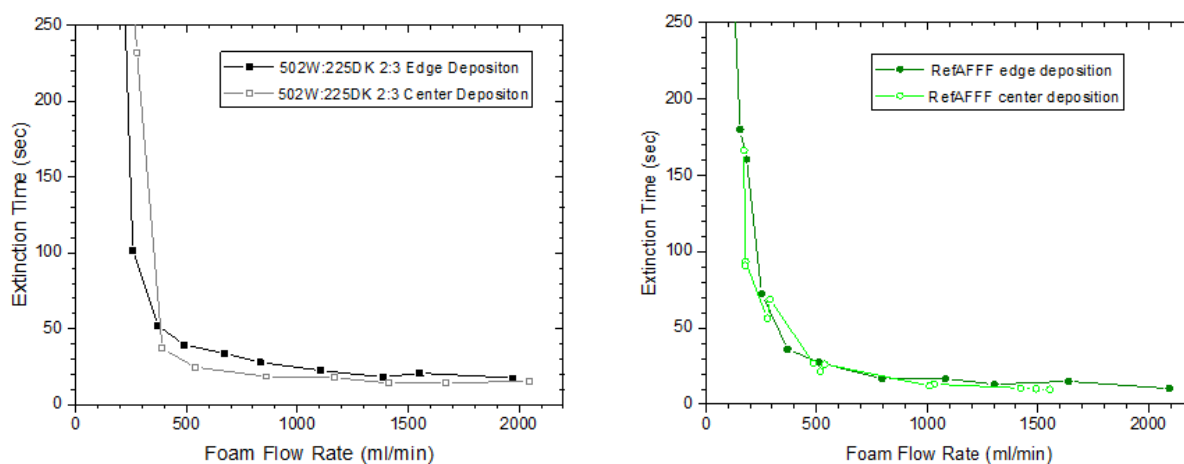


Figure 116. Fire extinction testing of 502W – Glucopon 225DK (left) and RefAFFF (right) foam formulations shown in columns 1 and 4 of Table 58 respectively. Center vs edge foam deposition effects on extinction time versus foam flow rate profiles.

shows slowest foam degradation for C9G2 among different tail lengths. But, Figure 107 shows no clear trend; both C8G2 and C12G2 have the slowest fuel transport rates among different tail lengths. Figure 117 shows that the effects of tail length on fire extinction time are less pronounced among the alkylmonoglycosides examined; C6G1, C7G1, and C8G1. No clear differences were seen in foam degradation and fuel transport rates with tail length for the monoglycosides in Figures 107 and 108 respectively. Figure 117 shows that increasing the tail length with the head size fixed did not improve the fire suppression performance over the 502W - Glucopon 225DK formulation.

In addition to the tail length, the polyglycoside has many structural features to vary. The simplest is the number linked glycoside rings forming the head. From Anatrache the analytical APG compounds are available as mono- and diglycosides as presented in Figure 98. Direct comparison between the pairs of C8G1 and C8G2 and of C6G1 and C6G2 are presented in Figure

118 and show that the diglycosides are more effective than the monoglycosides. However, the foam degradation and fuel transport rates shown in Figures 110 and 106 respectively do not show significant differences between the mono- and di- glycosides. Also, Figure 118 shows that neither of the glycosides closes the fire extinction profile gap with the 502W-Glucopon 225DK formulation. Finally, within the diglycoside series C8 alkyl groups with a branched, cyclic and sulfur for oxygen linkage substitution were tested. Figure 119 shows the fire extinction times increase in the order n- < thio- < cyclic- < iso- at a fixed foam flow rate and is consistent with fuel transport rates shown in Figure 108. But, the degradation rates shown in Figure 112 are not significantly different among the tail variations.

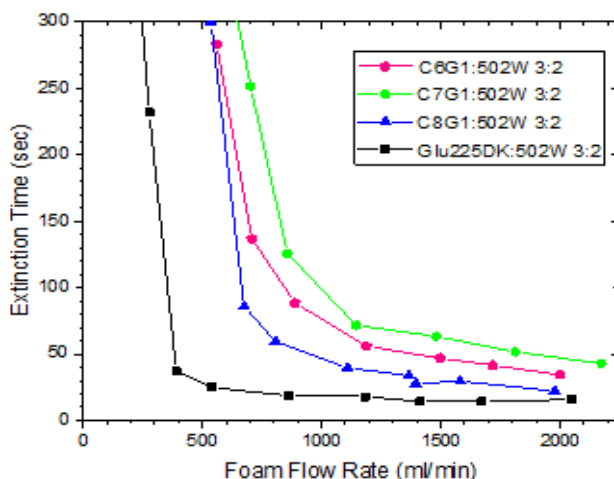


Figure 117. The effect of alkyl tail length of monoglycoside on fire extinction time versus foam application rate for formulations shown in column 3, Table 58. Foams were deposited at the pool edge.

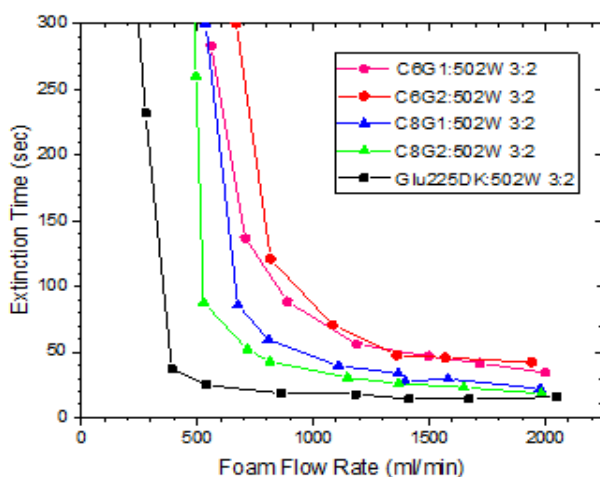


Figure 118. The effect of glycoside head size on fire extinction time versus foam application rate for formulations shown in column 3, Table 58 with edge deposition of the foam.

