FINAL REPORT

Fluorine-Free Aqueous Film Forming Foam

SERDP Project WP-2738

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14. ABSTRACT Fluorine-free fire-fighting foam formulations containing primary and secondary surfactants, solvents and polymers have been evaluated using surface chemistry techniques to understand their behavior in aqueous solution, and at air/water and fuel/water interfaces in fresh and salt water. These physical measurements determine foam stability to fuel, spreading and fire performance. Experimental formulations tested in the 28ft^2 MIL-PRF 24385F fire test gave extinguishment times of 36" and burnback of 477" on heptane in fresh water, and 75" extinguishment and 286" burnback on gasoline in salt water. Further work is needed to reduce extinguishment times to approach the current MIL-PRF 24385F fluorine-free specification.

A life cycle assessment using the method described in ISO 14040 and 14044 compared the environmental impact of AFFF and fluorine-free foams and identified routes to improving environmental performance. AFFF foams typically had greater impact on resource depletion, environmental quality and human health. A model AFFF foam containing C6 fluorosurfactant exposed to fire did not show evidence of new fluorocarbon species. Water draining from the foam is initially severely depleted in fluorocarbon content, with implications for clean-up of spent foam

15. SUBJECT TERMS

Fire-fighting foams, fluorine-free, MIL-PRF 24385F, fire testing, life cycle analysis, fluorosurfactant

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List of Acronyms

AFFF	Aqueous film-forming foam
CAS	Chemical abstract service
DALY	Disability adjusted life years
DSA	Drop Shape analyzer
DST	Dynamic surface tension
EN	European norms
ERA	Environmental risk assessment
F3	Fluorine-free foam
FTS	Fluoro-telemor surfactant
FtSaB	Fluorotelomer sulfonamido betaine surfactant
GWP	Global warming potential
HPLC-MS qToF	High performance Liquid Chromatography Mass Spectrometry Quadrupole Time of Flight
HC	Hydrocarbon surfactant
ICAO	International Civil Aviation Organization
IMO	International Maritime Organization
KW	Kilowatt
LC_{50}	Lethal concentration, 50 %
LCA	Life cycle analysis
LCI	Life cycle inventory
Mil-spec	Military specification
MSDS	Material safety data sheet
NO_x	Nitrous oxides
NFPA	National Fire prevention association
NMVOCs	non-methane volatile organic compounds
ODP	Ozone depletion potential
OECD	Organization for Economic Cooperation and Development
PFOA	Perfluorooctanoic acid
PFAS	Per- and polyfluorinated compounds
PFHxA	Perfluorohexanoic acid
PM	Particulate matter
PM2.5	Particulate matter <2.5 μm
PM10	Particulate matter <10 μm
POPs	Persistent organic pollutants
SON	Statement of Need
UL	Underwriters Laboratory
VOC	Volatile organic compound

Disclaimer

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Keywords

Fire-fighting foams, fluorine-free, MIL-PFF 24385F, fire testing, life cycle analysis, fluorosurfactant

1. ABSTRACT

Objective

The objective of this project was to increase our understanding of specific physical and chemical processes that underlie fire-fighting foams, and how specific components of a foam formulation can deliver the properties required for good fire performance whilst minimizing environmental burdens. Model fluorine-free foam formulations were developed and optimized for fire performance in the MIL-PRF 24385F 28ft^2 test.

A life cycle assessment compared the environmental impact of AFFF and fluorine-free foams in order to identify routes of improving environmental performance.

Technical Approach

The generation and deployment of fluorine-free fire-fighting foam was broken down into individual processes. For each, the desirable physical properties were hypothesized and tested with laboratory physical measurements and small-scale fire tests. All foam components were limited to readily biodegradable surfactants, solvents, polymers and other additives.

Life cycle analysis of fire-fighting foams used the method described in ISO 14040 and 14044.

Results

Model foam formulations of increasing complexity were evaluated using surface chemistry techniques to understand their behavior in aqueous solution, and at air/water and fuel/water interfaces in fresh and salt water. These physical measurements were correlated with key foam properties such as foam stability to fuel, spreading and with fire performance requirements of extinguishment and burnback times. The roles of primary and secondary surfactants, solvents and water-soluble polymers were tested.

Statistical optimization of one formulation gave an extinguishment time of 36” in fresh water in the 28ft^2 MIL-PRF 24385F fire test on heptane and burnback of 477”. An alternative formulation gave 75” extinguishment and 286” burnback on gasoline in salt water.

Data on the manufacture of AFFF and fluorine-free foams have been collected and the ReCiPe method used to compare environmental mid and endpoints. AFFF foams typically had greater impact on resource depletion, environmental quality and human health. A model AFFF foam containing C6 fluorosurfactant exposed to fire did not show evidence of new fluorocarbon species. Water draining from the foam is initially severely depleted in fluorocarbon content, with implications for clean-up of spent foam.

Benefits

The project has given a better understanding of the role of specific foam components in delivering the properties required of a fire-fighting foam, and show that foams based on hydrocarbon surfactants can extinguish within 30-60”, and give burnback times longer than 360”.

The life cycle analysis shows that the manufacture of fluorocarbons imposes higher environmental cost than hydrocarbon surfactants.

2. EXECUTIVE SUMMARY

The environmental issue being addressed is the use of fluorosurfactants and fluoropolymers in aqueous film-forming foams (AFFF) for fire suppression. All current foams that meet the requirements of MIL-PRF 24385F contain fluorocarbons.

Historically, AFFF foams contained fluorocarbons with a C_8F_{17}- chain to give the foam good heat stability and the very low surface tension required for film formation on hydrocarbon fuels. It is known that these fluorocarbons degrade in the environment to form perfluorooctanoic acid, PFOA. More recent AFFF foams have replaced the C_8F_{17}- chains with materials containing 6:2 fluorotelomer chains, $C_6F_{13}C_2H_4$-. These surfactants partially break down in the environment, via 6:2 fluorotelomer sulfonate, eventually to perfluorohexanoic acid, PFHxA.

Foams containing only hydrocarbon surfactants would be expected to fully biodegrade in the environment within a short space of time. Existing hydrocarbon surfactants that are used in other applications such as detergents and personal care products have relatively well established toxicology properties, and would not require lengthy and expensive toxicology testing programs.

Objectives (SON)

The Statement of Need (SON) is to develop a fluorine-free surfactant formulation for use in Aqueous Film Forming Foam (AFFF) fire-suppression operations. Proposed research should identify and test fluorine-free surfactants for use in AFFF that meet the performance requirements defined in MIL-PRF-24385F. New formulations must be compatible with existing AFFF and supporting equipment. Proposers should include testing to validate persistence and aquatic toxicity of alternative materials.

In addition, an assessment of the human health and environmental impacts of proposed ingredients, formulations, and byproducts should be included. A baseline lifecycle framework must identify the elements of a life cycle inventory that are already known, those that will be investigated during the course of the project, and those that are beyond the scope of the proposed work.

Technical approach - Scientific Understanding

This project aims to use scientific methods to increase understanding of the physical and chemical processes that underlie fluorine-free fire-fighting foams, and use it to develop a fluorine-free surfactant formulation that meets the fire performance requirements defined in MIL-PRF 24385F. National Foam have already developed and manufacture fluorine-free foams for use in commercial aviation (ICAO B and C), petrochemical (UL, LASTfire), Maritime (IMO), and Fire and Rescue (EN 1568) applications. This project builds on National Foam existing in-house knowledge, expertise and products to address the MIL-PRF 24385F specification.

The generation and deployment of fluorine-free fire-fighting foam has been broken down into individual stages. For each stage, the desirable physical properties have been hypothesized and tested through physical chemistry measurements and small-scale laboratory tests that give quantitative data. The project aims to understand the relationships determining:

Surfactant formulation → surface chemistry → Foam physical properties
fire performance. ←

The scope is limited to existing readily biodegradable surfactants, solvents, polymers and other additives that do not contain fluorine.

The importance of physical properties including dynamic surface tension, critical micelle concentration, bubble size distribution, foam rheology, and vapor diffusion rates have been tested in the laboratory using model formulations and tests of increasing complexity.

Results and Discussion

Task 1. Purchase equipment

Two key pieces of equipment were identified as essential in measuring and understanding foam properties. A rheometer, Malvern Kinexus Pro+ C25 with rotating cylinder and vane has been purchased. This measures fundamental rheological properties of foams and concentrates such as viscosity vs shear rate, yield stress and viscoelasticity. An optical microscope, Olympus BX53M with software to analyze bubble size distribution has also been acquired. This allows a visual study of foam interaction with hydrocarbon fuel, and statistical analysis of bubble size distribution.

Task 2. Primary surfactant package–correlate formulation with physical properties and foam quality

The surface chemistry properties of a range of single surfactants have been investigated by measuring dynamic and equilibrium surface tensions, determining the critical micelle concentration, diffusion coefficient and packing of surfactant molecules at the air–water interface.

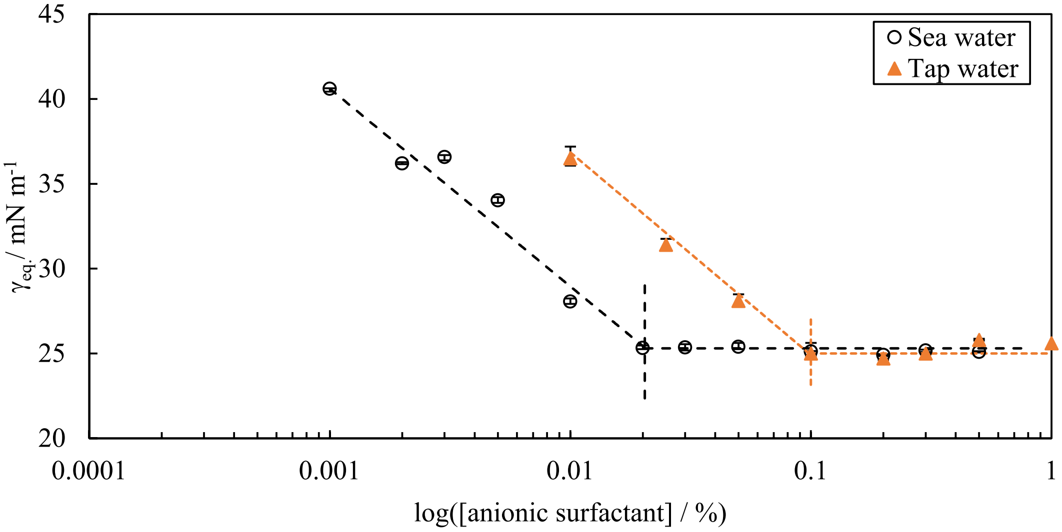


Figure 1. Determination of critical micelle concentration of an anionic surfactant in fresh and sea water.

The effect of adding hydrocarbon fuel, heptane or gasoline, to the foam structure and stability has been examined by optical microscopy. If the fuel is able to spread across the aqueous phase, it can destroy the bubble structure and collapse the foam. Figure 2 shows on the left a foam destroyed by entering of fuel into bubbles. On the right fuel droplets are contained within the foam structure and the foam is stable.

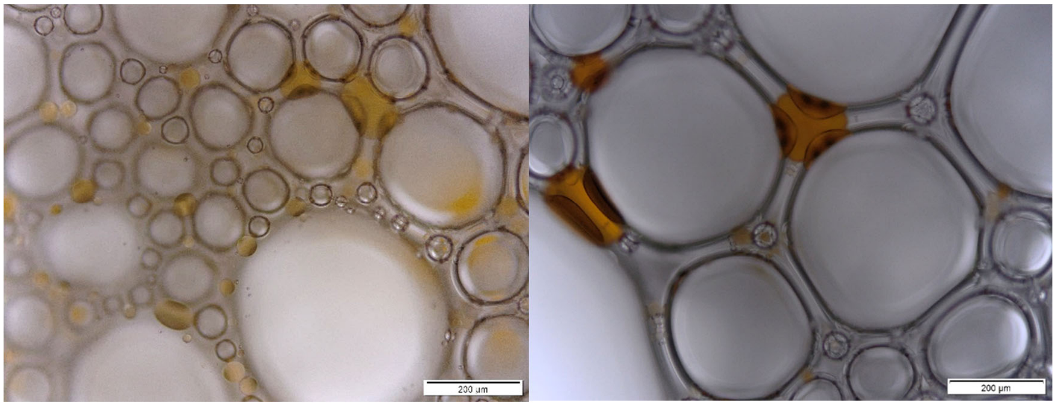


Figure 2. Optical microscopy of foam interaction with heptane dyed orange. Unstable foam on the left, stable foam on the right.

A small-scale fire test has been used to understand how foam behaves at a fuel surface. The surfactant structure and foam physical properties have been correlated with the microscopy images and the fire spreading and extinguishment performance. Systems have been selected with various hydrophilic groups that display the properties required for a fire-fighting foam.

Figure 3. Small scale lab test of extinguishment and foam stability on fire.

Task 3. Solvents – correlate formulation with physical properties and foam quality

Glycol ethers are used in fluorocarbon-based foams as foam boosters, increasing the expansion ratio significantly. The mechanism is believed to be an increase in the solubility of the fluorocarbon molecules in the aqueous foaming solution, raising the critical micelle concentration and allowing greater diffusion of fluorocarbons to the newly formed air–water interface. This phenomenon has been observed in fluorine-free foams but is less significant since hydrocarbon surfactants have greater solubility and mobility in water than fluorocarbons. A more important effect is that of fuel emulsification; this occurs when the foam strikes the burning or hot fuel, leading to fuel pick up. It is enhanced by the presence of solvent molecules. Foams containing fluorine are able to trap the fuel within the foam lamellae, and reduce the ignition or foam destruction of the fuel droplets. Hydrocarbon foams do not have this ability and fuel pick-up can seriously affect foam performance. This will be particularly marked when the foam concentrate is proportioned at a “rich” rate. Other mechanisms for increasing expansion ratio have been explored. Foams intended to be proportioned with sea water benefit overall from the presence of a solvent, and will be included in sea water formulations.

Task 4. Secondary surfactants – correlate formulation with physical properties and foam quality

Examination of mixed surfactant systems has focused on mixtures of a primary surfactant package that is responsible for generating a high expansion ratio in the first few seconds of foam life and a secondary package that thickens and stabilizes the foam over a longer time period. The ratio of the two co-surfactants, and effects of concentration and pH have been studied. A secondary surfactant is added to the formulation to increase foam elasticity and stability to fuel. The secondary surfactant adsorbs more slowly at the air–water interface by mechanisms such as lower aqueous solubility, lower critical micelle concentration or slower diffusion to the surface. Some secondary surfactants may be polymeric, and may rearrange or denature at the interface.

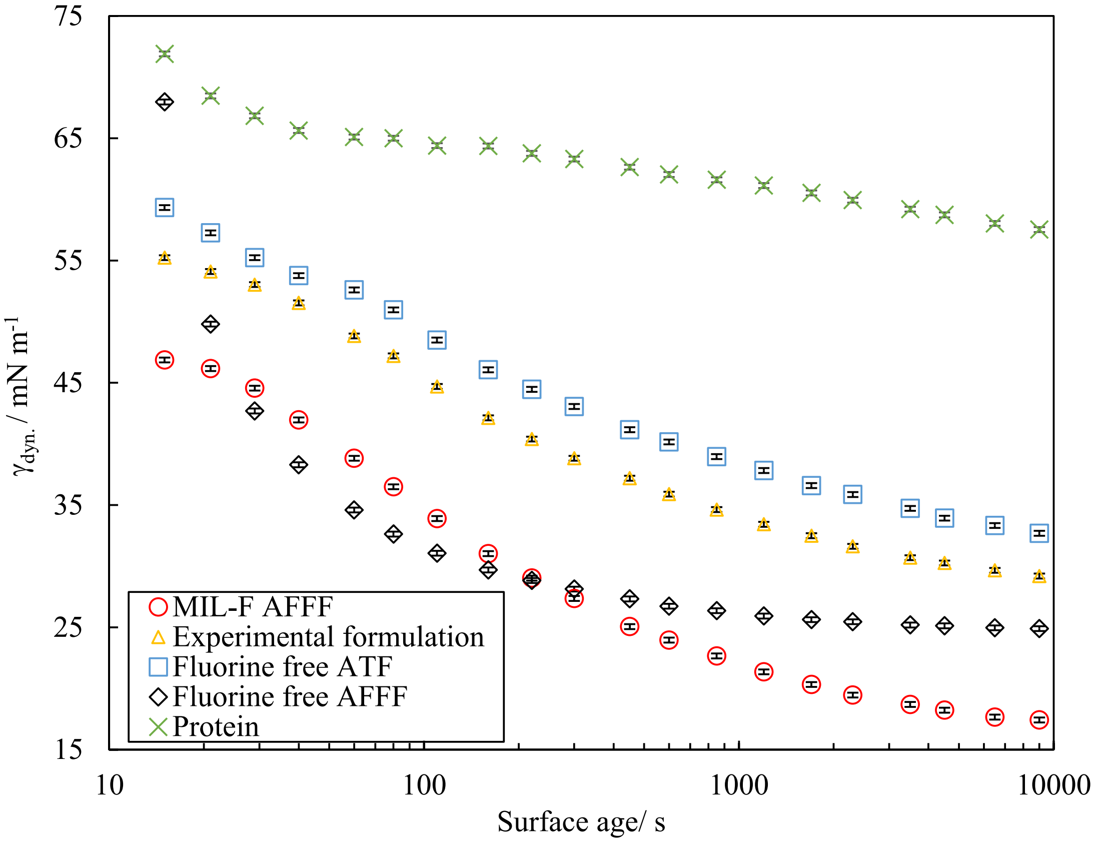


Figure 4. Dynamic surface tension of mixtures of surfactants illustrating the differences between foam types.

The formulation has been correlated with fire performance by lab scale testing in a 79 or 113 cm^2 brass pan on heptane to measure extinguishment time, the ability of the foam to edge seal at the rim of the pan and to resist destruction by hot fuel. This test allows differentiation of formulations based on properties and fire performance.

Two mixed surfactant packages have been identified with properties for deployment in fresh and sea water respectively.

Task 5. Select polymers

Incorporating polymers increases foam viscosity, stability to fuel, and during a fire test will reduce disruption of the blanket by freshly applied foam. A wide range of water-soluble polymers have been screened for their ability to affect foam properties and performance. A base formulation was prepared containing the preferred primary surfactant package, and polymers were added. This solution was charged to a laboratory branch pipe and foam prepared using the standard MIL-PRF 24385F nozzle. Key foam properties including expansion ratio and drainage time were measured, as well as rheological properties such as foam viscosity and yield stress.

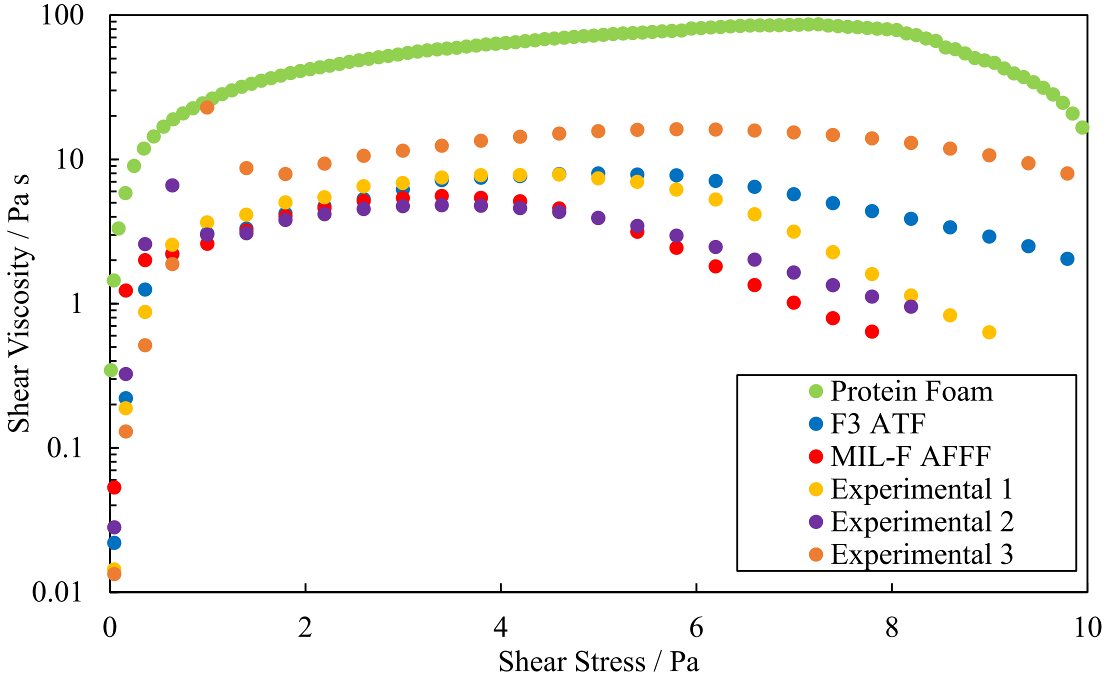


Figure 5. Yield stress of formulations containing polymers.