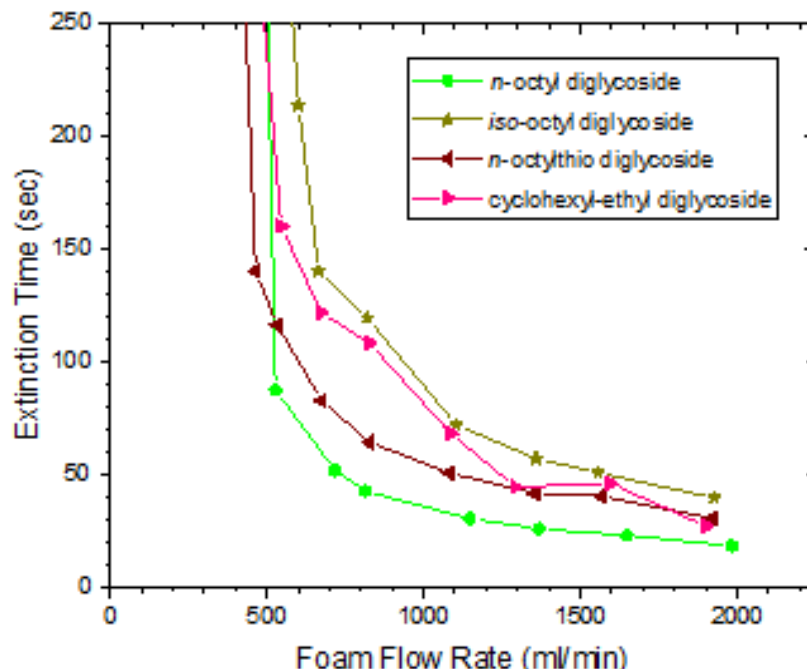


Figure 119. The effect of varying tail geometry of diglycoside compounds with linear, branched alkyl chain, cyclic, and sulfur atom substitution on fire extinction time versus foam application rate for formulations shown in column 3, Table 58 with edge deposition of the foam.

Figures 120 and 121 show quantitatively the effects of varying tail and head sizes of the alkylglycoside structure on extinction time using the monodispersed materials. They show that the extinction times for the monodispersed are higher than the polydispersed. The monodispersed octyltriglycoside was synthesized by Dr. Matthew Davis, NAWC, China Lake because it is not available commercially. With head size fixed, as the tail size increases, the extinction time goes through a minimum as shown in Figure 120. Similarly, the extinction time exhibits a minimum as the head size is varied, with the tail size fixed as shown in Figure 121. The tail and head size effects appear to be more pronounced at high and low foam flow rates respectively. For comparison the Glucopon225DK's extinction times at three foam application rates are represented as a rectangular box in Figures 120 and 121. Clearly, the Glucopon extinction times are significantly smaller than the monodispersed alkyl glycosides and some of the possible reasons are discussed below.

Amphiphilicity is necessary to make large foam volumes for a given amount of solution. For amphiphilicity, the hydrophobicity of tail should be in balance with the hydrophilicity of the head. As the tail size increases the balance shifts from head to tail and may be causing the minimum in extinction time. A similar phenomena could be happening when head size is increased with the tail size fixed. This suggests, both head and tail sizes should be changed simultaneously to maintain the amphiphilic balance rather than varying one at a time as was done in the current report.

A second reason for the difference between monodispersed glycosides and Glucopon225DK extinction times has to do with polydispersity of Glucopon225DK. Previously, we showed that there is synergisms between alkyl glycoside and trisiloxane polyoxyethylene

(502W) surfactants that reduce the extinction time for the mixture relative to the individual components. There could be a geometrical fit between these two surfactants because 502W is polydispersed molecules with fat tail and skinny heads of different sizes while Glucopon225DK has the opposite geometry (fat heads and skinny tails of different sizes). When a monodispersed alkylglycoside is mixed with the polydispersed 502W trisiloxane surfactant, a mismatch in geometry results and could lead to smaller degree of synergism compared to the mixtures with polydispersed Glucopon225DK. Further work should be performed to understand this by inducing polydispersity by mixing different monodispersed glycosides.

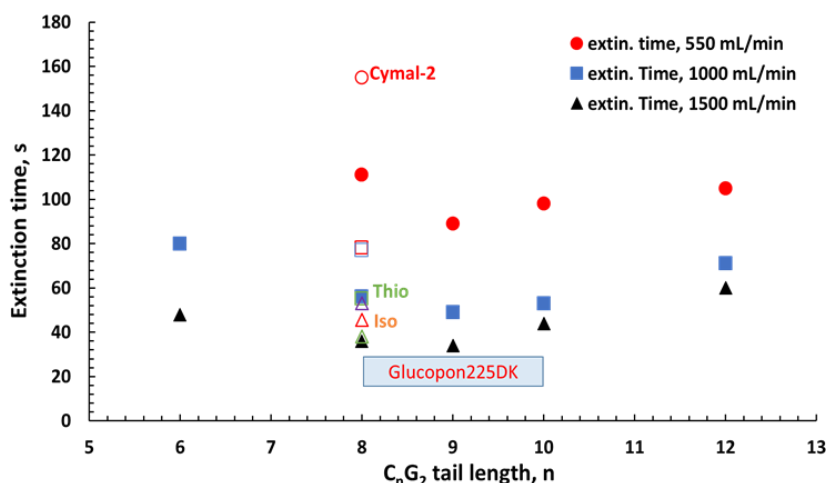


Figure 120. The effect of tail length of monodispersed alkylglycosides on heptane fire extinction time at different foam application rates relative to the polydispersed Glucopon225DK with edge deposition. For comparison, the Glucopon225DK's extinction times at three foam application rates fall within the rectangular box.

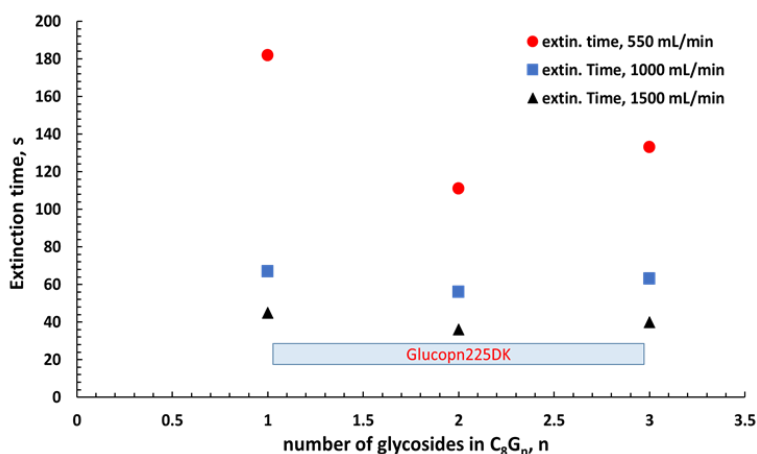


Figure 121. The effect of head size of monodispersed alkylglycosides on heptane fire extinction time at different foam application rates relative to the polydispersed Glucopon225DK with edge deposition. For comparison, the Glucopon225DK's extinction times at three foam application rates fall within the rectangular box.

During the fire extinction experiments discussed above, times for full coverage of the pool surface by foam were also recorded and are shown in Figure 122. They show a significant effect

due to changes in alkylglycoside chemical structure. The polydispersed GlucoPON225DK has the fastest spread relative to the monodispersed glycosides.

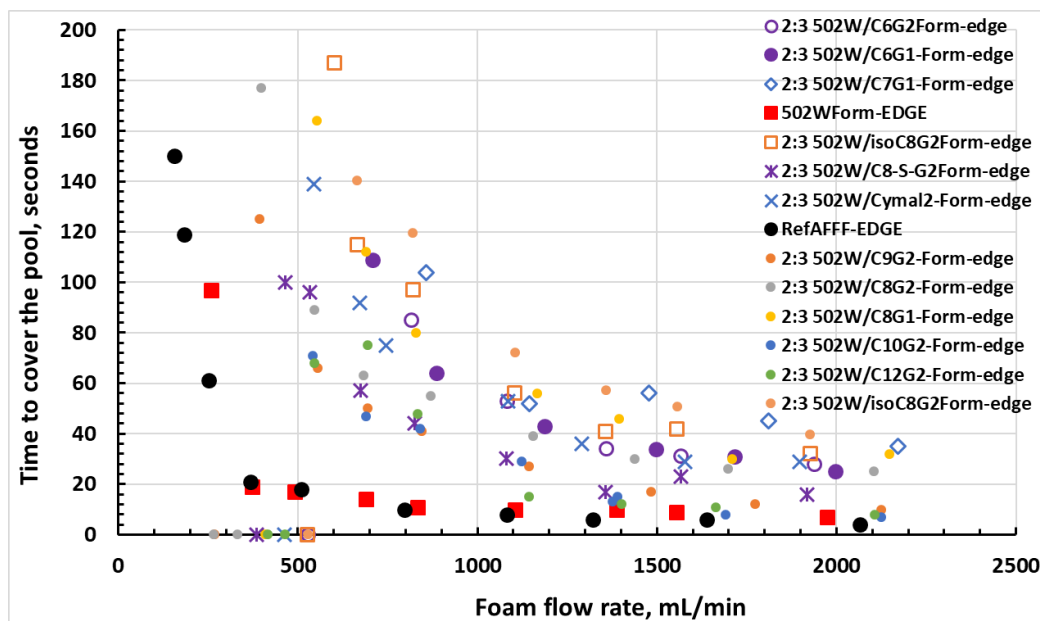


Figure 122. The effect glycoside head and tail variations on foam coverage time versus foam flow rate with edge deposition of the foam.

Figures 123 and 124 show that foam coverage times for the monodispersed alkylglycoside containing siloxane formulations are significantly longer compared to the polydispersed GlucoPON225DK especially at low foam application rates.

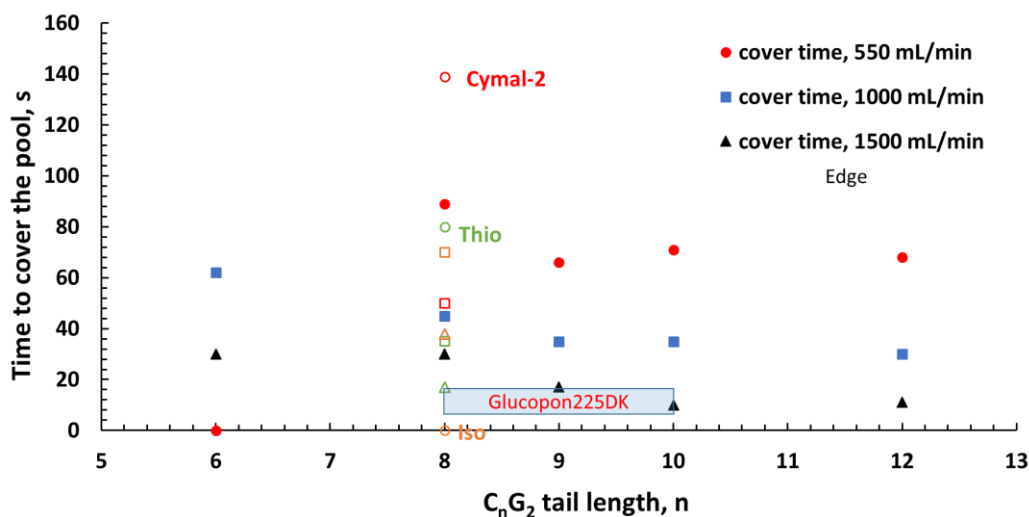


Figure 123. The effect alkylglycoside tail variations on foam coverage time versus foam flow rate relative to GlucoPON225DK with edge deposition of the foam. For comparison, the GlucoPON225DK's coverage times at three foam application rates fall within the rectangular box.

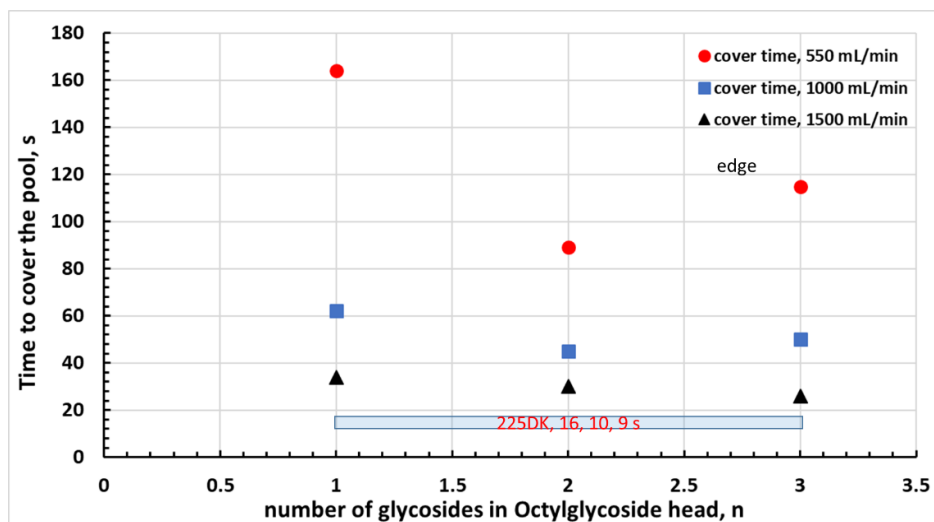


Figure 124. The effect alkylglycoside head size variations on foam coverage time versus foam flow rate relative to Glucopon225DK with edge deposition of the foam. For comparison, the Glucopon225DK's extinction times at three foam application rates fall within the rectangular box.