Lab scale tests of the stability of the foam on hot heptane were conducted to test the ability of the polymer to improve foam stability on fuel.

Other stabilizing mechanisms apart from polymers have been evaluated. A modified clay shows promise in stabilizing the foam to hot or burning fuel. Cellulosic fibers did not improve foam properties or fire performance.

Larger quantities of the experimental formulations were prepared, and full scale MIL-PRF 24385F 28 ft^2 fire tests carried out. The best performance was extinguishment in 48 seconds (target <35) and burnback 9 minutes (target >6). Based on these tests, three polymers were progressed.

Task 6. Experimental foam formulations

Foam formulations consist of:

- Primary hydrocarbon surfactant package to generate a foam with a high expansion ratio
- Secondary surfactants to improve foam properties
- Solvent to increase component solubility in sea water
- Polymers or clays to alter foam rheology and stability to fuel

Several experimental formulations were tested in the MIL-PRF 24385F 28ft^2 fire test on heptane fuel, using the exact conditions specified in the standard – nozzle, application rate, fuel volume and pan size. The fastest extinguishment time was recorded as 39 seconds, and this formulation was selected for optimization using a design of experiment statistical method.

Figure 6. 28ft^2 MIL-PRF 24385F fire tests showing 90%, 99% control, extinguishment and burnback.

Task 7. Statistical analysis

Eight formulations were prepared with high (+) and low (-) concentrations of each component. Each formulation was tested in a 28ft^2 fire test, and foam properties measured. The statistical analysis assumes a linear relationship between concentration and properties, but the analysis showed there was a more complex, quadratic relationship. This required the preparation of four more formulations to fully characterize the relationship between component concentration and foam properties.

Formulation	Primary surfactant	Secondary surfactant	Polymer
1	+	+	+
2	+	+	-
3	+	-	+
4	+	-	-
5	-	+	+
6	-	+	-
7	-	-	+
8	-	-	-

The optimized formulation was identified and forecast to give an extinguishment time of 29 seconds. This formulation was prepared and tested, with a measured extinguishment time of 36 seconds.

Lab scale foam generation and small scale fire tests have been carried out on the foam concentrated proportioned at half (lean) and five times (rich) the nominal proportioning rate.

Proportioning rate	Expansion ratio	Drainage time (m:s)	Lab extinguishment time on heptane (s)
Lean x0.5	8.74	6:12	11
Normal x1	9.00	6:19	13
Rich x5	9.03	6:03	13

Based on small scale tests no significant differences were observed but this needs to be confirmed on a large scale.

Persistence and aquatic toxicity.

All components of the experimental formulations are completely biodegradable in the natural environment over a short period of time. No components are bioaccumulative in living organisms.

Task 8. Gather data on foam manufacture

Data collection for the components of four fire-fighting foams was completed. This covers two fluorinated AFFF foams certified to MIL-PRF-24385 and ICAO B standards and two fluorine-free foams certified to UL162 and ICAO B standards. Data are available for raw material, energy and water usage for the synthesis of fluorocarbon telomer 6:2 FTS, conversion of this to fluorosurfactants has assumed conventional synthetic routes. Other components such as solvents and hydrocarbon surfactants have used figures from databases and literature.

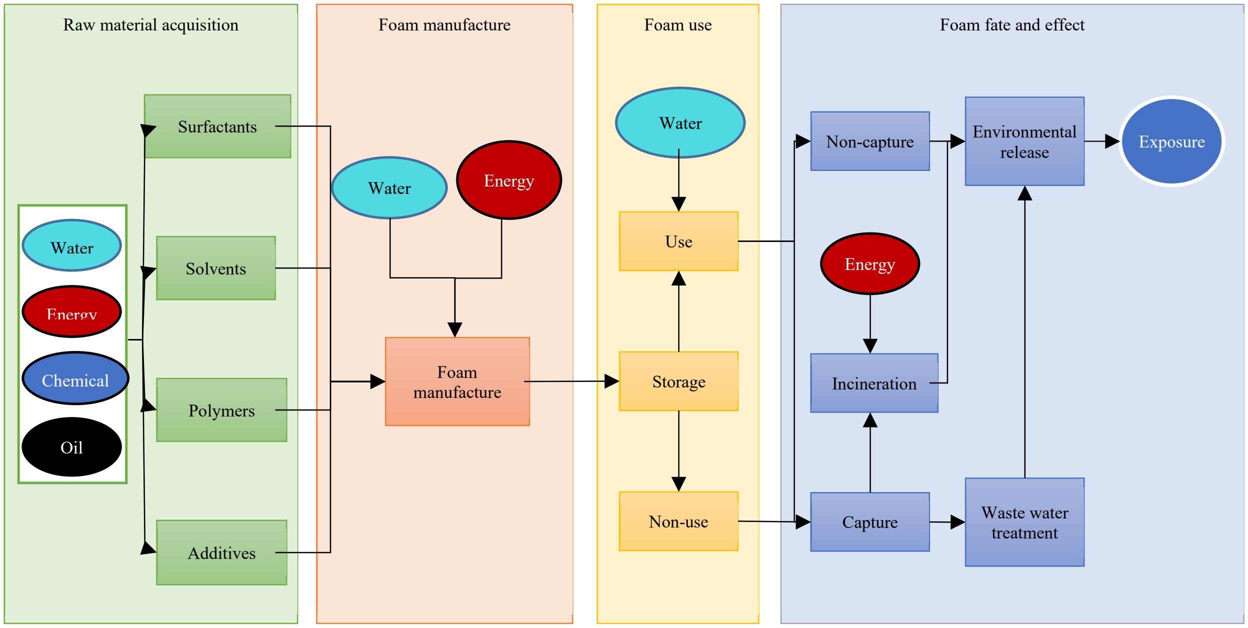


Figure 7. Fire-fighting foam product flow.

Task 9. Fate of foam components

To understand the fate of fluorocarbons applied to a hydrocarbon fire, a PFAS analysis method using HPLC-MS qToF has been developed.

The concentration of 6:2 FtSaB draining from foam has been quantified. Fig 8 shows that initial drainage is severely depleted in 6:2 FtSaB due to adsorption at the air/water interface. As the foam ages, the concentration in the drained solution increases.

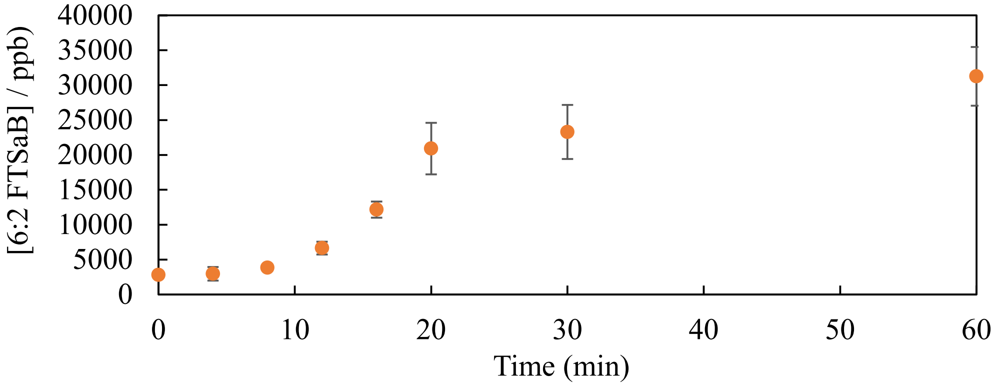


Figure 8. Drainage of 6:2 FtSaB from aged foam.

Task 10. Persistence and toxicity of foam components

Components of fluorine-free foams are all readily or inherently biodegradable, on a timescale that is too fast to make intermediate breakdown products a subject of concern.

No gaps in persistence data have been identified that would require additional toxicity testing.

Task 11. Exposure model

Available information has been drawn from literature to better understand the potential impact of PFAS use in firefighting foam products. The fate and transport mechanisms are key to the global distribution of PFAS compounds and are influenced by the nature of the environment to which they are exposed

The ReCiPe method was used to compare 2 fluorosurfactant foam products with 2 fluorine-free foam products. Midpoint and endpoints were calculated for each life cycle stage on individualist (10 year), hierarchist (100 year), and egalitarian (1000 year) bases using ReCiPe methodology, the Ecoinvent database and peer-reviewed publications as data sources. The stages considered within the life cycle assessment were: constituent acquisition, manufacture, use, and disposal. The study found that constituent acquisition represented the predominant contributor to detrimental impact of environmental quality, human health, and resource depletion. On a volume basis (per L foam), the AFFF products performed poorly relative to the fluorine-free products, however, when considered according to functional unit (performance based: determined by the quantity of foam required to control and extinguish a 10 m^2 heptane fire for 1 h), there was less difference between the 4 products,

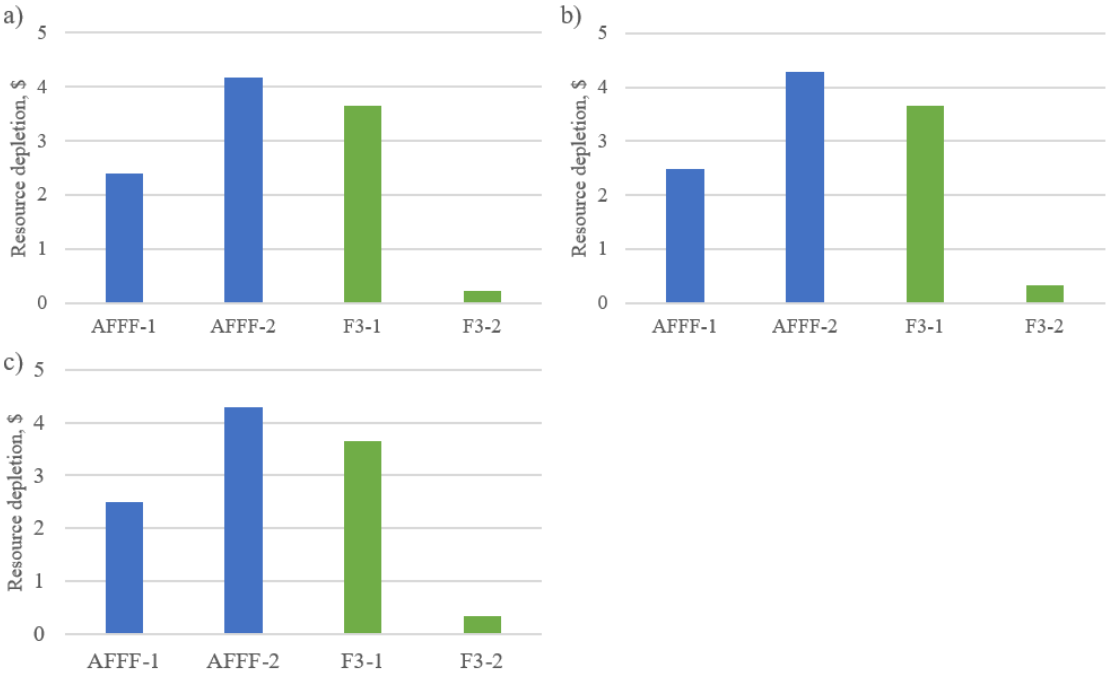


Figure 9. Endpoint characterisation for the resource depletion for a) individualistic, b) hierarchist, and c) egalitarian time scales for Scenario 1 in dollars ($).

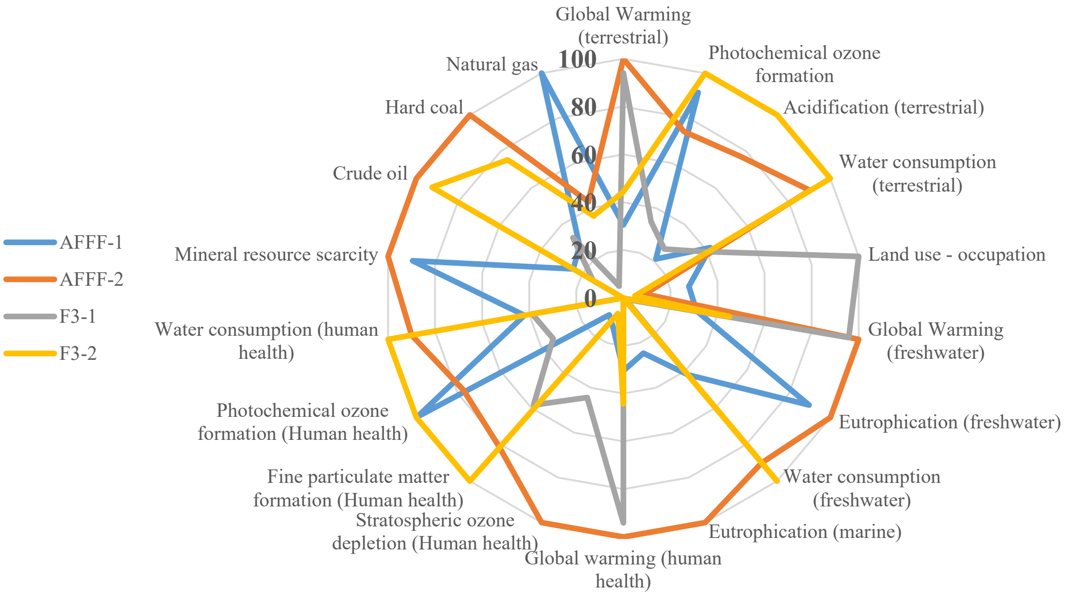


Figure 10. Relative midpoint categories for Scenario 2 using the hierarchist timescale.

Task 12. Toxic effects

Environmental and human toxicology were excluded from the LCA. Nevertheless, the biodegradable nature of fluorine-free foam products alongside the results of the LCA suggest they are more environmentally sustainable than AFFF foam products.

Bioconcentration of PFAS compounds has been observed as they are transferred from low to higher trophic levels organisms. Typically, studies show bioaccumulation of PFAS are within proteins rather than lipids, which is common for other POPs. A key human exposure pathway for PFAS is via drinking water and aquatic products, such as fish. The presence of PFAS within soils and sediment may contribute indirectly through uptake by crop plants destined for human consumption.

Fluorine-free foams utilize hydrocarbon surfactant alternatives in place alongside the traditional PFAS-based surfactants. The environmental fate and effect of hydrocarbon surfactants and their metabolites is highly dependent on their physicochemical properties. Hydrocarbon (HC) surfactants are present within both fluorine and fluorine-free foam formulations, where they provide increased detergency and solubilization. HC surfactants in foams are typically sodium alkyl sulfates comprising a mixture of homologues (C8, C10 or C12). Their prolific utilization and consumption has led to the detection of surfactants and their metabolites at various concentrations in numerous geographies and environmental matrices.

Task 13. Identify improvements

Improvements have been identified in the following areas: The energy required in manufacture of raw materials can vary substantially depending on the source of the raw material. Raw materials from natural resources, preferably plant-based, have lower environmental impact than those from oil, which are in turn better than those from minerals. Fluorocarbons have particularly high energy requirements since they are derived from fluorspar. Spent foam solution or unused foam concentrate can be allowed to biodegrade naturally if all components are biodegradable, with little environmental cost. Persistent materials that require incineration or another method of destruction are much more energy-intensive. Overall, foam formulations that do not contain fluorine result in lower resource depletion than fluorine-containing foams. The concentration of fluorosurfactant (6:2 FTSaB) in foam solution applied to a model fire was much lower in the early drainage samples. This has potentially significant implications for both foam clean-up and understanding the behavior of the foam-system.

Implications for future research

The results of this project demonstrate that fire-fighting foams developed without the use of fluorocarbon surfactants or polymers can give high levels of fire performance in the standard MIL-PRF 24385F 28 ft^2 fire tests in fresh water on heptane fuel. Foam is generated using the standard 2 gallon per minute nozzle with spreader tip and delivered at the normal application rate. These foams can be formulated as 3 or 6 % foam concentrates with flowable characteristics, and can be proportioned using current proportioners.

Experimental formulations produce extinguishment times on heptane are around 35 seconds, further optimization of the formulation and fire-fighting method might reduce this to potentially 30 seconds. Burnback times comfortably exceed the target of 6 minutes and do not require improvement.

Further research into performance in sea water is required to develop foams for use in sea-based operations. Optimization of performance on gasoline will be required should future specifications require gasoline as test fuel.

Large scale fire performance at lean and rich proportioning, and after ageing has not yet been established. Corrosion performance has not been measured, although addition of suitable iron and copper corrosion inhibitors generally satisfies this requirement.

The life cycle analysis should be extended to cover environmental and human toxicology effects.

Benefits

This project demonstrates that fire-fighting foams based on hydrocarbon surfactants can deliver fire performance in MIL-PRF 24385F 28ft^2 tests approaching that of an AFFF in fresh water. Foam concentrates can be deployed as drop in replacements for use in existing hardware.

These new foams will continue to ensure the protection of DoD personnel and assets at airfields and other land-based operations without use of persistent materials and potential long term damage to the environment.

The use of existing surfactants, already used in other industries, gives a rapid and low cost route to deployment without the need for extensive testing of toxicological and environmental properties.

Supporting new formulations with life cycle assessments ensures that the environmental burdens associated with the manufacture and use of fire-fighting foams can be measured and controlled.

3. OBJECTIVES

This research has been performed in response to Statement of Need Number WPSON-17-01, October 29, 2015, Fluorine-free aqueous film-forming foam. This SON required the development of a fluorine-free surfactant formulation for use in Aqueous Film-Forming Foam (AFFF) fire suppression operations. Persistence and aquatic toxicity of the materials used should be assessed. A lifecycle framework and inventory were also requested.

3.1. Understanding fire-fighting foam

The first objective of this project is to gain a better scientific understanding of the physical and chemical processes that underlie fire-fighting foams. The importance of properties including dynamic surface tension, bubble size distribution, foam rheology, and vapor diffusion rates will be tested in the laboratory using model formulations of increasing complexity:

Fire performance	Foam property	Physical property measured	Technique
Control	Expansion ratio, spreading	Dynamic surface tension, critical micelle concentration, surface excess	Bubble tensiometer, Wilhelmy plate
Control, extinguishment	Spreading	Yield stress	Rheology
Extinguishment	Foam stability to fuel	Foam / fuel interaction	Microscopy
Burnback	Vapor diffusion	Vapor permeability	Drager tube

Table 3.1. The key principles relating fire performance to physical chemistry of foam.

This study will also show how the components of a foam formulation can deliver the physical properties required for good fire performance.

Outdoor 28ft^2 fire testing will be performed on promising experimental formulations. One formulation will be optimized using statistical methods to develop a fluorine-free surfactant formulation that meets the performance requirements defined in MIL-PRF 24385F.