This could be due to differences in foam degradation rates and in foam expansion ratios which can affect rheological properties of spreading. Also, Figure 123 shows that there does not appear to be a minimum in coverage time as the tail size is increased, with head size fixed, unlike the minimum in fire extinction time shown in Figure 120. However, Figure 124 shows that there is a minimum with increased head size, with tail size fixed, similar to extinction time versus head size at low foam application rates shown in Figure 121. Figure 125 and 126 show the ratio of pool coverage time and fire extinction time. As one may expect, the ratio gets close to 1 at low foam application rates indicating the influence of spreading on fire extinction. At high foam application rates, foam spreading plays less significant role.

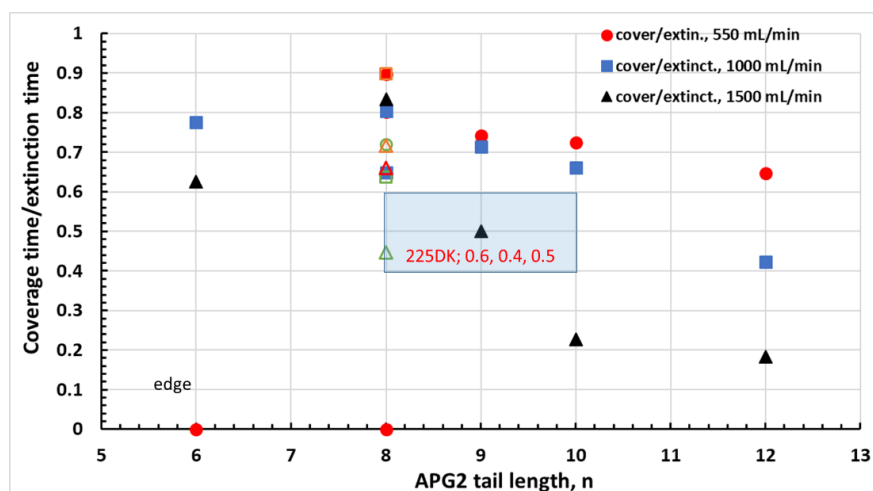


Figure 125. Coverage time as a fraction of extinction time and the effects alkylglycoside tail variations with edge foam deposition.

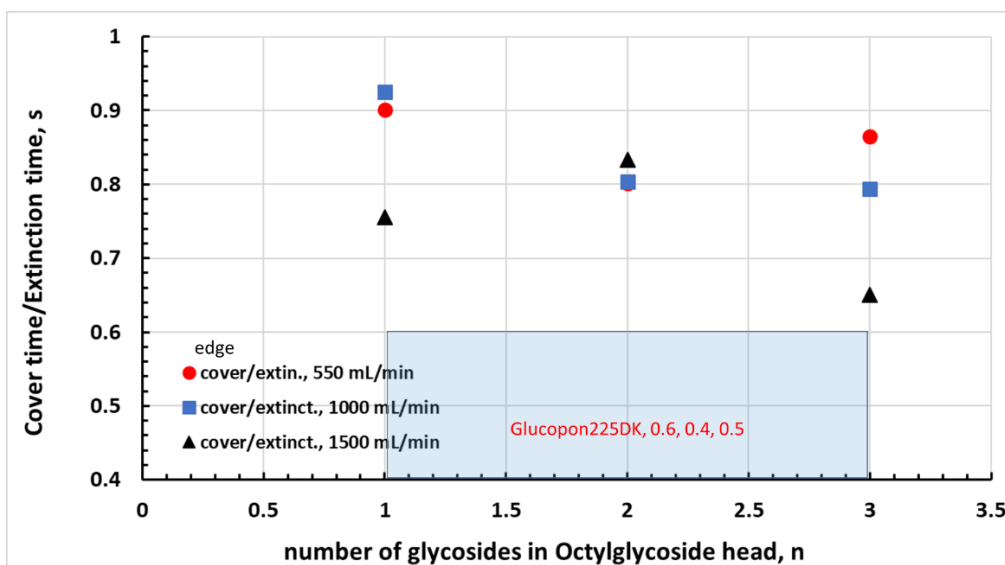


Figure 126. Coverage time as a fraction of extinction time and the effects alkylglycoside head size variation with edge foam deposition.

5.11. Hydrolytic Stability of Siloxane Surfactants

Siloxanes are prone to undergo hydrolysis in dilute solutions especially that are acidic or basic. While that may be helpful in breaking it down in nature in aqueous environment, it can limit its shelf life, which is one of the MilSpec requirements.

5.11.1. Analytically Tracking Hydrolytic Susceptibility

A very important property and issue is the comparative hydrolytic susceptibility of the branched and linear trisiloxane functional groups of the surfactant tail. Hydrolyzed surfactants lose their ability to form foams and suppress fires. While the hydrolysis of the Si-O-Si bonds via combination with one water molecule to yield two Si-OH functionalities is very simple in concept, when it is incorporated into a surfactant system, it becomes somewhat complex for several reasons. This reaction is very pH sensitive being strongly catalyzed by acid and base. Micelle formation provides variable levels of hydrolysis protection depending on size, shape, surfactant diffusion rates and surfactant critical micelle concentration. The silicic acid decomposition products may condense into a complex mixture of other products. Silicone surfactant hydrolysis studies are mostly limited to correlations of solution surface tension changes with aging time of the solution and do not address the role the micelle plays. Finally, higher molecular weight surfactants (particularly those of commercial origin) involve dispersity in isomer and chain length structures and lower levels of purity. In this work, we synthesized, purified and characterized low molecular weight (oxyethylene chain length $n = 2$) representatives of the branched and linear trisiloxane and of the tetrasilane classes of silicon surfactants. We also developed NMR technique, which is more definitive for observing hydrolysis than surface-tension correlation. As a reaction diagnostic, methyl groups bonded to the silicon nucleus can serve as a probe of cleavage of the Si-O-Si bond via their ^1H NMR chemical shifts of reagent and product.

To monitor the hydrolysis of the *B*-HMTS(CH₂)₃(OE)₂-OH, *L*-HMTS(CH₂)₃(OE)₂-OH surfactants by the Si-CH₃ proton resonances conditions (solvent, concentration, pH, temperature and observation time) need to be designated so that the result is physically meaningful and within

the operational capability of the NMR technique. To be physically meaningful from the perspective fluorine-free foam concentrate for use in fire suppression, a concentration corresponding to that used in a 1 to 6% proportioning rate is a range to target. This concentration is higher than the CMC of practically all surfactants designed for foams meaning that most of the surfactant will reside in micelles in a water medium. This concentration is well within the NMR sensitivity limits, but surfactants residing in micelles display resonances that are somewhat broadened and displaced in chemical shift compared with spectra of the unimolecular dissolved surfactant. Also, some surfactants form opaque emulsions or two phase systems due to lack of this level of micelle solubility in water. This limited micelle solubility is observed with the short ($n = 2$) oxyethylene chain length surfactants in that these three surfactants form hazy to opaque mixtures in D_2O in the 1-6% concentration range. Recording spectra of such mixtures is complicated by broad overlapping peaks originating from suspended droplets and micelles superimposing on low intensity narrow peaks from dissolved surfactant. To obtain a comparative analysis for the *B*- and *L*-HMTS(CH₂)₃(OE)₂-OH surfactants, we switched to an organic solvent into which a small quantity of water was added. Water saturated CDCl₃ was observed to provide ¹H NMR spectra of these molecularly dissolved surfactants identical to those in Figure 85 without the broad resonances attributed to micelle formation.

Concentrating on the -SiCH₃ region (0.2 to -0.1 ppm) of the spectrum, the spectra as a function of time were recorded as depicted in Figure 127. The initial spectra consist of three -SiCH₃ resonances for *L*-HMTS(CH₂)₃(OE)₂-OH and of two resonances -SiCH₃ for *B*-HMTS(CH₂)₃(OE)₂-OH with assignments indicated in Figure 85. After 9 hr, the first indication of hydrolysis for *L*-HMTS(CH₂)₃(OE)₂-OH is observed with the appearance and growth of a new resonance at 0.08 ppm and several more in the range 0.06 to 0.03 ppm between the second and third initial resonances at 0.07 and 0.01 ppm respectively. These new hydrolysis-associated resonances grow rapidly in intensity as the successive spectrum at 27.5 hr indicates. By comparison, the *B*-HMTS(CH₂)₃(OE)₂-OH 9 hr spectrum exhibits a very weak new resonance at 0.6 ppm which increases in intensity much more slowly. After 231 hr, the spectral change has subsided. To determine whether hydrolysis was complete, 100 μ l volume of HCl vapor from head space of concentrated HCl container was taken and mixed in the NMR cell solution. This resulted in little change in the *L*-HMTS(CH₂)₃(OE)₂-OH spectrum but an appreciable change particularly after 12 hr in the *B*-HMTS(CH₂)₃(OE)₂-OH spectrum. This experiment demonstrates that the linear trisiloxane surfactant is significantly more susceptible to hydrolysis than the branched trisiloxane surfactant. This susceptibility appears to correlate with a protective steric hindrance of the branched isomer.

Conducting this NMR hydrolysis assessment in the aqueous phase is more complicated and is also illustrated in Figure 128 for the short and long chain ($n = 2$ and 12.3) oxyethylene-*B*-HMTSF surfactants. The $n = 2$ surfactants are less water-soluble, and the 1% solution preparation results in a fine hazy suspension rather than a clear solution. The initial spectrum reflects the micelle/microdroplet effect. For the *B*-HMTS(CH₂)₃(OE)₂-OH surfactant it consists of the two -SiCH₃ resonances being broadened and shifted up field to 0.28 and 0.20 ppm. Over the 400 hr period the *B*-HMTS(CH₂)₃(OE)₂-OH undergoes a gradual hydrolysis with its spectral features resembling those of the hydrolysis depicted in Figure 127.

The $n = 12.3$ long chain surfactants are water-soluble at 3% composition forming clear transparent solutions. The freshly prepared $B\text{-HMTS}(\text{CH}_2)_3(\text{OE})_{12.3}\text{-OH}$ solution yields a spectrum composed of two somewhat broadened signals corresponding to the two types of $-\text{SiCH}_3$ groups residing in a micelle. Over the 450 hr aging time these initial signals slowly diminish with the appearance of other resonances which correlate with a complex hydrolysis process.