3.2. Development of a fluorine-free fire-fighting foam

Fluorine free foam can be defined as a product which has no fluoro-containing constituents and manufactured on a designated line which has not been used to manufacturer any fluorine-containing product. Furthermore, trace amounts of fluorine may be present due to water contamination

A true fluorine-free drop-in replacement for existing applications of AFFF will provide fire performance equivalent to the current MIL-PRF 24385F standard, at current application rates with existing equipment and will be effective on both heptane and unleaded gasoline fuels. The foam concentrates will be sufficiently mobile to be used through existing proportioners to give both 3 % and 6 % foam solutions. Foam will be generated through existing devices such as aspirating nozzles and some non-aspirating devices such as sprinkler heads.

3.3. Environmental impacts of fire-fighting foams

A life cycle assessment will compare the environmental impact of manufacturing the raw materials and the foam concentrate for both fluorinated and fluorine-free foam concentrates and identify routes to new foams that have lower environmental burdens. This will include resource depletion such as energy and water usage.

3.4. Working hypotheses

The successful deployment of fire-fighting foam to extinguish a fire involves a series of complex surface chemistry processes. Four key desirable properties have been hypothesized:

A. *The surfactant / solvent system must lower the surface tension very rapidly to stabilize air bubbles, giving a foam with high expansion rate, and small, monodisperse bubble structure.*
B. *The interfacial tension must be as high as possible to minimize fuel pick-up on application and foam destruction by fuel.*
C. *The foam must spread rapidly over the fuel for rapid extinguishment, but must then solidify for good burnback protection. This requires a low yield stress and viscosity and is also helped by rapid dynamic surface tension.*
D. *The layer of surfactants and/or polymers adsorbed at the air/water interface must be deep and/or tightly packed to reduce fuel vapor diffusion to the surface, giving high surface viscosity and give good burnback resistance.*

4. BACKGROUND

4.1. Environmental Issue

MIL-PRF 24385F specifies a range of fire tests and physical properties that are required for a fire-fighting foam concentrate to qualify for use by the military to extinguish liquid fuel fires. The specification requires the foam concentrate to contain fluorocarbons, and also contains clauses such as the requirement for a positive spreading coefficient of +3 mN/m on cyclohexane that currently cannot be reached without using fluorosurfactants. Even without these requirements, the fire performance required, particularly the extinguishment time, cannot currently be met without the use of fluorocarbon surfactants.

The very first AFFF foams developed by Naval Research Laboratory and the 3M Company contained fluorosurfactants such as PFOS synthesized by an electrochemical technique. A subsequent technology used a telomer process to synthesize fluorocarbons with a perfluoro chain, of length 6 to 12 carbons and a C_2H_4 spacer before the hydrophilic part of the molecule. Fluorocarbons give the foam good heat stability and the very low surface tension required for film formation on hydrocarbon fuels. It is known that the C8 telomer fluorocarbons cannot form PFOS, but instead degrade in the environment to form perfluorooctanoic acid, PFOA, which is persistent, toxic and bioaccumulative. More recent AFFF foams have replaced the C_8F_{17}- chains with materials containing pure 6:2 fluorotelomer chains, $C_6F_{13}C_2H_4$-. These short-chain surfactants also partially break down in the environment, via the intermediate 6:2 fluorotelomer sulfonate and eventually to perfluorohexanoic acid, PFHxA.

Silicone-based surfactants are capable of giving low surface tensions, and have been proposed as an alternative material for AFFF foams. However, the poly(dimethoxysiloxane) group is also man-made, and has no biological degradation routes. Under the precautionary principle, foams should not contain any persistent materials, therefore silicone surfactants will only be considered if they can demonstrate ready biodegradability in the environment.

Foams containing only hydrocarbon surfactants would be expected to fully biodegrade in the environment within a short space of time since there are known biological routes to break down hydrocarbon chains. However, some surfactants have higher acute aquatic toxicity than fluorocarbons. The hydrophilic head group structure and hydrocarbon chain length affect aquatic toxicity, with amphoterics being particularly toxic to algae. The ecotoxicity of other components such as solvents and metal salts must also be taken into account.

4.2. Previous work

National Foam Inc. is part of the Angus International Group of Companies, and has consistently been at the forefront of developing and launching more environmentally friendly fire-fighting foam concentrates. Angus introduced the first ever commercially available fluorine-free fire-fighting foam, Syndura, in 2002. This foam was used at 6 % and passed fire tests to UL 162, ICAO A and EN 1568 3 methods. Respondol ATF 3F 3/6, launched in 2016 was the first fluorine-free foam to achieve 1A ratings across the board in EN 1568 Parts 3 and 4, in fresh and sea water on heptane, acetone and IPA. Universal ^{F3} Green 3%-3% is the only fluorine-free foam concentrate listed to UL162 at 3 % on both hydrocarbon and polar solvents in fresh and salt water. These formulations contain a blend of hydrocarbon surfactants and a polysaccharide and rely on slow drainage for foam longevity. In 2015, Jetfoam was developed, a foam concentrate containing only hydrocarbon surfactants and solvent with no fluorocarbons or polymers. This foam was unique in two respects – it is the world's first Newtonian fluorine-free foam, and the first that is able to film-form on Avtur aviation fuel. Avio ^{F3} Green FHC 3%, launched in 2019 is the world's only fluorine-free foam that has been independently assessed as passing the ICAO C standard.

Product	**Type**	**Approvals**	**Surface tension γ_s (mN/m)**	**Interfacial tension γ_i (mN/m)**	**Spreading coefficient on Avtur mN/m**	**Film-forming?**
Aer-O-Water 3EM	C6 AFFF	MIL-PRF 24385F	16.5	3.0	+8.5	Yes
Jetfoam 3	Newtonian F-free	ICAO B	23.5	0.2	+4.3	Yes
Avio ^{F3} Green FHC 3%	Newtonian F-free	ICAO C	22.7	0.2	+5.1	Yes
Respondol ATF 3/3	Pseudo-plastic F-free	UL162 EN1568	28.5	3.5	-4	No

Table 4.1. Surface properties of fire-fighting foams at 20 °C. Spreading coefficient = 28.0 – ($\gamma_s + \gamma_i$) mN/m.

Table 4.1 gives the surface and interfacial tensions of various fire-fighting foams on Avtur. Avio ^{F3} Green FHC 3% has passed the ICAO C test and has already been adopted by many international airports, but would not meet the whole of the current MIL-PRF 24385F standard. Angus International aim to develop innovative fire-fighting foams through an understanding of the scientific principles that determine foam properties and performance. Angus International recently funded work at Bristol University into the surface and colloid chemistry of fire-fighting foams[1], and have partnered Manchester Metropolitan University to study in depth the analysis and environmental impact of foams. The combination of science base and deep knowledge of fire-fighting foams has allowed the development of the best-performing fluorine-free foams in the world today.

There have been several third party test programs, to evaluate the performance of commercially available fluorine-free foams in a range of applications and test methods. These test programs demonstrate that current fluorine-free foams are able to meet many of the standard test protocols, in some cases with performance equal to or better than fluorocarbon containing foams. However, there are significant variations in the performance of commercial foams from different manufacturers.

To date, there are no current commercial fluorine-free foams that meet the performance standards of MIL-PRF 24385F. National Foam strives to develop a stronger understanding of the relation between foam components, physical chemistry, foam properties and fire performance to develop a formulation to meet the MIL-PRF 24385F specification.

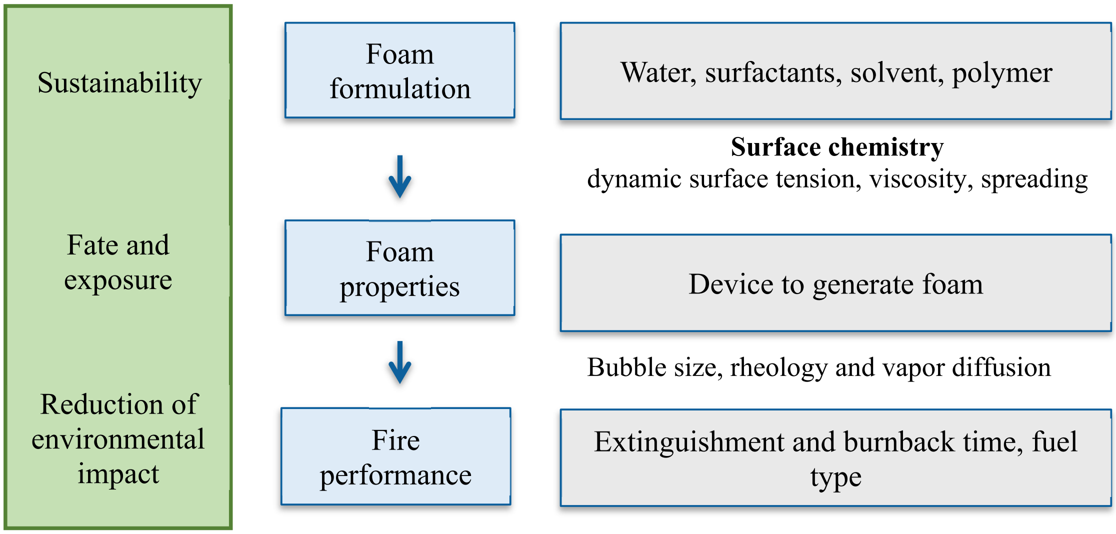


Figure 4.1. Relationship between foam formulation components, foam physical properties and fire performance.

To improve performance, and to completely satisfy the standards of MIL-PRF 24385F will require further understanding of the underlying physical chemistry and challenges of fluorine-free fire-fighting foams.

Heightened awareness of sustainability and environmental protection associated with product manufacture and use has led to increasing implementation of life cycle assessment (LCA) methodology. Life cycle assessment is defined as a way of quantifying potential environmental impacts over the life cycle of a product.[2] This can help improve the understanding of the potential environmental impacts of a product from the raw material acquisition through production, use, and final disposal.

4.3. State of the science and current gaps in understanding

The scientific literature contains many reports of attempts to understand the science of fire-fighting foams. Lattimer[3] broke down the overall fire performance into individual steps which could be treated separately. The role and importance of properties such as dynamic surface tension [4], interfacial tension [5,6], film formation, [7] spreading coefficient, bubble size[8], vapor diffusion and foam rheology[9] have all been discussed. Jho correlated rate of spreading of AFFF foams with dynamic surface and interfacial tensions.[10] Meeten used vane rheometry to measure yield stress of foams.[11] Schaefer published a summary of required properties of fire-fighting foams.[12]

A significant gap is the correlation of the foam formulation with the physical properties. Foam formulations are proprietary and guarded closely by foam manufacturers. Much of the academic work is therefore unable to correlate foam properties with components. The effects of polymers have been studied[13] but little has been published concerning the roles of surfactant types and solvents. There is no published life cycle assessment of a fire-fighting foam.

Foaming of high salinity aqueous solutions has not been widely reported, although the properties of saline surfactant solutions have been extensively studied for use in enhanced oil recovery to improve flooding of porous oil-bearing rocks.[14-17] Important properties such as oil entering and spreading coefficients have been reported and give valuable direction to formulating a foam in sea water.[18,19]

4.4. Fire-fighting foam formulations

Foam manufacturers rarely publish information concerning foam formulations, but the patent literature gives some indications of the components used in commercial fire-fighting foams.

Pure liquids do not foam. The presence of a surfactant that lowers aqueous surface tension is required to generate foam. A wide range of surfactants have been patented for use in fire-fighting foams. Alkyl sulfates are widely used, both alone and in conjunction with nonionic alkylpolyglycosides or amphoteric amine oxides or betaines.

Secondary surfactants can be used to alter foam properties, such as fatty amines. Polymers stiffen foams and retard drainage, examples include chitosan, poly(acrylic), poly(ethylene oxide) and polysaccharides including pectin, diutan gum, xanthan and carbonized sugar.[20]

Solberg have used a mixture of surfactants, such as amphoteric and anionic along with solvents and xanthan gum to formulate their leading fluorine free formulation, this formulation also used carbonized sugar as a polymer to alter the foam properties.[21] The formulation can be found in Table 4.2, the patent lists 7 surfactants, 3 polysaccharides; including the use of carbonized sugar, solvents and water.

Material	%w/w
Water	60 – 80
Diethylene glycol mono butyl ether	7-14
Xanthan gum (Keltrol)	0–4
Starch (Cerestar)	0–4
Carbonised sugar blend	3–20
Diethanolamine lauryl sulfate	0–5
Sodium decyl ethoxy sulfate	0–5
Cocamido propyl betaine	0–5
Cocamido propyl hydroxyl sultaine	0–5
Sodium octyl sulfate	0–5
Sodium decyl sulfate	0–5
Alkyl polyglycoside (C_8 - C_{16})	0–5

Table 4.2. Formulation details of Solberg leading fluorine free formulation. Showing the complex mixture of components.[21]

Comparison of AFFF and fluorine-free foams has focused on differences in performance. Williams measured extinguishment times on fuels of varying surface tension.[7] He calculated that on a 28ft^2 pan, film formation reduces extinguishment times by 5 to 12 seconds compared with non film-forming foams. Schaefer[12] investigated sealability of fluorine-containing and fluorine-free foams, and Sheng[22] compared spread on a heptane surface of fluorinated and fluorine-free foams.

4.5. Current gaps in formulation knowledge

There are no reported surfactants that can lower surface tension sufficiently to film-form on fuels such as gasoline or heptane, apart from fluorocarbons. Siloxanes reduce aqueous surface tension to around 20 mN/m, and can film-form on cyclohexane but not on gasoline.[23] It is considered highly challenging to develop effective formulations which film-form on a gasoline fire without using fluorine.

5. Materials and Methods

5.1. Physical chemistry of hydrocarbon surfactants

5.1.1. Equilibrium surface tension

Measuring Surface Tension with the DCA-100 Contact Angle Tensiometer

The air–aqueous phase surface tension measurements were conducted using a DSA-100 tensiometer with a roughened Wilhelmy plate (platinum) at 25 °C (thermostatted by an LTD6G water bath (Grant, UK)). The plate was cleaned by washing with ethanol and water, then drying with the blue flame of a gas burner. A 60 x 40mm beaker is filled to the line with test solution. The plate is lowered into the test solution and measurement is started. The air–water surface tension was recorded periodically and the average equilibrium surface tension (after 300 s), was given in an information box. Three repeat measurements were made by generating a fresh interface and allowing it to reach equilibrium. An average equilibrium air–water surface tension was then used to determine the cmc of each surfactant.

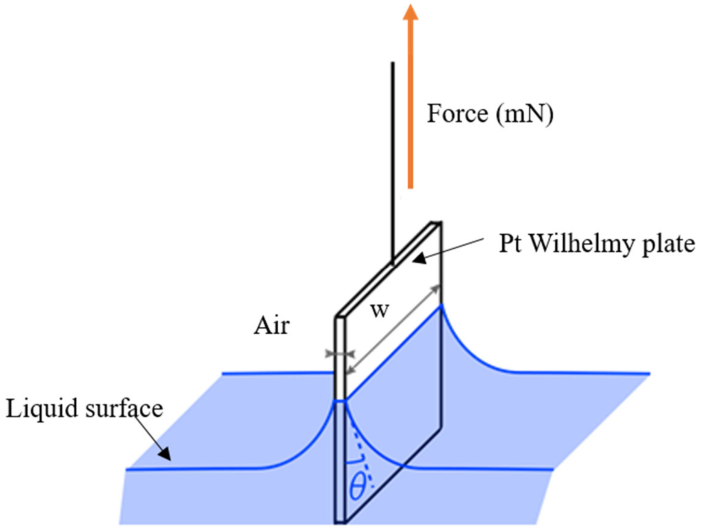


Figure 5.1. Principle of Wilhelmy plate surface tension measurement.

5.1.1.1. Critical micelle concentration

The equilibrium air–water surface tension is measured using the Wilhelmy plate method. The equilibrium air–water tension values are then plotted against log([surfactant] /%) as shown in

Figure 5.2. The cmc is determined at the point where the air–water surface tension remained constant, as this indicates the point at which the interface is saturated and further surfactant monomers will aggregate.

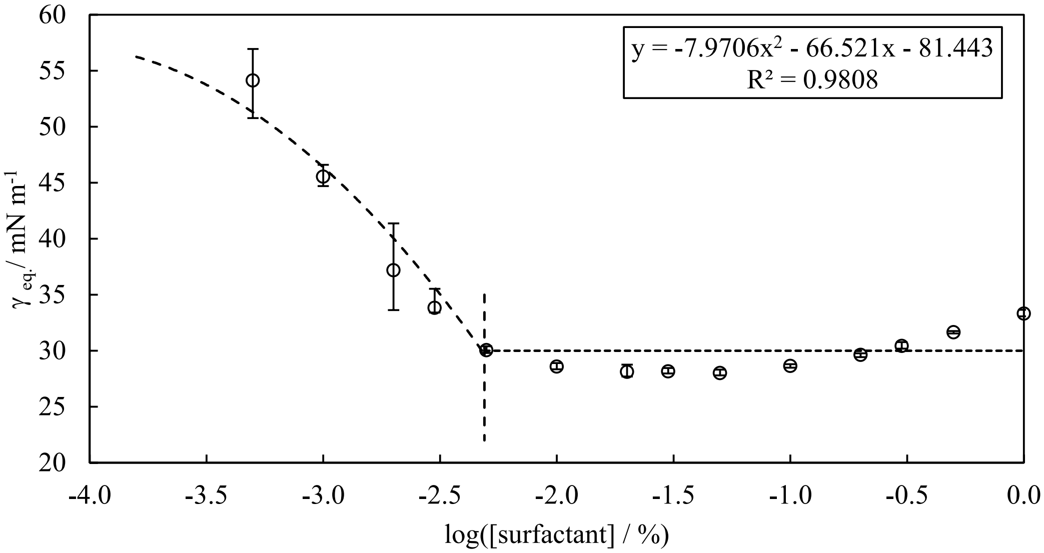


Figure 5.2. Average equilibrium surface tension after 5 mins as a function of [surfactant] in tap water using the Wilhelmy plate method at 20 °C.

5.1.1.2. Calculation of surface excess and surface area per molecule

For surfactant concentrations below the cmc, the surface excess concentration, Γ, at the interface can be determined from the slope of the surface tension vs. ln[surfactant] isotherm at constant temperature using the Gibbs' adsorption equation:

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln a}$$ **Equation 5.1**

where γ is the surface tension, R is the gas constant, T is absolute temperature and a is the activity of surfactant. For concentrations below those corresponding to either aggregate formation or phase separation, we assume that the solutions behave ideally, i.e. that activity and concentration of the surfactant can be equated.

An example calculation to determine the number of molecules at the air–water interface is shown below. A polynomial equation was used, with the Gibbs adsorption equation (Equation 5.1), to fit the surface tension values below the cmc. The polynomial equation was integrated and a factor of 2.303 was used to convert log([surfactant])]/ to ln ([surfactant]). Where R is the universal gas constant 3.145 J mol^{-1} K^{-1}, T is temperature (K), γ the surface tension at concentration, c.

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln c}$$

$$\Gamma = \left(-\frac{1}{1.38066\times10^{-23}\times293.15}\times\frac{-29.696828}{2.303}\right)\times 1\text{x}10^{-21}$$

$$\frac{d\gamma}{d\ln c} = -29.696828$$

$$\Gamma = 3.187 \text{ molecules nm}^{-2}$$

5.1.1.3. Surface area per molecule

The area per molecule (A) provides useful information on the degree of packing and the orientation of the adsorbed surfactant molecules at the interface when compared with the dimensions of the molecule. Using the surface excess concentrations, Γ, in molecules nm^{-2}, the molecular area occupied by surfactant, A, (nm^2) can be calculated using Equation 5.2:

$$A = \frac{1}{\Gamma} \qquad \textbf{Equation 5.2}$$

Additionally, the surface excess concentrations at surface saturation Γ_m, and the area per molecule at the interface at surface saturation A_m, are useful measures of the effectiveness of adsorption of the surfactant at the air-water interface as they indicate the maximum value that the adsorption can reach.

Example calculations of the number of molecules and area per molecule are shown below:

[surfactant] / %	**log([surfactant] / %)**	**(dγ/dlogC)/mN m^{-1}**	**Γ/molecules nm^{-2}**	**A / nm^2**
0.0010	-3.0	-18.697	2.006	0.499
0.0020	-2.6	-23.496	2.521	0.396
0.0030	-2.5	-26.303	2.822	0.354
0.0049	-2.3	-29.696	3.187	0.313

5.1.2. Dynamic surface tension

In firefighting conditions, the dynamic properties are also important due to the short timescale between the foam being produced and being applied to the hot fuel surface.[24] Dynamic surface tension gives information about the mobility of the surfactants, and how quickly they reduce the surface tension.

The dynamic surface tension (DST) of aqueous surfactant solutions was measured using a bubble pressure tensiometer (Sita Proline 115). The DST was measured from 15 ms to 20 s. Measurements were conducted at 20 °C thermostatted using a Grant waterbath. Three repeat measurements were made and the dynamic surface tension reported as the average of the three readings.

5.1.2.1. Diffusion coefficient

In dilute solutions, the transfer of the surfactant molecules from the bulk onto the surface is usually governed by diffusion. Initially, the surfactant molecules that are closer to the surface are adsorbed.[25] As a result, the bulk concentration of the surfactant just below the surface becomes much smaller than that far from the surface. This generates a significant concentration gradient and, therefore, a strong diffusion flux of surfactant molecules from the bulk towards the surface. The adsorbed amount of surfactant rapidly increases and the decrease of the dynamic surface tension with the time is very fast. At longer times, the surfactant concentration in the bulk starts to equilibrate; the concentration gradient and the diffusion flux of surfactant towards the interface diminish in magnitude thus slowing down the adsorption.

The time for reaching the equilibrium surface tension may vary from a fraction of a second to many hours depending on the surfactant type and its concentration, and can be quantified by calculating the diffusion coefficient (D).[25]

$$D = (\frac{\gamma_o - \gamma_t}{2R.T.c})\pi.t^{-1}$$

Equation 5.3

Where γ_o is the air–water surface tension in the absence of surfactant, (N m^{-1}), γ_t the air–water surface tension, (N m^{-1}) at time t, T the temperature (in Kelvin) and c the concentration of the surfactant (mol m^{-3}).

5.1.3. Interfacial tension

The interfacial tension is a measure of the interaction between two immiscible liquids. In the presence of surfactant, the interfacial tension will change depending on the affinity of the surfactant molecules with each phase.[26,24]

A known volume of the higher density phase liquid is added to a beaker (60 x 40mm). The platinum ring is immersed into the solution, the second liquid with a lower density is carefully added up to the second line. A force maximum F_{max} occurs when the lamella, which is produced when the ring moves through the phase boundary between the two liquids, is aligned vertically to the ring plane.

This maximum correlates with the interfacial tension ($\gamma_{int.}$) according to the following equation:

$$\gamma_{\text{int}} = \frac{\mathrm{F}}{L\cos\theta}$$ **Equation 5.4**

The wetted length L of the ring is the sum of the inner and outer circumference. Platinum-iridium is used as the material for the ring, as this alloy is optimally wettable due to its very high surface free energy and therefore generally forms a contact angle θ of 0° (cos θ = 1) with liquids. The material is also chemically inert and easy to clean. A correction factor is used as the weight of the liquid of the lamella increases the measured force, and because the force maximum does not occur at the inside and outside of the lamella at the same time.

5.2. Foam properties

5.2.1. Foam generation

Prepare 1 liter of premix at the intended use strength (usually 3 or 6%). Viscous liquids should be weighed out using the SG value (e.g. 1.09). Ensure that the premix solution is at 20 ± 2 °C and is thoroughly mixed with all the foam concentrate fully dispersed. Pour the premix into a standard laboratory foam generator fitted with a UK Defense Standard 42-40 or MIL-PRF 24385F Branch pipe fitted with a full flow outlet. Pressurize the foam generator to 100 psi and generate a foam sample into the NFPA 1630 ml drainage pan.

5.2.2. Expansion ratio

The expansion ratio is a measure of the foam and can be calculated using Equation 5.5

$$E = \frac{\text{Volume of pan / mL}}{\text{Foam weight / g}}$$ **Equation 5.5**

5.2.3. Drainage time

Place the drainage pan onto the ring on the retort stand. Position a 100 ml measuring cylinder beneath the drainage outlet. Allow the liquid to drain from the bubble structure and collect it in the measuring cylinder. Record the temperature of the foam in the drainage pan.

As liquid drains from the foam, adjust the drainage outlet valve to control the flow so that the foam/water interface is visible in the drainage tube between the drainage tap and the body of the drainage pan. Do not allow foam to enter the measuring cylinder.

25 % Drainage time (D_{25}) is the time taken to collect a quarter of the foam sample weight (expressed in ml) in the measuring cylinder placed beneath the drainage outlet.

$$D_{25} = \frac{\text{Sample weight}}{4}$$ **Equation 5.6**

25 % drainage times are expressed as decimal minutes at 20 °C (e.g. 6.52 mins at 20 °C). The drainage rate is affected by changes in foam temperature, if the temperature varied from 20 °C, the stability was corrected by ± 2.5 % for every 1 °C difference.

5.2.4. Bubble size distribution, optical microscopy

Optical microscopy was used to investigate the foam bubble structure, including the bubble size and polydispersity and the effect the presence of fuel has on the properties. An Olympus optical (model BX53M) microscope fitted with 2.5×, 5×, and 10× magnification objectives was used to view samples using transmitted visible light. Images were taken using a SC50 CMOS color camera and processed using Stream imaging software. Samples were viewed on a planar glass microscope slide of dimensions 26 × 76 mm, cleaned with acetone and dried before use. The foam sample was generated using a standard device and a sample was transferred to the glass slide.

5.2.5. Rheology

The rheological properties of the foam were investigated using Malvern Kinexus Pro+ and measurements were analyzed using Rspace software.

5.2.5.1. Yield stress

Yield stress is a measure of the foam ability to flow over a surface and is determined from a plot of the change in viscosity with increasing shear stress.[27]

A vane geometry was placed into the rheometer and a zero gap measurement initiated. Enter shear rate ramp properties and the rheometer will then measure the viscosity vs shear stress. Foam was generated using the standard method and collected into a small jug. Ensure foam is at 25 °C. A known volume of foam sample was measured into a beaker of known dimensions, being careful not to spill or damage the geometry until about 1 cm below the rim which will ensure correct loading. Foams that drain quickly will need to be measured as quickly as possible.

5.2.6. Resistance to fuel destruction

Microscopy was used to investigate the foam-fuel interaction and the resistance to fuel destruction. The fuel was dyed orange with 0.1 g solvent orange dye powder in 100 mL fuel and a small sample was added to the foam.

The bubble size and foam structure was examined using an Olympus optical (model BX53M) microscope as outlined in Section 5.2.4.

5.2.7. Vapor suppression

The resistance to fuel destruction is correlated to the amount of fuel vapors permeating through the foam blanket and can be measured using Draeger tubes.

The set-up is shown in Figure 5.3. 30 mL fuel was placed at the bottom of a round bottom flask, 40 mL foam applied on top and rapidly sealed with the gas detection tube. The color change (orange to brown) was monitored over time and correlated to the gas permeating though the foam blanket.

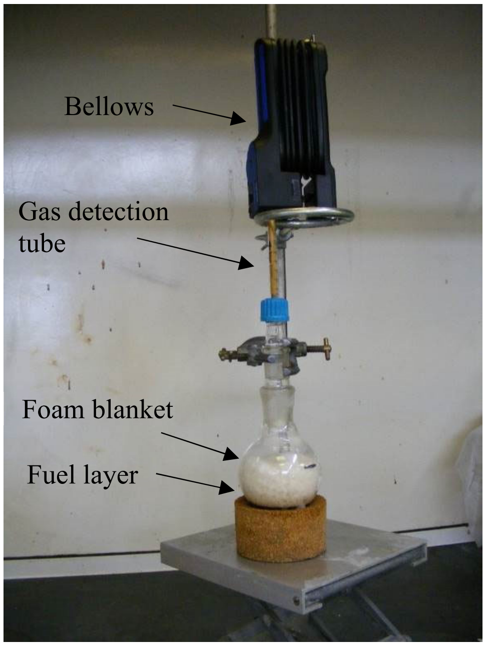


Figure 5.3. Measurement of fuel vapor diffusion through a foam blanket.

5.3. Fire performance

5.3.1. Lab scale fire tests

Laboratory based fire tests were used to compare the firefighting properties of formulations and correlate to changes in surfactant structure and related properties. Foam was generated as described above.

30 mL of fuel (Heptane and Gasoline are normally used) was added into a brass pan of either 79 or 113 cm^2 surface area x 4 cm high with a 1mm wall thickness. Ensure that the fuel temperature is in the range 20°C ± 2°C.

The foam was generated from the branch pipe into a small jug and 120 mL foam was carefully poured into the syringe Acrylic tube, (4.5cm internal diameter x 15.5cm long,). Level off the foam across the open end of the syringe. Ignite the fuel in the pan using a wax taper and simultaneously start the stopwatch. After 10 seconds has elapsed rest the syringe nozzle on the side of the pan and expel the foam smoothly onto the burning fuel to cover the pan. Delivery of the foam should be completed within 2 seconds. Record the time at which fire is controlled and extinguished. Leave the foam sat on the hot fuel and record the time that the first hole appears in the foam blanket exposing the fuel. An example is shown in Figure 5.4.

Figure 5.4. Laboratory small scale fire test. (a) 10 s preburn, (b) application of foam, (c) measurement of extinguishment and burnback.

5.3.2. Full scale 28ft^2 fire tests

Tests were carried out following the procedure described in MIL-PRF-24385F(SH) AMENDMENT 1 5 August 1994.[28]

Tests were conducted outdoors when the wind was below 10 miles / hour in the absence of precipitation.

The fire test was conducted in a level, circular pan 6 feet in diameter, fabricated from l/4-inch thick steel with a 4-inch high side. A shallow water layer was used to protect the pan bottom and to ensure complete coverage of the area with fuel. The nozzle used for foam application was the 2 gal/min device shown.

Foam was generated at 23 ± 5.0 °C from solutions made with fresh or sea water, as required, at concentration values of 3 or 6 %. 10 gallons of heptane or unleaded gasoline were used.

The fuel was ignited and allowed to burn freely for 10 seconds. After the preburn period, the fire was attacked and extinguished as expeditiously as possible and the times required for 90 % control, 99 % control and extinguishment were recorded. Foam application continued for a total of 90 seconds.

Burnback procedure. Within 60 seconds of the completion of foam application, a burning pan (1-foot in diameter with 2-inch side) containing one gallon of unleaded gasoline or heptane was placed in the center of the pan. The pan was not removed. The burnback time is that time at which it is estimated that 7 square feet (25 %) of the total area was involved in flames.

6. RESULTS AND DISCUSSION

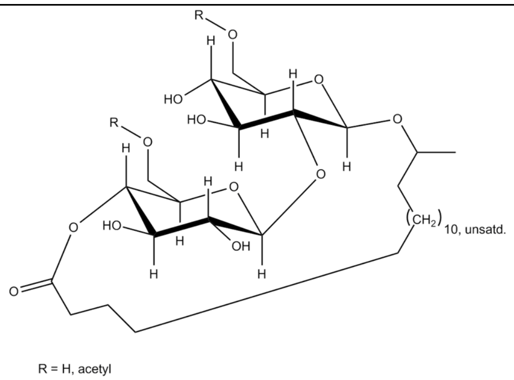
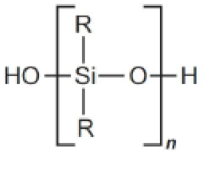
6.1. Selection of primary surfactant package

Fluorine-free foams are complex formulations with multiple components, each providing different properties to the foam concentrate, the foaming solution and the foam. These components all work together as a holistic mixture. Nevertheless, it is possible to deconstruct the foam into key components, each with a defined function. This approach allows each component to be studied separately, prior to combining all the foam components.

The major components, with their function, are:

Primary surfactant – generates foam with a high expansion ratio, good spreading and provides some foam stability to fuel.
Secondary surfactant – thickens foam after initial foam generation to increase fuel stability
Solvent – increases solubility of surfactants and polymers to improve foam properties
Polymer – thickens foam, slows drainage, improves vapor resistance

The role of the primary surfactant package in a foam formulation is to generate a high expansion ratio as the foam leaves the nozzle, producing a large volume of foam and a thick foam blanket. Spreading of a non film-forming foam is driven by hydrostatic pressure, a thicker blanket exerts more pressure and will spread more quickly. A thick blanket will also form a stronger barrier to fuel vapor diffusion. The physical chemical properties of a wide range of commercially available surfactants were evaluated to identify which classes of surfactants have potential for use in fire-fighting foams. Nonionic surfactants were not included in the screen since they are known to be poor foam generators, an example is shown in the table. All were used as received.

Chemical info	Structure
Alkyl sulfate C8 - C14 **(Anionic)**	n-C8-C14
Sodium sulfonate **(Anionic)**	n-C14-C18
Sodium alkyl ether sulfate (C12-C18) **(Anionic)**	n-C12-C18
Dioctyl sulfosuccinate. **(Anionic)**	
Alkyl polyglucoside **(Nonionic)**	 R = H, acetyl
Polydimethylsiloxane Copolymer **(Silicone)**	 $HO{-}[Si(R)_2{-}O]_n{-}H$

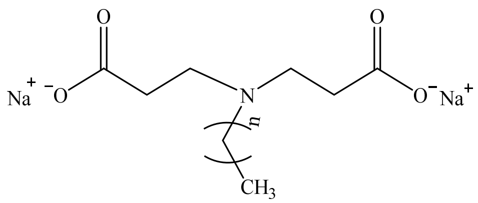
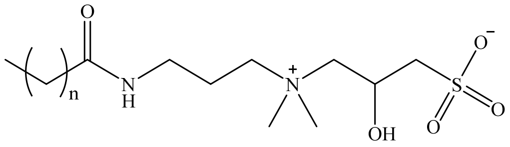
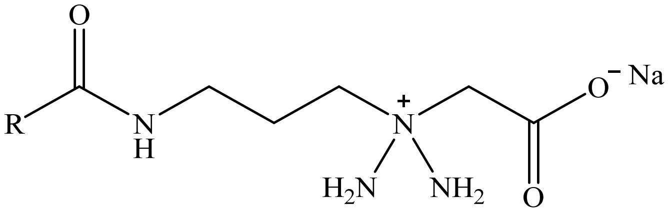
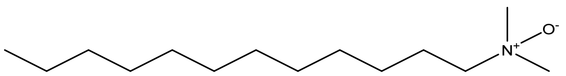
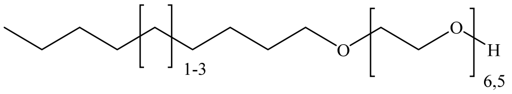
Chemical info	**Structure**
Reaction products of C12-18-(even numbered)-alkylamines and acrylic acid and sodium hydroxide, **(Amphoteric)**	
Cocamidopropyl Hydroxysultaine **(Amphoteric)**	
Cocamidopropyl betaine **(Amphoteric)**	
Amine oxide **(Amphoteric)**	
Ethoxylated alcohol High-performance, environmentally-friendly nonionic surfactant	

Table 6.1. Structures of surfactants.

6.1.2. Surfactant properties

The dynamic surface tension (DST) is an important parameter when studying firefighting foams. From the DST, information regarding the mobility of the surfactant can be obtained and correlated to the surfactant structure.[29,30] The DST was determined with a bubble tensiometer as described in Section 5.1.2. Figures 6.1 and 6.2 show the change in DST as a function of surfactant concentration for anionic and amphoteric surfactants. The diffusion coefficient was calculated for each surfactant after 20 s and 5 s.

From Figure 6.1. the greatest reduction in the air–water surface tension is observed with the di-chain anionic surfactant, it has a larger hydrophobic area than a single chain anionic surfactant, and hence there is a larger driving force at the air–water interface. From Figure 6.2 the DST does not reduce as quickly for amphoteric surfactants as observed with the anionic species. Furthermore, the addition of a sulfur group increases the air–water surface tension and slows down the adsorption at the air–water interface. This is due to the electronegativity of the sulfur group, which leads to more interactions in the bulk phase and less driving force to adsorb at the air–water interface.

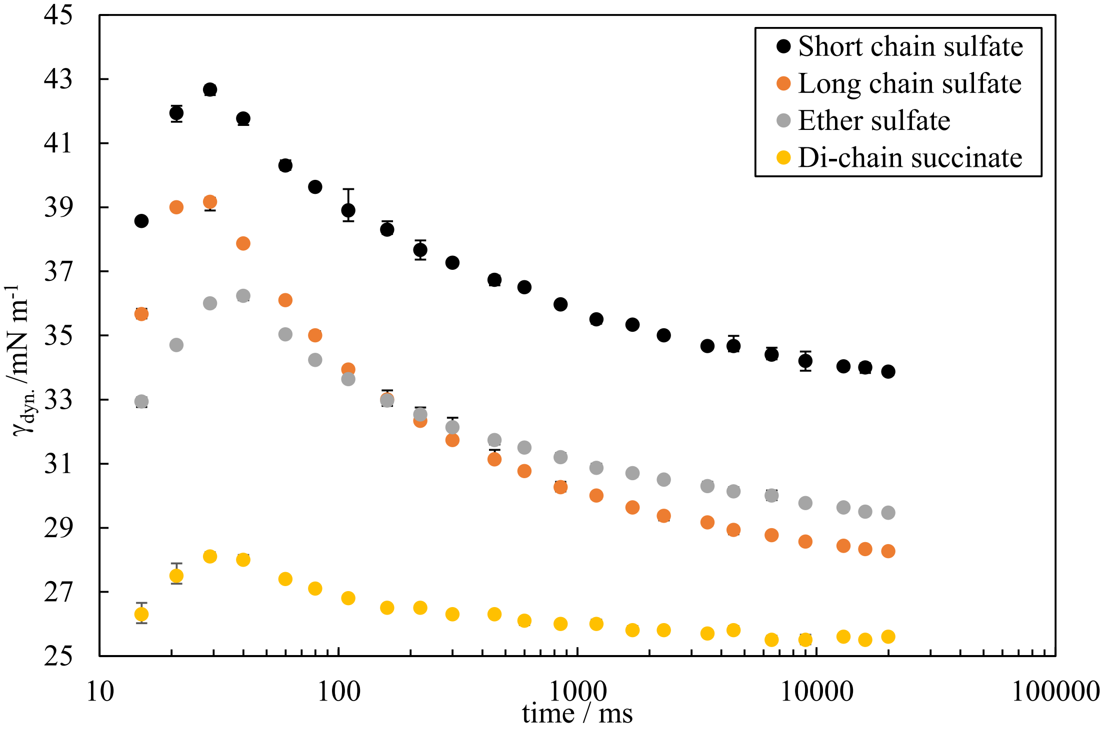


Figure 6.1. Change in air –water dynamic surface tension as a function of time for a range of anionic surfactants in tap water. Measured using bubble pressure tensiometer at 20 °C.