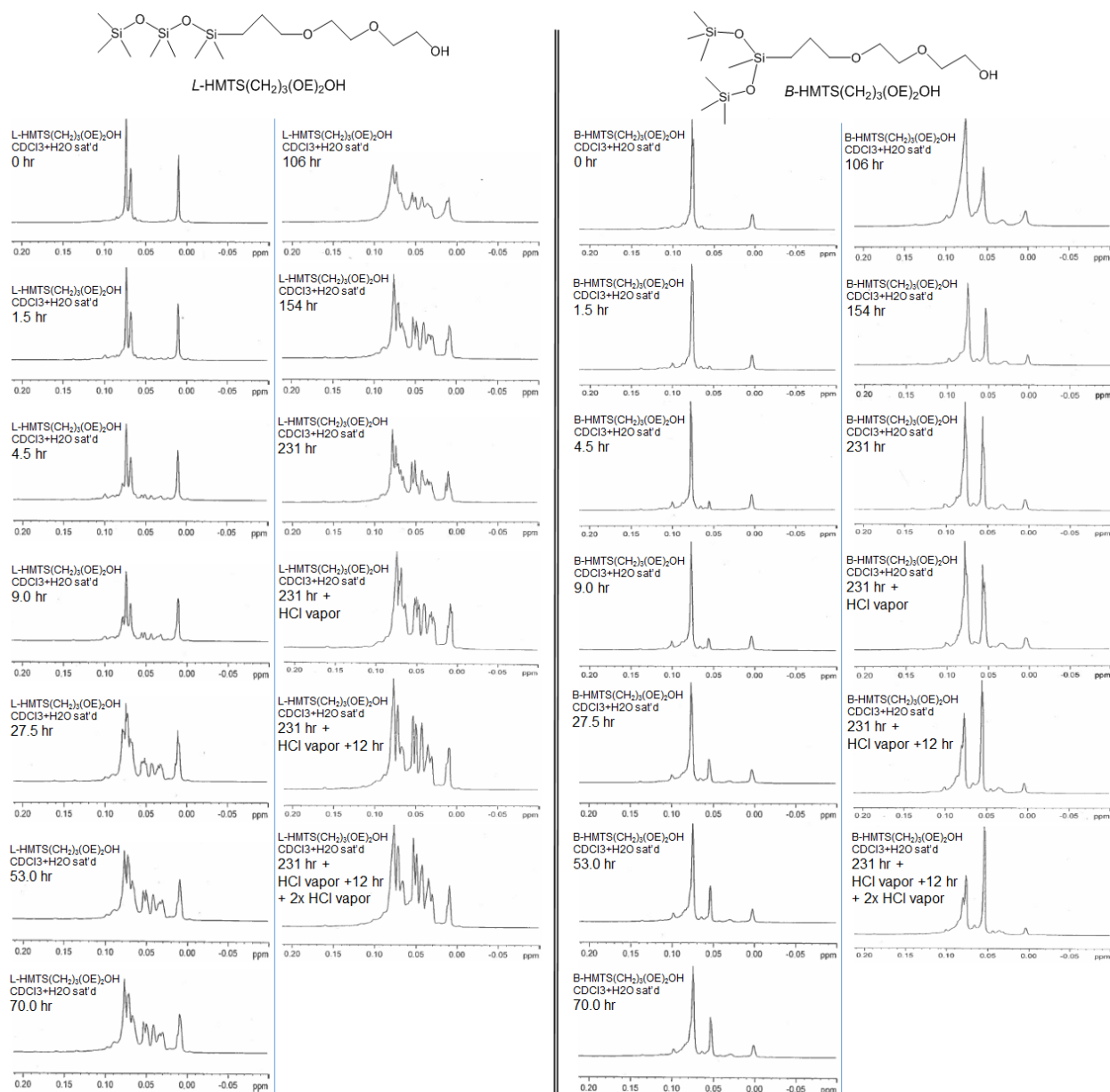


Figure 127. ^1H NMR spectra (–SiCH₃ region) of L and $B\text{-HMTS}(\text{CH}_2)_3(\text{OE})_2\text{-OH}$, and polydispersed $B\text{-HMTS}(\text{CH}_2)_3(\text{OE})_{12.3}\text{-OH}$ dissolved in H_2O -saturated CDCl_3 as a function of time illustrating hydrolysis of the trisiloxane group.

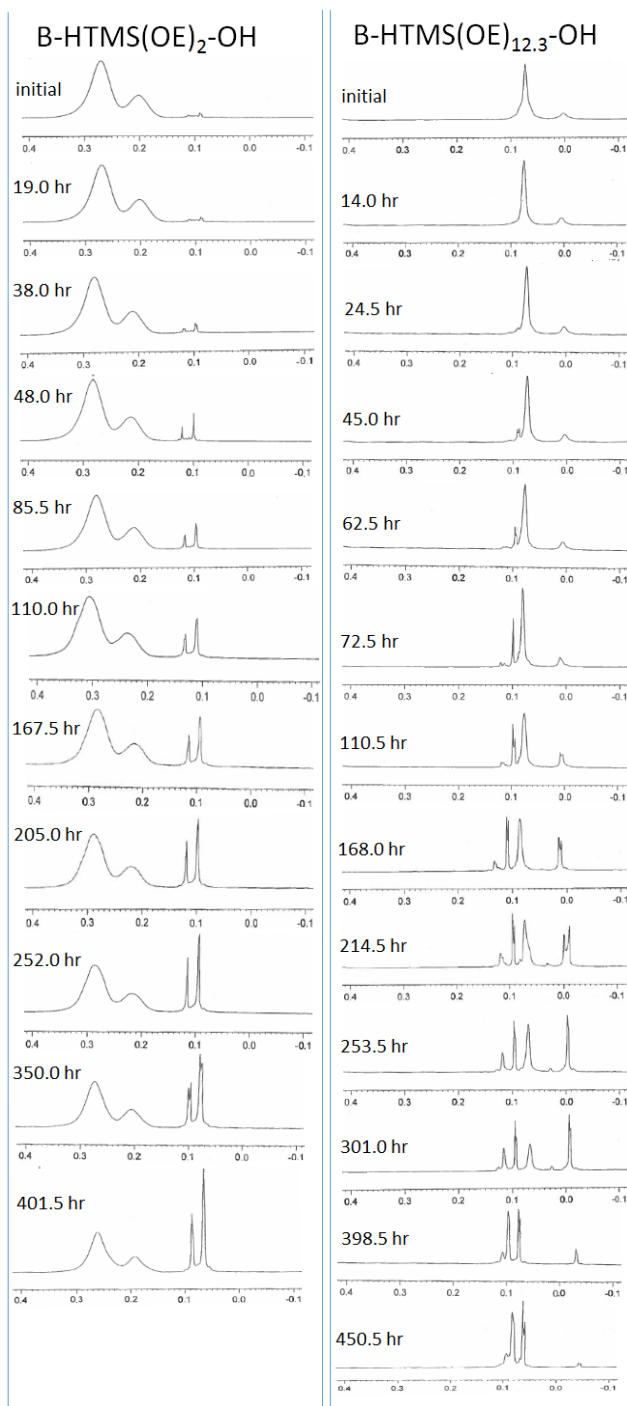


Figure 128. ^1H NMR spectra ($-\text{SiCH}_3$ region) of $B\text{-HMTS}(\text{CH}_2)_3(\text{OE})_n\text{-OH}$, $n = 2, 12.3$, dissolved in D_2O as a function of time illustrating hydrolysis of the trisiloxane group and micelle effect.

5.11.2. Accelerated Testing of Shelf-life

We conducted accelerated aged test listed in MIL-F-24385F with 3% concentrate of the surfactant formulations (column 1, Table 19). The accelerated aging was performed on the concentrates rather than the premix solutions. The surface and interfacial tensions were measured

on the premix solutions prepared by diluting the aged and fresh concentrates at 3% proportioning with distilled water and are listed in Table 61.

Table 61. Surface and Interfacial Tensions of 502W-Gluc225 and RefAFFF formulations listed in column 1, Table 19 after subjecting the 3% concentrates to accelerated aging test by holding the concentrate at 60 °C for 10 days in an oven as listed in MIL-F-24385F.

Foam Solution	Surface Tension (mN/m)	Interfacial Tension with Heptane (mN/m)
Ref AFFF	15.2	1.00
Ref AFFF Aged	15.4	1.60
NRL's silxoane502W-Gluc225 formulation	22.4	2.29
NRL's Siloxane502W-Gluc225 Form Aged	25.1	3.80

Table 61 shows that the 502W-Gluc225 formulation's surface tension increased only slightly by 2.7 mN/m before and after the concentrate was subjected to the accelerated aging. As expected, the surface tension of the RefAFFF containing the fluorocarbon surfactant was unchanged by the accelerated aging test.