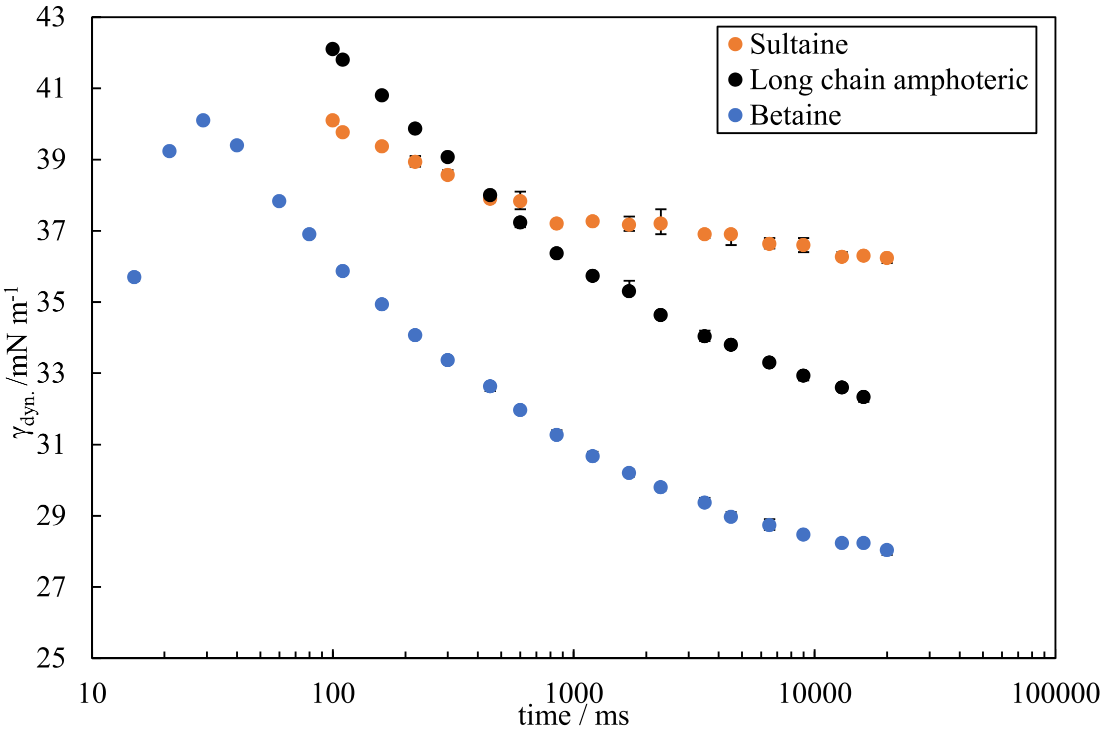


Figure 6.2. Change in air–water dynamic surface tension as a function of time for a range of amphoteric surfactants. Measured using bubble pressure tensiometer at 20 °C.

The air-water equilibrium surface tension was measured using the Wilhelmy plate method described in 5.1.1. From these measurements, the critical micelle concentration (cmc) was determined by plotting the change in the surface tension (γ) as a function of the natural logarithm of initial aqueous surfactant concentration. As shown in Figure 6.3, below the cmc, the surface tension steadily decreases with increasing surfactant concentration up to the cmc. Above the cmc, aggregates are formed and the concentration of monomers in the bulk solution does not change and the surface excess concentration is unaffected and the surface tension remains constant as seen in Figure 6.3. The gradient of the line below the cmc (dγ/dlnc) allows calculation of the surface excess, and the area per molecule adsorbed at the interface.

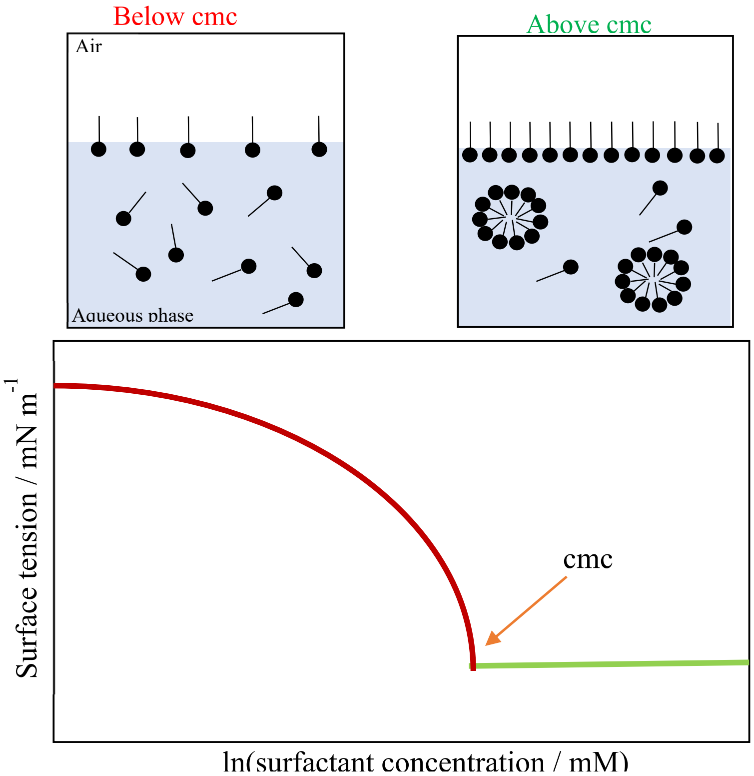


Figure 6.3. Change in surface tension (γ) as the concentration of surfactant increases. Below the cmc, the monomers adsorb at the air–water interface lowering the surface tension (left).

Above the cmc, the additional surfactant monomers form micelles and the monomer surface tension remains constant (right).

Nonionics generally have very low cmc values and are poor foamers. Table 6.2 summarizes the surface properties of single surfactants in fresh water at air–water interface measured at 20 °C.

Surfactant type	**$\gamma_{dyn. (1\% 20 s)}$ / mN m^{-1}**	**γ_{cmc} / mN m^{-1}**	**cmc / wt.%**	**Γ_m / molecules nm^{-2}**	**A_m / nm^2**	**D @ 20 s / m^2 s^{-1}**	**D @ 5 mins / m^2 s^{-1}**
Anionic short single chain	33.87	28.9	0.0158	0.894	1.119	9.03×10^{-16}	9.03×10^{-17}
Anionic long single chain	29.46	26.5	0.0152	3.194	0.313	1.46×10^{-15}	9.83×10^{-17}
Anionic double chain	25.33	24.8	0.1	1.370	0.730	3.94×10^{-15}	2.58×10^{-16}
Siloxane 1	19.970	20.06	0.794	0.030	32.878	1.00×10^{-14}	6.66×10^{-16}
Siloxane 2	21.700	21.45	0.095	0.109	9.115	1.71×10^{-14}	1.16×10^{-15}
Siloxane 3	31.43	23.54	0.300	0.436	2.295	1.86×10^{-14}	1.61×10^{-15}
Long chain amphoteric	32.67	30.10	0.005	3.406	0.294	1.02×10^{-15}	1.14×10^{-16}
Sultaine	36.23	36.1	0.117	0.421	2.374	2.68×10^{-15}	1.77×10^{-16}
Betaine	28.130	28.30	0.300	0.429	2.331	2.61×10^{-15}	1.68×10^{-16}
Polymeric surfactant 1	26.13	27.20	8.913×10^{-4}	3.28	0.305	3.12×10^{-15}	1.99×10^{-16}
Polymeric surfactant 2	56.37	52.1	0.989	0.43	2.329	Unable to determine due to lack of structural information	
Polymeric surfactant 3	37.47	33.90	0.199	0.57	1.745		

Table 6.2. Summary of surfactant properties of a range of surfactants measured at 20 °C.

The aggregation behavior of a series of siloxane surfactants, Silsurf A008-UP, A208 and C208 was also investigated. From Figures 6.4 and 6.5 as the relative molecular weight increases, both the equilibrium and dynamic air–water surface tension increase, which correlates to an increase number of molecules at the air–water interface and an increase in the cmc. This series of surfactants reduces the surface tension considerably as they are very surface active.

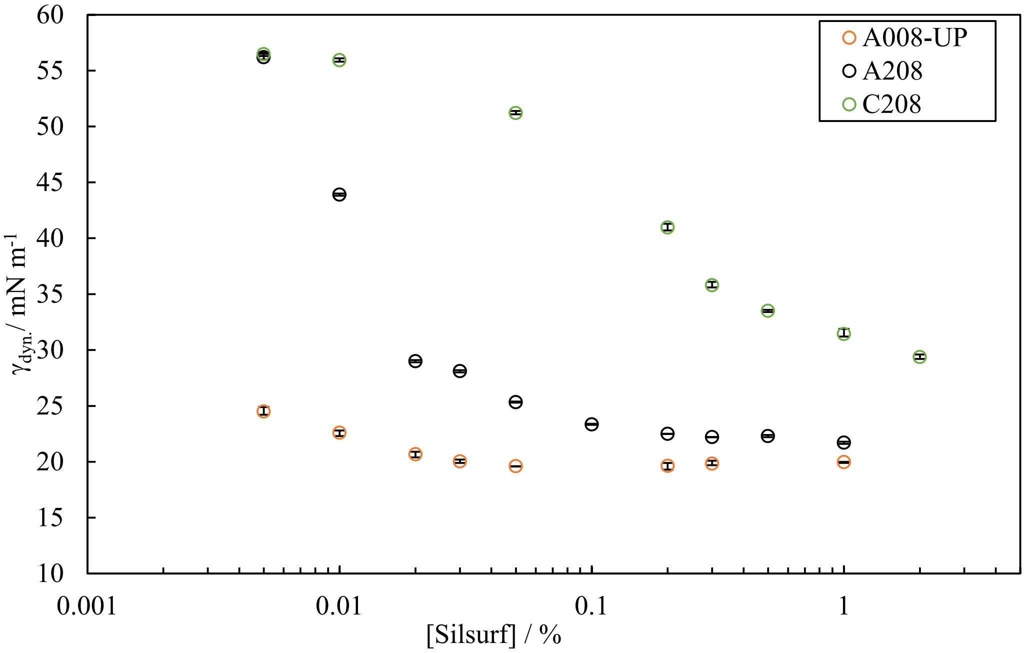


Figure 6.4. Average–air water dynamic surface tension as a function of Silsurf concentration in tap water at 20 °C.

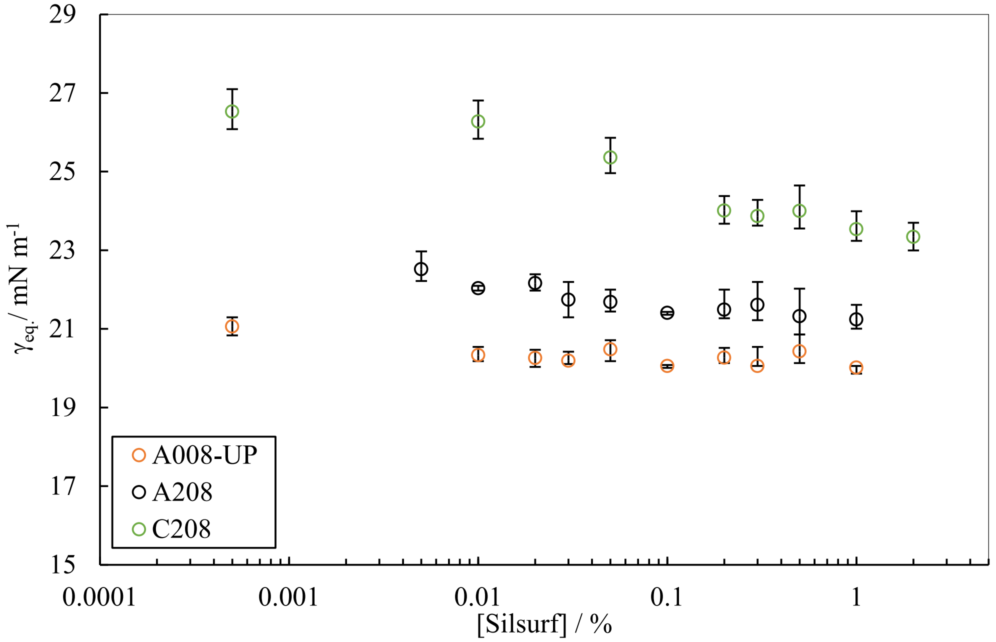


Figure 6.5. Average–air water equilibrium surface tension as a function of Silsurf concentration in tap water at 20 °C.

6.1.3. Foam properties

The foam properties of each surfactant solution in fresh water was prepared, and foam was generated using the branch pipe described in Section 5.2. The expansion ratio and quarter drainage time were measured at 20 °C. Table 6.3. summarizes the foam properties observed.

Surfactant name	Expansion ratio	Foam stability 25% drainage time / s
Long chain sulfate	9.96	205
Short chain sulfate	8.30	225
Ether sulfate	9.70	216
Di-chain succinate	9.95	208
Long chain amphoteric	9.62	190
Sultaine	9.79	167
Betaine	9.83	240
Siloxane 1	3.30	61
Siloxane 2	4.26	67
Siloxane 3	5.81	65

Table 6.3. Foam properties of a range of surfactants.

The series of anionic and amphoteric species exhibit excellent foaming characteristics, which can be correlated to the surface aggregation behavior. Generally, as the hydrophobicity of the molecule increases, the driving force to adsorb at the air–water surface increases and hence the air–water surface tension is considerably reduced.[31,32] Furthermore, the expansion ratio increases with cmc. Above the cmc the air-water surface is saturated and further surfactant molecules form aggregates in the bulk phase and hence the addition of surfactant molecules above the cmc, do not contribute to the foam properties. Finally, the foam stability increases with increasing surfactant hydrophobic chain length, which again can be attributed to the hydrophobic effect.

From Table 6.2, as the cmc increased from 0.005% (long chain amphoteric) to 0.3% (betaine) there was an increase in the foam stability. Comparing the structures of the three amphoteric, the betaine has the lowest air–water surface tension at both 20 s and 5 mins, this can be correlated to the foam properties, in particular the stability, alongside the packing at the foam interface, and the mobility. For the anionic species, the expansion ratio increased with increasing chain length, however the presence of ether groups reduces the expansion ratio due to the presence of hydrophilic oxygen groups which reduces the affinity to adsorb at the air-water surface.

The foam properties of a series of siloxanes and non ionic surfactants was also investigated, however very poor foam was produced. Both silicone and non-ionic surfactants are often used as a wetting[33,34] or spreading agent due to the very low air–water surface tension, and are not used to directly stabilize a foam.[22] This correlates with the behavior observed with the silsurf series, whereby the surface tension was considerably reduced, but a stable foam was not able to be produced. [35,36] Silicones rapidly reduce the surface tension, hence as the foam expands and surface area increases, the surfactant monomers adsorb and desorb too rapidly. Consequently, there is no surface tension gradient, and such, the Gibbs film elasticity is non-existent and therefore a stable foam cannot be formed

Polymeric surfactants 2 and 3 do not foam. This can be correlated to their behavior at the air–water interface. From Table 6.2 both the dynamic and equilibrium air–water surface tensions are too high and it is not energetically favorable to adsorb at the air–water interface. Both molecules are large and bulky, as shown by the larger area per molecule, and are slow to adsorb at the air–water interface, hence unable to form a stable foam.[37]

6.1.4. Mixed surfactant systems

Mixtures of surfactants are known to foam better than individual species. Strongly interacting surfactants give low equilibrium surface tensions, but the initial rate of surface tension reduction is slower. Weakly interacting surfactants behave as the more mobile component over short timescales, and the more strongly adsorbing component over longer periods. Figure 6.7 shows the effect of a 1:1 ratio of amphoteric and anionic surfactant.

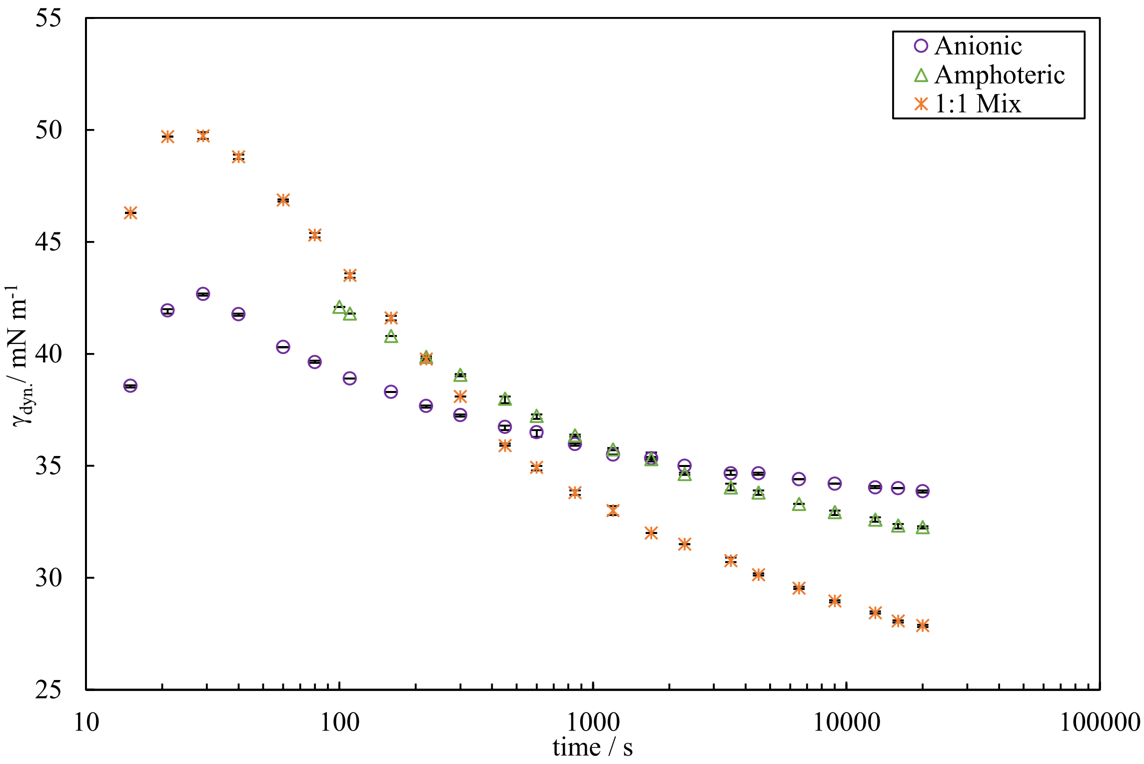


Figure 6.6. Behavior of single and mixed systems at the air-water interface and the effect on the dynamic surface tension.

The anionic surfactant alone gives the most rapid surface tension reduction, and over the first 250 ms gives the lowest surface tension. However, it only reaches an equilibrium surface tension of around 34 mN/m. The amphoteric alone adsorbs more slowly at the air / water interface, and reaches 33 mN/m. The mixture is initially slow but gives the lowest surface tension. This behavior can be explained in terms of the interaction between the two surfactants. Interactions in solution will lower the cmc, reduce the concentration of surfactant monomers in bulk solution, and give slow rate of diffusion to the interface. Once adsorbed however, that same interaction between the two surfactants results in a stable condensed surfactant layer with very low surface tension of 27 mN/m. This is a good example of how increasing the degree of order in the surfactant package can affect physical behavior.

Rapid surface tension reduction is believed to be a key property in foam spreading. As the foam spreads across the fuel, new air/water and fuel/water interfaces are generated. At t=0, before any surfactant adsorption has occurred these interfaces have high surface energies. The energy required to form these new surfaces opposes foam flow and introduces an elastic component to the foam rheology. Rapid reduction of these surface energies allows spreading and gives the foam a more viscous rheology.

The ratio of a mixture also has an effect on the foam properties, as shown in Table 6.4, in fresh water, a 2:1 ratio significantly increases the foam stability, this is due to more efficient packing at the air-water interface.

Ratio of surfactants	Expansion ratio	Drainage	Expansion ratio	Drainage
	Fresh water		Sea water	
2:1	8.96	5:58	8.36	3:50
1:1	9.01	3:48	8.17	4:00
1:2	9.00	3:46	8.15	3:26

Table 6.4. Foam properties of a mixture of surfactants at different ratio in fresh and sea water.

The property of anionic and amphoteric surfactants to co-adsorb has been exploited in national Foam's Avio F3 Green KHC 3% foam concentrate that passes the ICAO C standard.

6.1.5. Conclusions

A wide range of single surfactants have been screened for the properties required in a primary surfactant of a fire-fighting foam formulation. Nonionic, siloxane and polymeric surfactants did not have suitable properties and will not be progressed further. Nonionic and polymeric surfactants do not have the surface tension reduction required to generate good quality foam, however may have use as secondary surfactants.

Anionic surfactants foam well in fresh water but not in salt water due to micelle stabilization in high ionic strength aqueous environments.

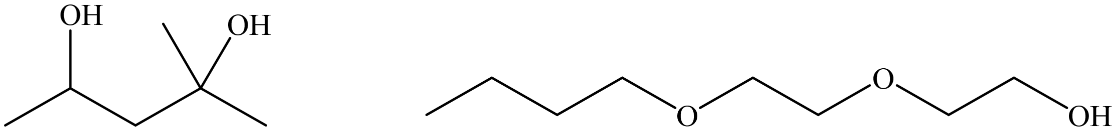
Amphoteric surfactants foam well in both fresh and salt water, but do not give such rapid surface tension reduction as anionics.

Mixtures of anionic and amphoterics can give low equilibrium surface tensions due to an electrostatic interaction in the condensed monolayer at the air / water interface. However this same effect can significantly retard diffusion to the interface, giving slow dynamics.

6.2. Effects of solvents on physical properties

6.2.1. Glycol solvents

Glycol or alcohol ether solvents are added to a foam formulation to increase the surfactant cmc and improve the foam properties. Preliminary investigations on the effect of the solvent on the foam and surfactant properties was carried out by comparing the two most commonly used glycol products, hexylene glycol and butyldiglycol, with four surfactants (anionic and amphoteric). Table 6.5 compares the foam and surfactant properties in the presence of hexylene glycol and butyldiglycol.



Hexylene glycol

Butyl diglycol

Figure 6.7. Chemical structures of hexylene glycol (left) and butyl diglycol (right).

Formulations prepared with hexylene glycol lead to a reduction in the foam properties for both the anionic and amphoteric surfactants when compared with butyl diglycol. This behavior is reflected in a change in the surfactant behavior at the air–water surface. In most cases, formulations containing hexylene glycol have a slower dynamic surface tension and do not reduce the air–water surface tension as far, this implies that the molecules diffuse to the interface slower and the packing at the interface is less ordered, which is confirmed in the number of molecules adsorbed at the interface (Γ) and the area per molecule. From Figure 6.7, hexylene glycol is a more hydrophilic moiety and hence the driving force to adsorb at the air-water interface is reduced, furthermore, the linearity of butyl diglycol will lead to a more densely packed monolayer of surfactant and glycol at the interface. Therefore butyl diglycol is a more efficient and effective foam boosting solvent than hexylene glycol

Surfactant type	**Solvent**	**Expansion ratio**	**Foam stability / s**	**$\gamma_{dyn.}$ (1 % 20 s) / mN m^{-1}**	**cmc / wt.%**	**Γ_m / molecules nm^{-2}**	**A_m / nm^2**
Amphoteric	BG	9.62	190	32.67	0.005	3.406	0.294
	HG	8.16	180	34.13	0.010	1.047	0.955
Amphoteric	BG	9.83	240	28.03	0.300	0.429	2.331
	HG	8.29	225	28.13	0.295	0.146	6.84
Anionic	BG	8.30	225	33.87	0.016	0.894	1.119
	HG	8.44	215	34.00	0.008	0.752	1.329
Anionic	BG	9.95	208	25.27	0.1	1.370	0.73
	HG	8.54	205	25.60	0.1	1.042	0.98

Table 6.5. Surfactant and foam properties for four surfactants with either butyldiglycol (BG) or hexylene glycol (HG), measured at 20 °C in fresh water.

The solvent is being chosen on the basis that it should increase the surfactant critical micelle concentration (cmc) and thereby increase the available surfactant monomer concentration at the air/water interface. An alternative method for determining the effect of each solvent on increasing the cmc, is a parameter known as the cohesive energy density (C) and has been measured for various solvents.

Those with a low value of C, are referred to as water structure makers and tend to lower the surfactant cmc, whereas those with a high value of C are known as water structure breakers and tend to increase the surfactant cmc.

The solvents have been incorporated into a single surfactant model formulation to assess their foam stability on hot petrol and shown in Table 6.6: The quarter drainage time is a quantitative measure of the foam blanket stability.

Generally, those solvents with a higher cohesive energy density give rise to the most stable foams on hot gasoline

Solvent	C (N/m^2)	% loss in quarter drainage time
Formamide	1.719	38.5
Glycerol	1.534	44.3
MPG	1.103	38.1
Hexylene glycol	0.669	30.4
Butyl diglycol	0.527	56.3
Hexyl diglycol	0.475	50.7

Table 6.6. Cohesive energy of a range of solvents and the resulting foam stability.

6.2.2. Effects of salt water

The MIL-PRF 24385F specification requires firefighting foam to perform in both fresh and salt water. Hence it is necessary to understand the surfactant and foam behavior in the presence of salt. Preliminary investigations were carried out with two surfactants, an anionic and amphoteric surfactant. The foam properties of a di-chain anionic surfactant in both fresh and sea water are compared in Table 6.7 and it can be observed that the foam properties, particularly expansion ratio, are greatly reduced in the presence of sea water. This can be explained by examining the aggregation behavior as shown in Table 6.8. The cmc of an anionic surfactant in fresh and sea water is shown in Figure 6.5.

[Anionic] / %	Water type	Expansion ratio	Foam stability / s
0.1	Fresh water	6.92	79
0.5		9.58	230
1		9.95	208
0.3	Sea water	6.18	200
0.5		6.10	206
1		6.52	211

Table 6.7. Foam properties of anionic surfactant in aqueous solutions at 20 °C.

Water type	**$\gamma_{dyn. (1\ \%\ 20\ s)}$ / mN m^{-1}**	**γ_{cmc} / mN m^{-1}**	**cmc / %**	**Γ / molecules nm^{-2}**	**A / nm^{2}**
Fresh water	25.60	25.0	0.1	1.37	0.730
Salt water	24.77	25.3	0.019	1.42	0.703

Table. 6.8. Physical properties of anionic surfactant in fresh and sea water measured at 20 °C.

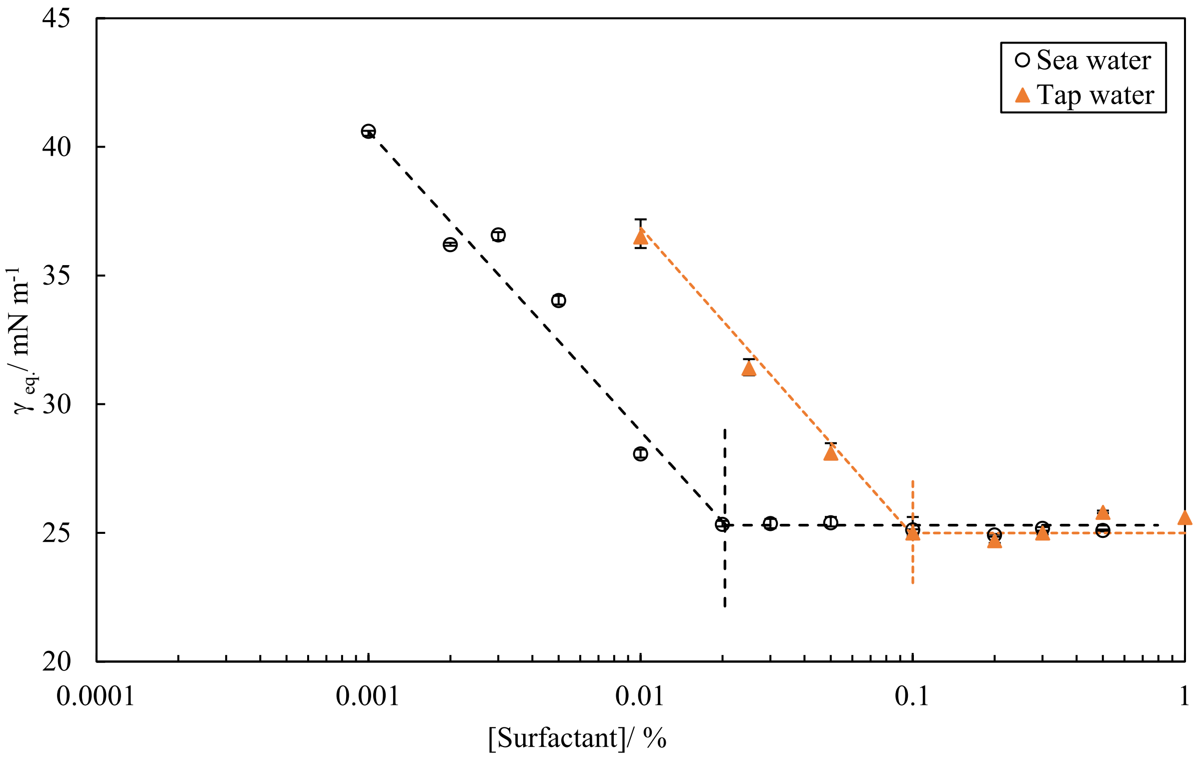


Figure 6.8. Comparison of the cmc of an anionic surfactant in aqueous solution determined by the Wilhelmy plate method at 20 °C.

Figure 6.8 shows that the cmc is considerably reduced in sea water. This is a common phenomenon observed with ionic surfactants. Micelle formation in aqueous solution is an entropy-driven process. The hydrophobic tails in the center of the micelle have more degrees of freedom of movement in this environment than in the bulk water phase. However, there is an enthalpy penalty, since the polar head groups are very closely aligned on the outer surface of the micelle. The presence of salt water screens the electrostatic repulsion between surfactant head groups hence the repulsion between the head groups is shielded leading to a greater driving force to aggregate, and the cmc is observed at a much lower concentration of surfactant. This has a significant impact on the formation of foam, as a lower cmc results in less monomers available to adsorb at an air–water interface to stabilize the foam. Hence the foam quality and stability is reduced.

Amphoteric surfactants are also one of the more commonly used surfactants in firefighting formulations, thus the effect of sea water was investigated. Table 6.9 summarizes the foam properties at increasing concentrations in both fresh and sea water.

From Table 6.9, similar to the anionic surfactant, the expansion ratio decreases in the presence of salt, however, the stability of the foam in salt water was increased. The stability of the foam initially is attributed to a fast adsorption at the air–water surface tension. Figure 6.9 compares the dynamic air–water surface tension with time, from which it can be noted that the surface tension is reduced quicker in the presence of salt, which could account for the stability increase observed with amphoteric surfactant. The physical properties were also investigated and are summarized in Table 6.9, and Figure 6.8 compares the equilibrium phase behavior for both systems.

[Amphoteric surfactant] / %	**Water type**	**Expansion ratio**	**Foam stability / s**
0.3	Fresh water	9.48	180
0.5		9.68	185
1		9.62	190
0.3	Sea water	7.63	238
0.5		8.19	262
1		8.10	278

Table 6.9. Foam properties of amphoteric surfactant in aqueous solutions at 20 °C.

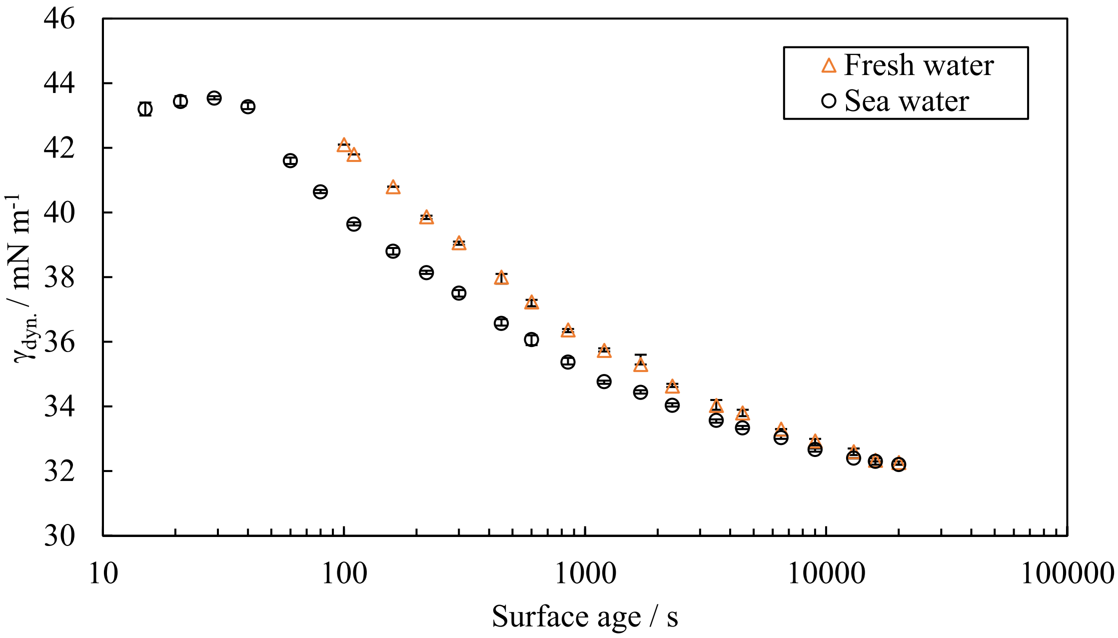


Figure 6.9. Change in air –water dynamic surface tension as a function of time for amphoteric surfactant in fresh (orange) and sea water (black). Measured using bubble pressure tensiometer at 20 °C.

Water	**cmc / %**	**Γ / molecules nm^{-2}**	**A / nm^2**
Fresh	0.0049	3.1865	0.314
Sea	0.0045	2.9735	0.336

Table 6.10. Physical properties of a single amphoteric surfactant in fresh and sea water measured at 20 °C.

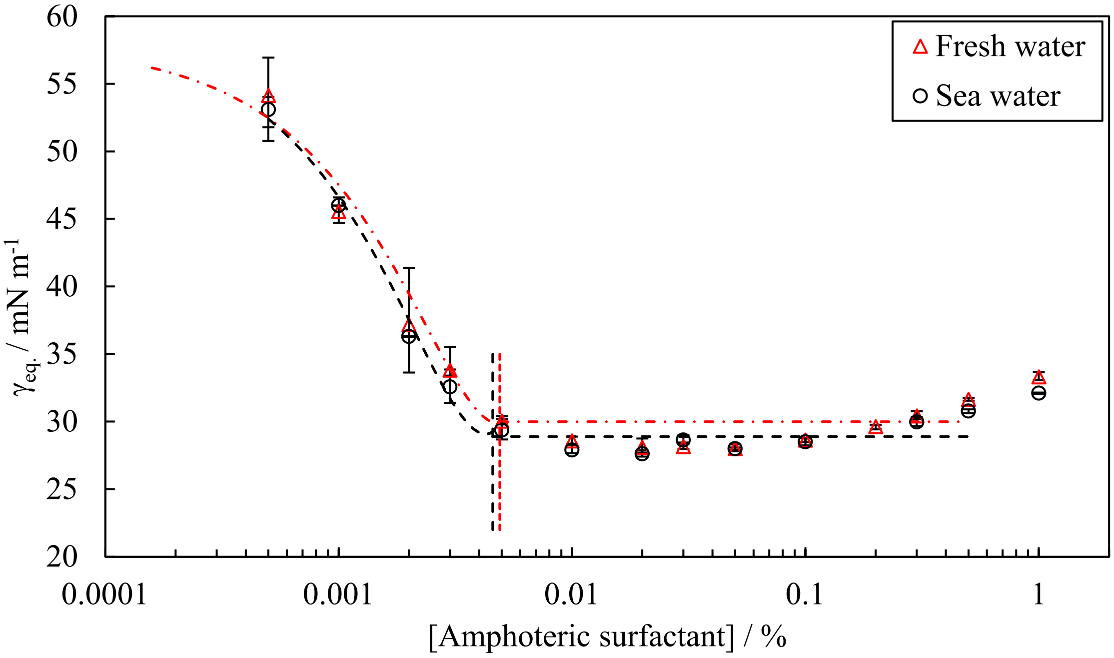


Figure 6.10. Comparison of the cmc of amphoteric surfactant in aqueous solution determined by the Wilhelmy plate method at 20 °C.

From Figure 6.10 and Table 6.10, the aggregation properties of amphoteric surfactant are not significantly affected by the presence of ions in salt water, unlike anionic surfactants. Therefore any observed affects are attributed to a "salting out" of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant.[38]

Salting in or salting out by an ion depends upon whether the ion is a water structure breaker or a water structure maker. Ions with a large ionic charge-radius ratio, such as F^-, are highly hydrated and are water structure makers. They salt out the hydrophobic groups of the monomeric form of the surfactant and decrease the cmc. Ions with a small ionic charge/radius ratio, such as CNS^-, are water structure breakers; they salt in the hydrophobic groups of the monomeric form of the surfactant and increase the cmc. The total effect of an electrolyte appears to approximate the sum of its effects on the various parts of the solute molecule in contact with the aqueous phase. In both the monomeric and micellar forms, the hydrophilic groups are in contact with the surrounding aqueous phase and may cancel each other out, whereas the hydrophobic groups are shielded when aggregates are present, thus are significantly affected by the addition of electrolyte to the aqueous phase below the cmc when they are in the monomeric form.[38]

Staszak *et al.* investigated the effect of sodium chloride on the surface properties of cocamidopropyl betaine.[39] The group observed that with the addition of a low concentration of salt, the change in the cmc was negligible, (cmc-0.28×10^{-3} M in water, 0.89×10^{-3} M in 0.01 M NaCl), it was noted a much larger concentration of NaCl was required to observe any changes (cmc-7.02×10^{-3} M in 2 M NaCl). This is very different behavior than observed for ionic surfactants, whereby only slight changes in the ionic strength of the solution have a marked effect on the aggregation behavior.

As requested in MIL-PRF 24385F specification, compatibility with sea water needs to be achieved. From equilibrium and dynamic surface tension measurements it was found out that the presence of salt in the solutions lessens the ability of both surfactants to reduce surface tension and decreases the CMC which is reflected in the low foam expansion ratio and poor foam stability achieved in the absence of solvent (Table 6.11).

Water type	**Solvent**	**Foam expansion**	**Stability / m:s**
Freshwater	0 % BG	9.14	6:08
Seawater	0 % BG	7.99	3:58
Seawater	5 % BG	8.40	9:59

Table 6.11. Effect of solvent on the foam properties in sea water using 1:1 ratio surfactants (anionic:amphoteric).

The foam bubble structure is also significantly altered in sea water. Figure 6.11 compares the formulation in fresh and seawater in the absence of solvent. It can be noted that in fresh water, the bubble size is much smaller and monodisperse compared to in seawater.

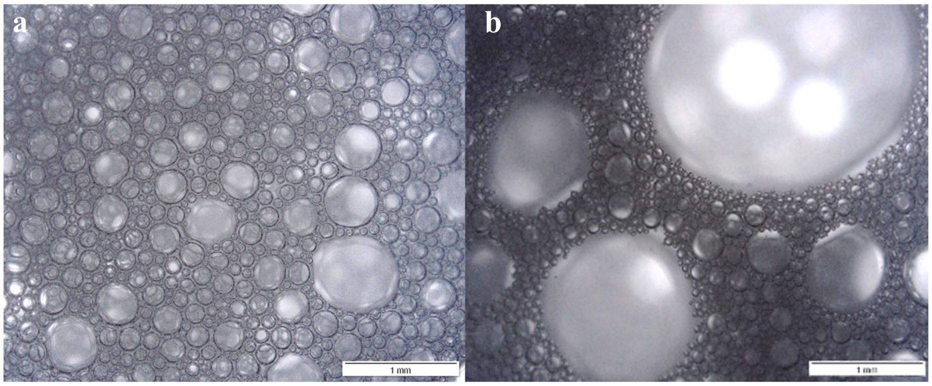


Figure 6.11. Optical images comparing foam structure in fresh (a) and seawater (b).