Foams were generated using aqueous solutions of surfactant formulations listed in Table 61 using sparging method. The expansion ratio (volume of foam/volume of liquid) was calculated by measuring the weight and volume of the foam. Table 62 shows that the expansion ratio decreased slightly after subjecting the 3% concentrates for the 502W-Gluc225 and RefAFFF formulations. Figure 129 shows that the liquid drainage with time are comparable among different formulations after the concentrates were subjected to the accelerated aging test.

Table 62. Foam expansion ratios for the aged (accelerated) 3% concentrate of 502W-Gluc225DK formulations listed in column 1, Table 19.

Foam Solution	Expansion Ratio
Ref AFFF Unaged	9.4
Ref AFFF Aged	9.30
502W Form Unaged	8.2
502W Form Aged	7.60

Figure 130 shows that the life time (time for 100% degradation of foam) foam generated from 502W-Gluc225 formulation reduced by a factor of 2 when subjected to the accelerated aging test. Similarly, the fuel transport rates of foams generated from 502W-Gluc225 and RefAFFF are unaffected by the accelerated aging as shown in Figure 130. The fuel transport rate is suppressed for a shorter time after the accelerated aging for foams generated from 502W-Gluc225 formulation consistent with shorter foam life time seen in Figure 130.

Figure 131 shows bench scale 19-cm heptane fire extinction times for the 502W-Gluc225 (shown in column 1, Table 19) and RefAFFF formulations before after subjecting the 3% concentrates to accelerated aging by holding the concentrates at 60 °C for 10 days and performing

fire extinction with foams generated from the premix solutions. It shows that the extinction times are not changed significantly after accelerated aging.

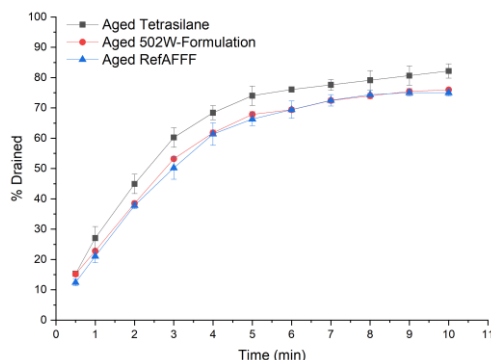


Figure 129. Liquid drainage from foams generated from premix solutions of different formulations after the concentrates were subjected to aging.

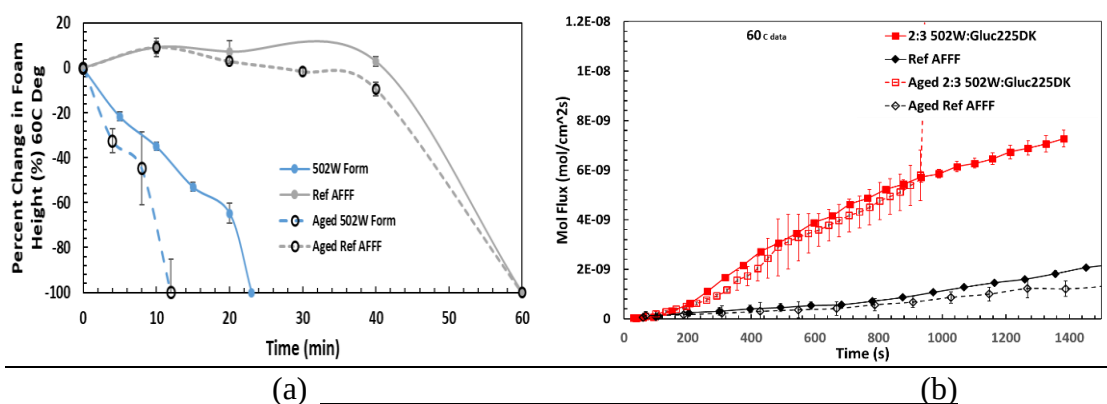


Figure 130. The effect of accelerated aging on foams generated from 502W-Gluc225 and RefAFFF formulations shown in column 1, Table 19, on (a) foam degradation, (b) heptane fuel transport through a 4-cm thick (initial thickness) foam layer covering a hot (60 °C) heptane pool.

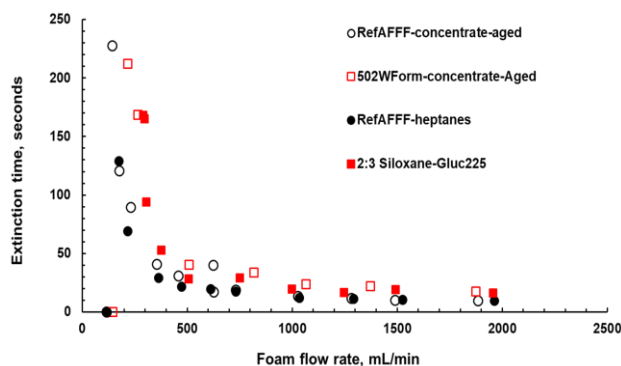


Figure 131. 19-cm heptane pool fire extinction before and after subjecting the 3% concentrates to accelerated aging. Data points along the x-axis represent no extinction in 5 min of foam application.

6. Conclusions

Current work showed that exploiting the chemical mechanisms is the key to developing fluorine-free foams that are equally effective in suppressing gasoline, heptane, and jet fuels and with an efficiency equal to AFFF. Future works should build on few general principles revealed in this work (1) surfactant's chemical structure has a significant effect on foam's ability to suppress fires, (2) when varying surfactant's chemical structure, head's hydrophilicity should be balanced with tail's hydrophobicity to preserve amphiphilicity, which affects interfacial activity and fire suppression, (3) increasing synergism between two types of surfactants adsorbed at an interface is the key to enhancing fire suppression, (4) surfactant head structures that suppress surfactant extraction by fuel can increase fire suppression, (5) surfactant structures that decrease fuel permeation through foams enhance fire suppression, and (6) foams cool pool surface rapidly and reduce fuel vapor pressure leading to enhanced fire suppression for high flash point fuels, whose fire extinction times are close to their pool coverage times.

Future works should focus on revealing the synergistic molecular interactions among different types of surfactants and fuels that control fuel permeation through foams and synergistic mechanisms of fire suppression. Increasing synergism between two types of surfactants for increased oleophobicity is crucial for improving fire suppression on a given fuel.