6.2.3. Conclusions

The foam properties are significantly affected by the presence of sea water. This has been attributed to a reduction in the critical micelle concentration of anionic surfactants. Amphoteric species foam well in fresh and salt water without the need for a solvent. Glycol solvents are often used as foam boosting solvents by increasing the cmc which can improve the properties in sea water, however there is some evidence they can increase fuel pick up when foam is forcefully applied to a fire.

Future formulations containing mixtures of amphoteric and anionic surfactants will be examined with alternative foam boosting species or in the absence of solvent molecules for fresh water only formulation.

6.3. Formulations with polymers

6.3.1. Polymers evaluated

Fluorine-free foams are formulated with polymers to slow down drainage, increase solution viscosity and provide structure to the foam. The effect on foam properties depends on the polymer structure, molecular weight, solubility and interactions with other formulation components. A wide range of polymer types were screened for their effects on foam properties.

Type of polymer	Mode of action	Examples
Associative type thickeners	Hydrophobic portions of polymer form 3D network	Borchi gel Thix 921
Natural gum NG	High MW to increase bulk solution viscosity	Polysaccharides - xanthan
Modified gums MG	Charged polymers interact with surfactants	Polysaccharides – guar, diutan
Acrylates	Charged polymers interact with surfactants	Texitryl 13-645
Zephrym	Polymeric surfactant	Zephrym
Cellulosics	High MW to increase bulk solution viscosity	Methocel
Surfactive	High MW to increase bulk solution viscosity	MM1000
SH succinoglycan	Rheology modifier	Rheozan
Polypeptides	Polymeric surfactant	Mirapol

Table 6.12. Initial screening of polymer types.

Those polymers that increased drainage times without any adverse impact on expansion ratio were then taken forward and their behavior on hot fuel was investigated with a small scale fire test. The extinguishment time on heptane, and time taken for the foam blanket to re-open were measured. Polymer formulations were tested initially without solvent, and then with solvent added.

6.3.2. Effect on foam properties

A formulation consisting of 10% of a primary surfactant and polymer without solvent was prepared. A control sample had no polymer, other samples contained 0.5 to 2% polymer. A single test was carried out on each formulation. Foam was generated in the laboratory using the standard MIL-PRF 24385F nozzle with spreader tip. Foam expansion ratio and drainage times were measured and compared with the control formulation.

Polymer type	Concentration	Expansion ratio	Drainage time (min:sec)
None (control)	None	7.98	3.17
Associative thickener 1	1%	8.63	2:53
Associative thickener 2	1%	8.45	2:33
Associative thickener 3	1%	8.08	3:10
Associative thickener 1	2 %	9.05	3:19
NG 1	0.5%	7.61	7:11
NG 2	1%	7.03	21.52
MG 1	1%	7.96	6.22
Acrylic 1	2%	8.59	4:49
Acrylic 2	2%	9.00	5:14
Acrylic 3	2%	7.92	4:46
Polymeric surfactant	1%	8.67	3:18
Cellulosic	0.5%	8.98	3:59
	1%	8.88	4:05
Surfactive	0.5%	8.86	6:59
	1%	8.76	10:22

Table 6.13. Foam properties of formulations prepared with polymers.

With no polymer, the expansion ratio is good, around 8. This is high enough to generate a volume of foam that is sufficient to fill the 28 or 50 ft^2 pan in the full scale fire tests. However the 25% drainage time is very rapid at around 3 minutes. This is not long enough to provide the required burnback time of 6 minutes. The aim of this test program is to identify polymers that can maintain the good expansion ratio and also significantly slow down drainage.

Associative thickeners did not improve foam drainage properties. The natural gum gave a slight reduction in expansion ratio but a very large increase in drainage time. The modified gum did not affect expansion ratio but gave a doubling of drainage time. Acrylic polymers slightly increased expansion ratio, presumably due to some surface activity. Drainage time was extended to around

5 minutes, but this is still too fast and these foams were concluded to not be stable enough to withstand the MIL-PRF 24385F testing. The polymeric surfactant did not increase drainage time.

Cellulosics gave a slight increase in both drainage and expansion ratio and a large increase in stability was observed with Surfactive polymer. Polymers which showed an improvement in physical properties were gums, cellulosics and Surfactive. These were taken forward to a small scale fire test.

Cellulosic Polymer		**Expansion ratio**	**Stability (25% drainage) / m:s**	**Fire testing (79cm^2/120mL foam)**	**Fire testing (113cm^2/120ml foam)**
Low molecular weight	0.5%	8.98	3’59”	Ext: 11’’/12’’ Reopen: 2’10’’/2’17’’	Ext: 13’’/14’’ Reopen: 1’34’’/1’57’’
	1%	8.88	4’05”	Ext: 11’’/10’’ Reopen: >4’ />4’	Ext: 9’’/10’’ Reopen: 2’32’’/3’01’’
Medium molecular weight	0.5%	8.92	3’58	Ext: 16’’/10’’ Reopen: 1’08’’/>4	Ext: No Ext/ No Ext Good control
	1%	8.87	4’12”	Ext: 10’’/11’’ Reopen: >4’ /3’38’’	Ext: No Ext/ No Ext Good control
High molecular weight	0.5%	8.95	4’05”	Ext: 11’’/10’’ Reopen: 3’10’’/>4’	Ext: No Ext/ No Ext Good control
	1 %	8.92	4’13	Ext: 10’’/10’’ Reopen: >4’/>4’	Ext: 11’’/No Ext’’ Reopen: 3’10’’/-

Table 6.14. Foam properties of formulations prepared with cellulosic-type polymers.

6.3.3. Fire testing of polymer-containing formulations

Foam was generated using the MIL-PRF 24385F nozzle and spreader tip, and fire performance evaluated in a lab scale heptane fire test. This involved noting the extinguishment time and the time for the foam blanket to reopen. This gives an indication of the foam stability to destruction by fuel.

The first series of tests focused on cellulosic polymers. Performance on the 79cm^2 pan was good, with all foams extinguishing the fire, and some maintaining foam blanket integrity longer than 4 minutes. However, on the more demanding 119cm^2 pan fire, some of the formulations did not extinguish and none were able to maintain the foam blanket for 4 minutes, which could be due to insufficient foam drainage.

The foam properties and fire performance of a range of higher molecular weight natural and modified gums were investigated and compared to the initial formulation with no polymer. Fire performance was measured using a small lab scale test, with a 79 cm^2 pan and heptane. The results are in Table 6.15.

Polymer		Expansion ratio	Stability / m:s	79 cm^2 pan
0%		8.65	02:59	No extinguishment
0.5 %	NG1	7.63	08:24	No extinguishment
	MG1	7.45	03:18	No extinguishment
	MG2	7.49	04:52	No extinguishment
	MG3	6.98	07:22	No extinguishment
	MG4	8.86	06:59	Ext: 13’’/14’’ Reopen: >4’/3’15
1%	NG1	7.07	19:16	Extinguished: 18 s Foam break down: 59 s
	MG1	7.05	04:18	No extinguishment
	MG2	7.46	06:14	Extinguished: 23 s Foam break down: 61 s

Polymer		Expansion ratio	Stability / m:s	79 cm^2 pan
	MG3	6.79	17:45	No extinguishment
	MG4	8.76	10:22	Ext: 13’’/14’’ Reopen: >4’/3’12
2%	NG1	6.33	> 45 min	Extinguished: 20 s Foam break down: 56 s
	MG2	7.78	05:01	No Extinguishment
	MG3	6.34	> 45 min	No extinguishment
	MG4	8.88	10:55	Ext: 10’’/12’’Reopen: 3’12/3’37

Table 6.15. Foam properties and lab fire performance of natural and modified gums without solvent.

Modified gums MG1 and MG2 had little effect on the foam drainage rate, MG3 gave long drainages but had a significant impact on expansion ratio, and failed to extinguish the small fires. This polymer is of too high a molecular weight, with the result that the foam solution is viscous. This reduced expansion ratio and retards foam spreading. No further development was carried out with these polymers. MG4 gave some promising results and will be investigated further in mixtures.

NG1 is a natural polysaccharide that has not had functional groups added to the backbone or side chains. This polymer had the greatest effect on drainage, which leads to good foam stability on the small scale lab fire test.

Microscopy was used to correlate the fire test results to the vapor suppression properties of each formulation. Figure 6.12 compares the effect of the addition of polymer to the vapor suppression properties. From Figure 6.12a, the fuel has a strong interaction with the foam blanket and moves from the foam lamellae into the bubbles, causing them to rupture. In comparison Figure 6.12b shows the effect of the addition of MG4 polymer, it can be observed that the foam walls are strengthened with the addition of the polymer, causing the fuel to remain in the foam lamellae and not diffuse into the foam bubble and destroy the foam structure. This explains the improvement of the mini fire test, from no extinguishment to extinguishment and some vapor suppression against hot fuel.

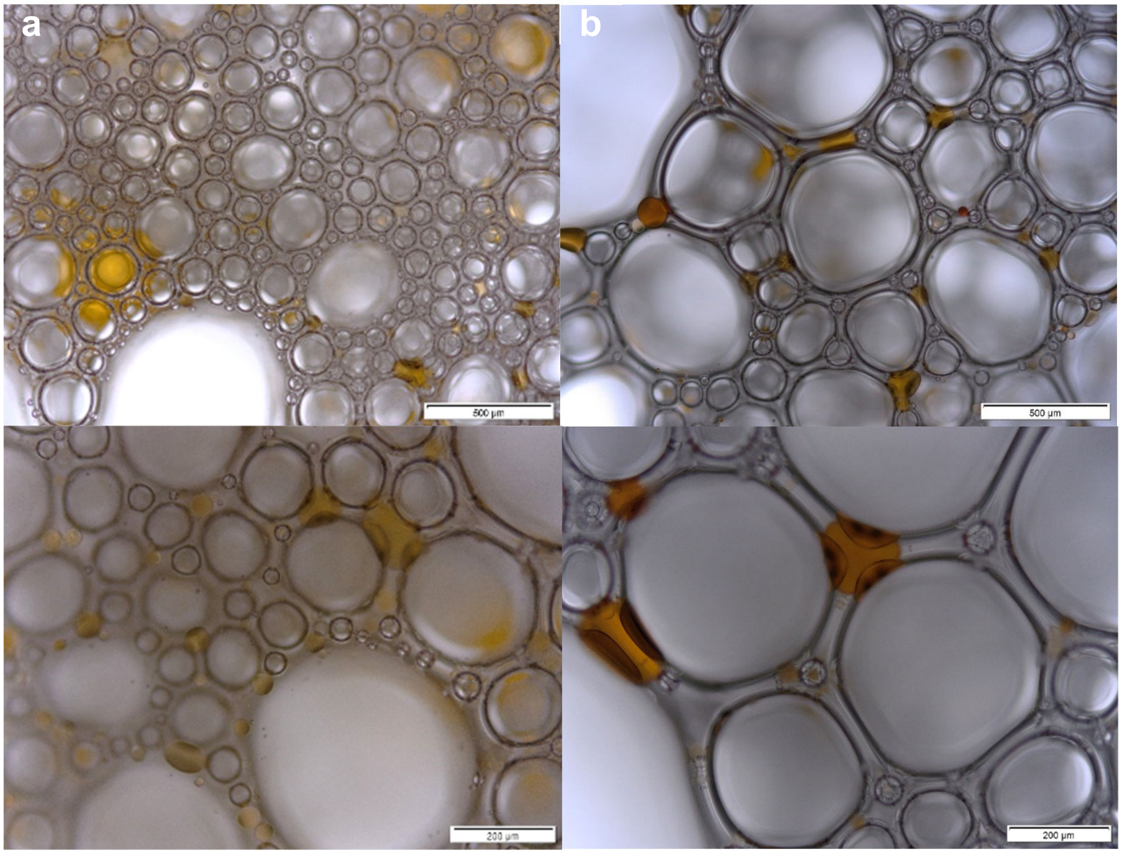


Figure 6.12. Optical micrograph of formulation without polymer (a), and the addition of MG4 polymer (b).

The addition of polymer has a marked impact on the foam properties of each formulation. In particular it increases the stability of foam, which increases the performance on small scale fire test. With no polymer there is no extinguishment as the foam is not stable to fuel. Too much polymer again leads to no extinguishment since the foam is too stiff and does not spread easily. An optimum concentration and type of polymer gives both fuel stability and spreading, and extinguishes the fire.

6.3.4 Effect of solvent on foam properties and small fire test

The addition of solvent is known to increase the expansion ratio and foam quality. The effect of adding a solvent to the formulation was explored with different grades of polymers. The solvents investigated were branched chain hexylene glycol (HG) or straight chain butyl digol (BG) and dipropylene methyl ether (DPM).

Polymer	Solvent	Expansion ratio	Stability (min:sec)	79 cm^2 pan
0% polymer	0 %	8.65	2:59	No extinguishment
1% NG	0 %	7.07	19:16	Extinguished: 18 s , Foam break down: 59 s
0.5% NG	5 % HG	7.82	17.50	No extinguishment
1% NG	0.5% HG	7.93	10.15	No extinguishment
	1% HG	7.68	40:25	Extinguished: 15 s, Foam break down: 50 s
	2% HG	7.45	> 60:00	Extinguished:18 s Foam break down: 56 s
	1% BG	7.45	20:34	No extinguishment
	2% BG	7.99	40.00	No extinguishment
1% NG2	10% HG	8.41	7:13	No extinguishment
1% NG3	1% HG	8.25	17:30	Extinguished:18 s Foam break down: 36 s
1% NG4	1% HG	7.75	32:15	Extinguished:15 s. Foam break down: 39 s
1% MG	0 %	7.46	6:14	Extinguished: 23 s. Foam break down: 61 s
1% MG	1% HG	8.32	4:16	No extinguishment
1% MG	2% HG	9.53	4:55	
1% MG	5% HG	10.24	5:52	Extinguished: 13 s Foam break down: 3:47 s

Polymer	**Solvent**	**Expansion ratio**	**Stability (min:sec)**	**79 cm^2 pan**
1% MG	10% HG	11.38	6:43	No extinguishment
1% MG	10% DPM	9.66	4:52	No extinguishment
1% MG	5% HG + 5% BG	10.21	5:23	Extinguished: 14 s Foam break down: 3:42 s
0.5% MG 2	0 %	9.08	4:45	Extinguished: 14/13'' Foam break down: 2'34''
1% MG 2	0 %	8.55	4:49	Extinguished: 11/14'' Foam break down: >4'
2% MG 2	0 %	8.55	4:58	Extinguished: 10/15'' Foam break down: >4'
1% MG 3	0 %	8.17	4:28	Extinguished: 15/16'' Foam break down: 2'52''
0.5% NG + 0.5% MG	0 %	8.28	9.09	Extinguished: 24 s Foam break down: 66 s

Table 6.16. Fire test MIL-PRF 24385F branch pipe/ 3% Foam solution in fresh water with solvent.

The addition of solvent generally improves the foam properties, especially the expansion ratio. However this has a detrimental effect on the fire test performance, which is due to an increase in fuel emulsification.

6.3.5 Full scale 28ft^2 fire tests

The lab scale testing allows the identification of promising experimental formulations, these were then assessed on a full scale 28ft^2 fire test. Criteria used to select formulations for larger scale testing were the expansion ratio, preferably above 8, the drainage time, preferably above 5 minutes and the small scale fire performance, achieving extinguishment and foam break down greater than one minute. The standard MIL PRF 24385F 28ft^2 fire test procedure, with heptane fuel was used. The formulations contained the same primary surfactant with each polymer and solvent. The results are shown in Table 6.17.

Polymer	**Solvent**	**Expansion ratio**	**Foam stability M:s**	**Control (30 s) / %**	**Ext. / s**	**Burnback / s**	**Comments**
None	1% HG	8.2	3:46	85%	85	170	Sloppy foam, holes in blanket reignited
None	1% HG	8.2	4:50	90%	76	210	Thicker foam, blanket more stable
6% MB	1% HG	8.2	6:20	90%	65	190	Similar to above
1% NG1	1% HG	7.9	11:07	85%	75	240	Poor foam properties
1% NG2	1% HG	8.1	31:14	95%	53	480	Fast control, edge flickers slow
2% NG2	1% HG	6.8	37:56	90%	70	1030	Low expansion, slow control
1% NG1	None	7.5	21:48	90%	48	540	
1% MG1	10% HG	9.1	8:15	80%	60	364	
1 % MG2	10 % HG	8.4	7:13	80 %	83	39	
2% Cell 1	10% HG	7.8	5:03		69	83	

Polymer	**Solvent**	**Expansion ratio**	**Foam stability M:s**	**Control (30 s) / %**	**Ext. / s**	**Burnback / s**	**Comments**
5% MG2	5% HG	8.7	5:53	75%	52	381	New foam breaks blanket
2% MG2 1% NG1	10% HG	7.9	3:20	70%	53	660	Low expansion, slow control
1% PEI	1% BG	5.3	3:15		92	324	
1% PEI	3% PEG	5.1	3:27		100	275	

Table 6.17. Fire performance on 28 ft^2 MIL-PRF 24385F pan with heptane with formulations containing polymers.

Formulations without polymer and low levels of solvent extinguished in 70 - 80 seconds, burnback was around 200 seconds. The addition of modified gum improved the burnback performance. Further work will be conducted using the modified polymers.

The synergistic effect of polymer mixtures was investigated using a mixture of natural polysaccharides, either straight chain or with side-groups. Solvent was used to improve the foam expansion ratio. The fire performance was investigated using the small lab scale test using heptane (Table 6.18).

Formulation		Expansion ratio	Stability / m:s	Extinguishment time on heptane 113 cm^2 pan.
Surfactant ratio Ampho : anionic	Polymer			
1:1	none	9.01	3'48"	No Ext
	MG2	7.54	34’02	9”, stable > 4’
	NG1 (10 % BG)	9.02	5’18”	No Ext
1:2	none	9	3’46”	18”, reopened after 2 min
2:1	none	8.96	5'58"	No Ext
	MG2	8.51	32'24"	14 “, stable > 4’
	NG1	8.92	4’00”	22”, reopened after 2 mins

Table 6.18. Lab scale fire performance of polymer blends.

From Table 6.18, a 1:1 ratio of surfactants gave the fastest extinguishment time. The addition of MG 2 type polymer reduced the expansion ratio, however increased the foam stability and fire performance. NG1 polymer had less effect on the foam expansion. Foam stability was increased less than MG2, which was reflected in the stability on hot fuel. MG2 showed high levels of fuel stability, further work will continue to explore the interactions between the 1:1 surfactant mixture and concentrations of MG2 polymer.

6.3.6. Physical properties of polymer formulation

Correlations between the physical properties of the foam and the fire test enable further understanding of the relationship and minimize the requirement to conduct large scale fire tests. Rheology can be used to understand the flow behavior and polymeric effects of the foam. Table 6.19 shows the yield stress as a function of the concentration of a natural gum compared to a fluoroprotein. Low shear rate gives information about the foam properties and high shear rate is useful for how the foam flows through a pipe or hose.

	NG (%)	Expansion ratio	Drainage	*Viscosity (cPs)		*Yield stress (Pa)
				1/s	10/s	
Fluorine free	0.0	7.98	3:17	3638	551	1.749
	0.5	7.61	7:07	2899	467	1.959
	1.0	7.03	19:52	2590	458	1.499
Fluoroprotein				11080	1420	8.101

Table 6.19. Measured yield stress of natural gums using a vane geometry at 25 °C.

From Table 6.19 as the concentration of polymer increases, the viscosity and yield stress of the foam decreases, the optimal concentration content was determined as 1%.

The dynamic surface tension is a key parameter for the foam expansion and spreading properties. From Figure 6.13, polymer slows down the rate of surface tension reduction; however the addition of solvent increases the rate of surface tension reduction.