We developed a simple, well-defined, Reference AFFF formulation containing a mixture fluorocarbon (tridecafluorooctyl sulfonamide alkylbetaine) and hydrocarbon (Alkyl poly glycoside, APG) surfactants, and a solvent (Diethylene glycol butyl ether). Unlike the proprietary commercial AFFF, the composition and chemical structures of the components of RefAFFF are precisely defined. This enabled us to show the roles of individual surfactants and solvent components in fire suppression. By substituting a fluorine-free candidate for the fluorocarbon in the RefAFFF formulation, we were able to compare fire suppression performance of the fluorine-free candidate directly with the fluorocarbon surfactant. The key insight obtained is that the chemical interactions between surfactants and fuels affect fire suppression significantly and that fire suppression is affected by the variation in chemical structures of the surfactants and fuels. One of the ways the chemical interactions affecting fire suppression involves a surfactant being extracted from foam by the fuel or fuel being extracted into the foam at an enhanced rate. The exchange of surfactant and fuel could lead to enhanced rate of permeation of fuel vapors through a foam layer and longer fire extinction times. The chemical interaction effects on fire suppression are significantly smaller for the RefAFFF containing the fluorocarbon surfactant compared to a fluorine-free substitute. This new approach unlocks chemical paths to improving fire suppression in contrast to the current approaches based on physical mechanisms such as aqueous film formation controlled by the spreading coefficient and foam's water content controlled by liquid drainage with the use of gums.

Trisiloxane oxyethylene with a terminal hydroxyl was investigated as a fluorine-free alternative to the fluorocarbon surfactant. The key insight is that chemical interactions between the trisiloxane and APG surfactants result in a dramatically enhanced fire suppression compared to the fire suppression using either the siloxane or APG components individually instead of the mixture. We call this as the synergistic effect and is specific to a fuel. The increased fire suppression is partly due to a dramatic reduction in foam degradation when the foam is exposed to fuel vapors. When the foams are generated using individual surfactant components, the foams

are degraded by the fuel vapors very quickly unlike the foams generated from the surfactant mixture. Thus, the synergistic interactions between the surfactants reduces foam degradation by a fuel. The reduced foam degradation enables foam to form a more effective and thicker barrier to fuel vapors, when the foam is applied on to a burning fuel pool. A more effective fuel barrier cuts-off fuel supply to the fire and extinguishing it more quickly. We hypothesized that the skinny oxyethylene head and large trisiloxane tail fits geometrically with the large head size and skinny alkyl tail of the APG to form a bi-layer at the bubble surface preventing fuel vapor permeation through the foam. Varying siloxane's head size and APG's tail and head sizes affected the degree of synergism and fire suppression.

In addition to the synergism, surfactant's amphiphilicity and polydispersity can affect fire suppression significantly. Both the siloxane's oxyethylene head APG's tail and head are polydispersed having a distribution of sizes. Increasing the average oxyethylene length of the siloxane surfactant in a siloxane-APG mixture resulted in minima in both the fuel transport rate and fire extinction time. This could be due to competition between the increased synergism and decreased amphiphilicity as the head size is increased with the tail size fixed. Slight minima in foam degradation rate and fire extinction time were also exhibited when we varied the head and tail sizes of monodispersed-APG. This is because we varied the alkyl tail size, with glycoside head size fixed, or varied the glycoside head size, with the alkyl tail length fixed. The variation of head or tail sizes one at a time could have affected the amphiphilicity of APG significantly. Furthermore, we employed monodispersed APG in a mixture containing polydispersed siloxane surfactant. This could have affected the geometrical matching between the two types of surfactants and could have affected the degree of synergisms. Indeed, when we increased the average glycoside head size of APG in the polydispersed siloxane-APG mixture, both foam degradation rate and the fire extinction times were reduced significantly due to increased synergistic effects.

To improve fire suppression to match that of AFFF, it is crucial to combine structurally compatible surfactants for increased synergistic effects and to suppress fuel/surfactant extraction. While the effects of chemical interactions among surfactants (in a mixture) and fuels on foam degradation, fuel transport, and fire suppression are explored by varying the surfactant-fuel chemical structures, the fundamental nature of the chemical interactions remains unclear. Without a fundamental understanding of the chemical interactions, it will remain empirical and irregular to find compatible surfactant structures for a given fuel. To this end, it is crucial to quantify the chemical interactions in a monodispersed system, which is much simpler than the polydispersed surfactants used in the current investigation. Within a simpler system, a systematic variation of surfactant structure using custom synthesis remains a challenge. Furthermore, investigating surfactants at an interface using Langmuir-Blodgett films, single lamella, and single bubble surface exposed to fuel vapors could provide new insights. A variety of analytical tools such as NMR, IR, contact angles, Atomic Force Microscope, Brewster Angle Microscope, and MRI techniques may reveal the fundamental nature of the chemical interactions. Modeling tools including machine learning in combination with the experimental methods need to be employed to further elucidate the complex phenomena involved in fire suppression with aqueous foams.

In an effort to evaluate the potential toxicity of the formulation, a series of acute and chronic toxicity tests were performed with the individual formulation components and the proposed end-use mixture. Toxicity tests were conducted with the cladoceran, *Ceriodaphnia*

dubia, the fathead minnow, *Pimephales promelas*, and the green algae, *Raphidocelis subcapitata*. Testing followed standard USEPA and OECD toxicity testing methodology. The study design of the mixture testing used a toxic unit (TU) approach where median-lethal effect concentrations (LC50s) for acute tests and 20% sublethal effect concentrations (EC20s) were identified for each compound singly (LC50 or EC20 quantified as one TU), followed by exposure to the prescribed mixture. The candidate end-use AFFF formulation mixture did not contain equivalent amounts of each single compound, therefore the TUs were of varying influence. Biological endpoints were assessed to determine whether the mixture exhibited additive (no difference in toxicity as a mixture), less-than-additive (reduced toxicity as a mixture), or more-than-additive (increased toxicity as a mixture) effects. The acute studies (toxicity based upon 48-hr or 96-hr survival) demonstrated that the mixture tested had additive or more-than-additive effects. In the chronic tests (72 h or 7 d), the scenario resulted in additive or less-than-additive effects. When comparing each species based upon measured mixture concentrations, *P. promelas* and *C. dubia* were more sensitive to chronic exposures versus acute exposures, while the algae, *R. subcapitata* was the least sensitive to the mixture tested.

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8. Productivity

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