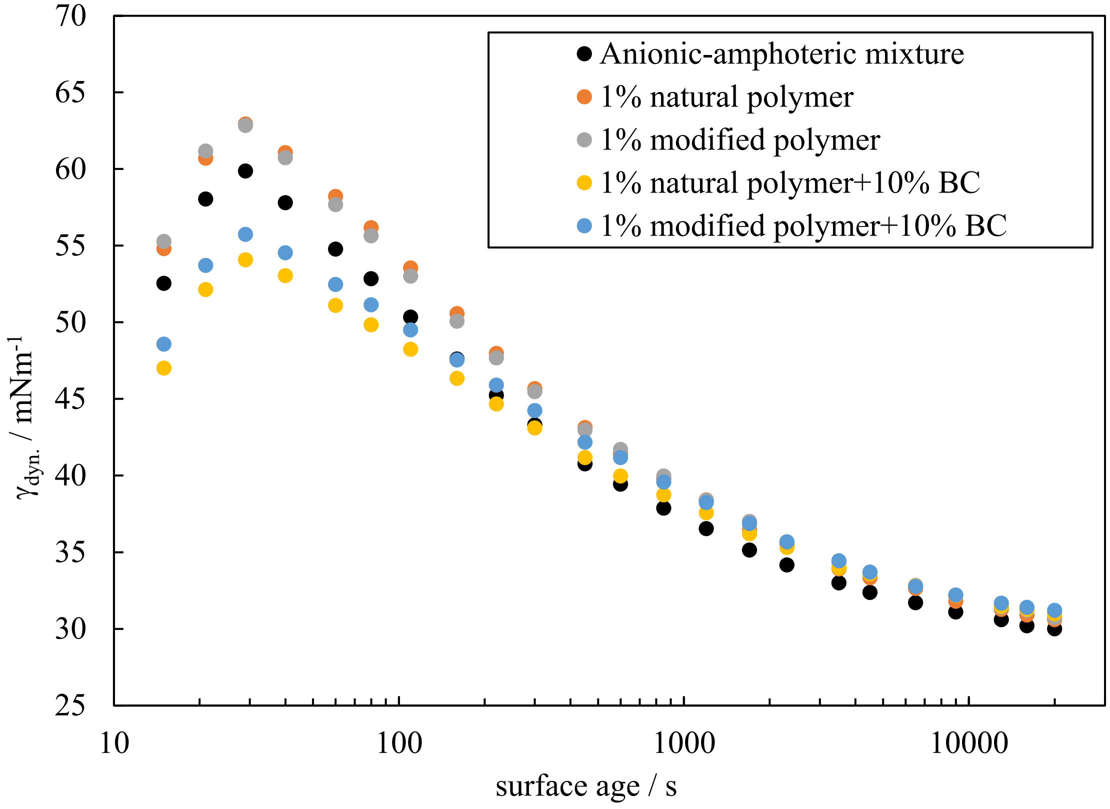


Figure 6.13. Effect of polymer and solvent on the dynamic surface tension.

Finally, the effect of pH on the foam properties was investigated for two polymers using the preferred surfactant package and 10 % solvent. As the pH was reduced below 6.5, the foam properties were significantly reduced. As the pH becomes more acidic, the surfactants become protonated and lose their charge, (salting out effect is observed), hence the number of interactions is significantly reduced.

pH-Premix	**Expansion ratio**		**Stability (25 % drainage) / m:s**	
	1 % MG4	1 % MG1	1 % MG4	1 % MG1
12	8.88	8.78	4' 08"	34'10"
11	8.69	8.74	8' 03"	17'16"
10	8.84	8.74	7' 30"	31'42"
7	8.72	8.91	7' 03"	27'44"
6.5	8.87	8.95	9' 01"	26'56"
4.9	5.24	5.44	1' 56"	3'22"

Table 6.20. Effect of pH on foam properties.

6.3.7. The addition of clay particles.

Clay particles are commonly used as rheology modifiers in aqueous systems and have been shown to possess cooling properties and high fuel tolerance,

A range of clay samples were received from Imerys Clay. The foam properties and vapor suppression characteristics of surfactant formulations containing each clay material have been investigated and the main results summarized in Table 6.21. The formulation of the foam concentrate contained 10% of anionic surfactant, 10% amphoteric surfactant, 15% clay, with no solvent added. Concentrate was diluted to 3% in fresh water for testing.

Sample	Expansion ratio	Foam stability / m:s	Fire Performance 113cm^2/120mL foam
E7992	8.47	12’14”	12” Reopen > 4 s
E8480	7.74	9’34”	10” Reopen >4
E8493	5.82	1’51”	No Ext. Large reopening.
E8483	8.89	4’39”	17". Reopen >4'
E8488	8.94	5’27”	12", Reopen >4'
E8003	7.99	8’32”	11", Reopen 3’49”
E8491	6.84	2’52”	11", Reopen >4'
E8492	7.7	5’48”	11" Reopen ~4’00”
E8481	8.92	4’30”	No Ext, Reopen >4'
E8501	8.33	4’36”	13", Reopen 1’13”

Table 6.21. Foam properties and lab-fire performance of a range of clay formulations. For each formulation a 10:10 Mixture of surfactants was used with 15 % clay added.

The best mineral performance was given by the E8003 and E8480 showing very good foam stability, quality and fuel stability. This was closely followed by the E8492 and E8488 which gives good foam stability and expansion ratio respectively. The addition of the Talc seemed to give average results as well as the modified Kaolin As seen in Figure 6.14, E8003 foam exhibits good fuel shedding characteristics, which correlates to the small scale fire performance. Whereas E8491 is a very poor quality foam that shows a significant amount of fuel emulsification, explaining the poor fire performance. Further formulation and stability investigations will be explored with the promising samples.

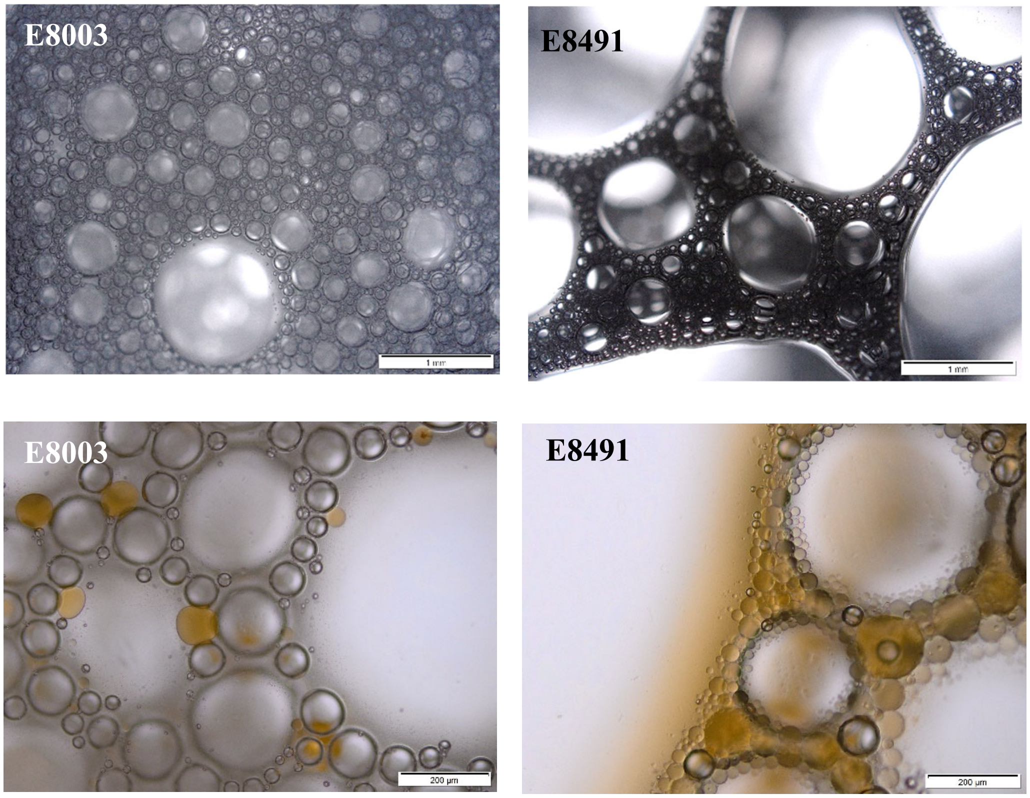


Figure 6.14. Microscope images showing the difference in bubble structure and fuel tolerance (on heptane) of a good (left) and a poor foam sample (right).

6.3.8. Performance in sea water.

The MIL-PRF 24385F specification requires a formulation to perform in both fresh and sea water. The preferred primary surfactant formulation was formulated with two different polysaccharides at 1% with increasing solvent concentration. The foam properties and fire performance in sea water in a small lab scale test were measured.

Polymer	Solvent (%)	Expansion ratio	25% drainage time / m:s	Fire performance on heptane 113 cm^2 pan.
1% NG1	0	4.16	5:12	Ext: 8 s / 9 s. Reopen> 3 min
1% NG1	5	6.85	8:45	Ext:11 s /12 s. Reopen> 3 min
1% NG1	10	7.53	20:8	Ext: 11 s. Reopen:>3 min
2% NG1	0	4.13	>30	Ext:8 s. Reopen > 4 min
1% MG1	0	4.30	1:30	Foam too poor to test
1% MG1	5	7.35	3:33	Ext:15 s. Reopen > 3min
1% MG1	10	8.53	4:10	Ext: 13 s. Reopen: 2:50

Table 6.22. Sea water effect in foam properties using the MIL-PRF 24385F branch pipe.

From Table 6.22, the foam stability was improved with the addition of 10 % solvent, this is because the solvent increases the solubility of surfactant in sea water, more surfactant molecules are available to adsorb at the air-water interface and stabilize the foam. The fire performance of two formulations with 10% solvent was investigated on the 28 ft^2 MIL- PRF 24385F test method. However, the formulations displayed poor foam properties using the MIL- PRF 24385F nozzle and poor fire performance.

	Primary surfactant MG 1% 10% solvent	Primary surfactant NG 1% 10% solvent
Expansion ratio	3.85	4:95
Drainage time (s)	2:20 (9ºC)	10:53 (10ºC)
Fuel temperature (ºC)	Poor foam properties. Fire test was not performed	24
% Control at 30 s		No extinguishment
Extinguishment time (s)		
Burnback time (m:s)		n/a

Table 6.23. 28ft^2 MIL- PRF 24385F test performed on heptane using sea water.

From Table 6.22. the foam expansion is significantly reduced for both systems, however when NG polymer is used, some foam stability is still observed. Whereas, the foam stability is significantly reduced with the MG polymer. The MG polymer forms a network with the surfactants in the foam lamellae, the increased concentration of electrolyte present in sea water screens the interactions between the polymer and surfactant, reducing the networking in the foam lamella, and hence reducing the foam stability.

6.3.9. Polypeptide polymers

Gas diffusion occurs more readily in foams with simple monolayer surfactant films rather than foams stabilized by thick, elastic crystalline gel phases or densely condensed surfactant phases. The former are exemplified by proteins, polymer films or hydrophilic particles.

Diffusion theory states that the rate of gas molecules moving through a liquid film is governed by the permeability of the monolayer, the area of the liquid film and the concentration gradient.[40] Furthermore Princen[41] has stated that the foam film permeability can be linked to Ostwald's solubility coefficient, the gas diffusion coefficient and the thickness of the liquid layer in the film.

Foam vapor barrier properties might be improved by making the bubble walls thicker and denser - this may partly explain why high molecular weight gums are effective. An alternative approach is to formulate an anionic surfactant with a polypeptide. Provided their natural incompatibility can be overcome, this combination might produce stable and long lasting expanded foams in both fresh and sea water. A stable formulation has been prepared for use at 6%. This formulation was tested in a 28ft^2 fire test on gasoline.

Expansion ratio	5.8
Drainage time	5'04"
Fuel temperature (°C)	12
% Control at 30 s	90
Extinguishment time (s)	87
Burnback time (m:s)	360

Table 6.24. Fire performance on gasoline of a formulation containing polypeptide.

The foam achieved rapid 90% control within 30 seconds, and extinguishment on 87 seconds. Burnback time was 360 seconds.

Considering this test was performed on gasoline, these are good results, and the polypeptide will be considered for further development.

6.3.10. Conclusions

This section of the project assessed a range of polymers for their effects on foam properties in fresh water. This included a mixture of polymer type, molecular weight distribution and concentration. The addition of polymer slows down the dynamic surface tension and in some cases, reduces the foam expansion, although the addition of a foam boosting solvent improves the foam properties. The fire performance of promising formulations was screened using a small-scale lab fire test, and the effect on extinguishment and blanket re-opening time was investigated. Full scale MIL- PRF 24385F 28ft^2 fire tests were conducted on the most promising polymer-solvent combinations, natural and modified polymers show promise, however edge sealing and fuel pick up due to the presence of solvent slowed down final extinguishment times. Mixtures of polymers were investigated and some synergistic behavior was observed. The physical properties, such as dynamic surface tension, viscosity and foam yield stress were measured and correlations between these properties and the fire performance have been made. Performance in sea water was significantly affected by the structure and charge of the polymer. A formulation containing a polypeptide gave reasonable performance on a 28ft^2 gasoline fire.

6.4 Effect of adding a secondary surfactant to the formulation

6.4.1. Adsorption of secondary surfactants

It is known that certain substances can, when formulated with surfactants, significantly change the structure of the adsorbed film, thus affecting the stability of the foam. For example, the incorporation of fatty acid or alcohol molecules in a surfactant adsorption layer increases the surface elasticity and renders the mixed adsorption monolayers tangentially immobile as shown in Figure 6.15.

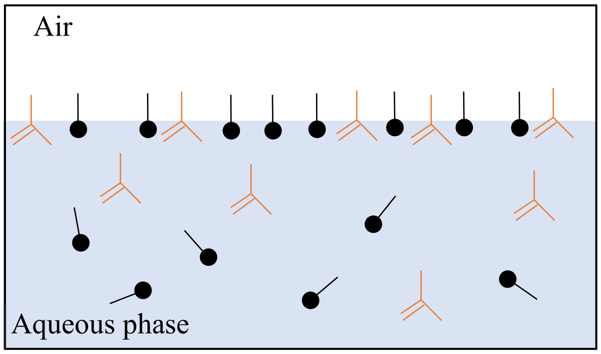


Figure 6.15. Interaction between charged surfactant and fatty alcohol (orange) at the air–water interface.

The effect of long chain fatty acids and fatty alcohols on the foam properties and fire performance were investigated. Increasing concentrations (from 0.1 - 1 %) of lauric acid LA, stearic acid SA, lauryl alcohol LAC and glycerol were added to a surfactant package and either natural polymer (NG) or modified polymer (MG1) polymer at 1 %. The results are summarized in Table 6.25.

Polymer	**Solvent**	**Fatty acid**	**Expansion ratio**	**Drainage time (min:sec)**	**Fire testing ($95cm^2$/120mL foam)**
MG1	10%	None	8.17	4:43	Ext: 13 s / 12 s Reopen: >4:00
	10%	0.2 % L.A	8.73	5:35	Ext: 13 s / 16 s Reopen: >4:00
	10%	0.5 % L.A	8.79	5:40	Ext: 13 s Reopen: 2:00
	10%	1.0 % L.A	8.87	5:41	Ext: 16 s / 18 s Reopen: 2:00
	10%	0.2 % LAC	8.89	6:41	Ext: 12 s / 16 s Reopen: 2:00
	10%	0.5 % LAC	8.83	7:08	Ext: 14 s / 16 s Reopen: 2:06

Polymer	**Solvent**	**Fatty acid**	**Expansion ratio**	**Drainage time (min:sec)**	**Fire testing ($95cm^2$/120mL foam)**
	10%	1.0 % LAC	8.68	9:01	No Ext
NG1	None	None	7.54	> 30 min	Ext: 11 s / 10 s Reopen: >4:00
	10%	None	8.97	> 30 min	Ext: 9 s / 11s Reopen: >4:00
	10%	0.5 % L.A	8.46	13:10	Ext: 9s / 7s Reopen: 3:08
	None	0.2% SA	7.90	28:17	Ext: 18s Reopen: 1:40
	None	0.5% SA	6.77	>30 min	Ext: 21s Reopen: 1:10
	None	0.5% LA	7.70	>30 min	Ext: 10s Reopen: 1:35
	None	0.5% LAC	8.89	>30 min	Ext: 16s / 13s Reopen: 2:30 – 4:00
	None	0.8% LAC	8.78	20:24	Ext: 17s / 13s Reopen: 2:30 – 4:00
	None	1.0% LAC	8.46	>30 min	Ext: 15s / 13s Reopen: 2:30 – 4:00
	1%	None	7.20	18.25	Ext: 27s Reopen: >9:00
MG1	None	1% glycerol	9.02	6:03	Ext: 15 s / 14s Reopen: >4:00

Polymer	Solvent	Fatty acid	Expansion ratio	Drainage time (min:sec)	Fire testing ($95cm^2$/120mL foam)
	None	2% glycerol	8.97	5:05	Ext: 13 s / 13s Reopen: >4:00
	None	5% glycerol	8.96	5:58	Ext: 13 s / 13s Reopen: >4:00

Table 6.25. Effect of the addition of fatty molecule.

From Table 6.25 the foam stability was generally increased by the addition of either long chain fatty acids and alcohol. Long chain stearic acid reduced foam stability on fuel, whereas the shorter lauric acid and lauryl alcohol both performed better, this can be attributed to the size of the small molecule added, the shorter molecules can form a more densely packed layer at the surface, hence increasing the fuel barrier. Rheology was used to investigate the influence of the small molecules on the viscosity of the foam. The foam viscosity was so high the blanket took longer to flow across the pan weakening the edges and thus weakening the blanket sitting on hot fuel. Figures 6.16 and 6.17 show the addition of fatty alcohol increases the foam viscosity and yield stress significantly more than the small acid species.

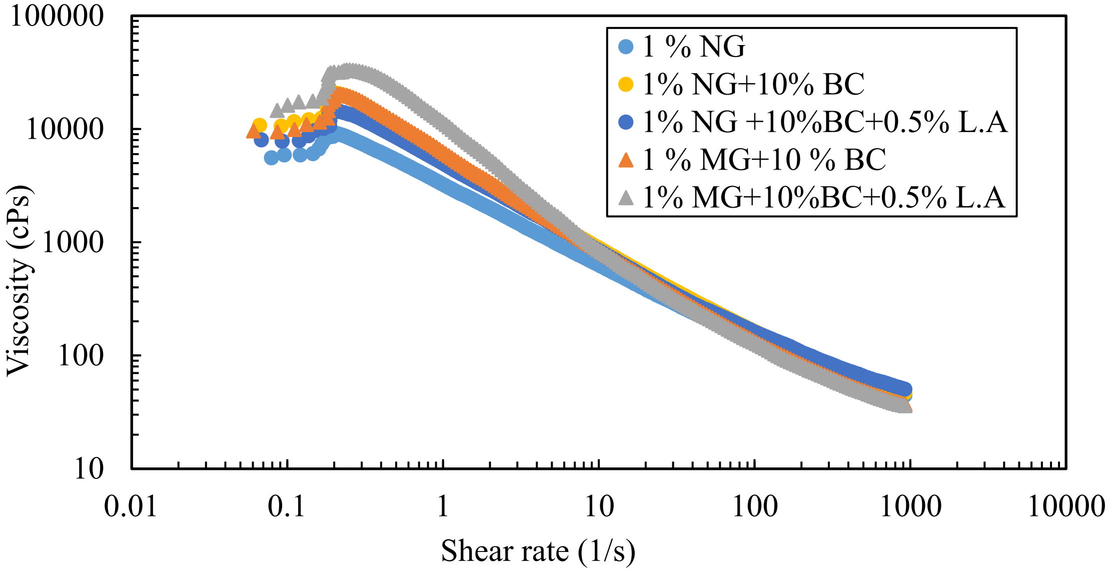


Figure 6.16. Viscosity vs shear rate of foams containing solvent and lauric acid.

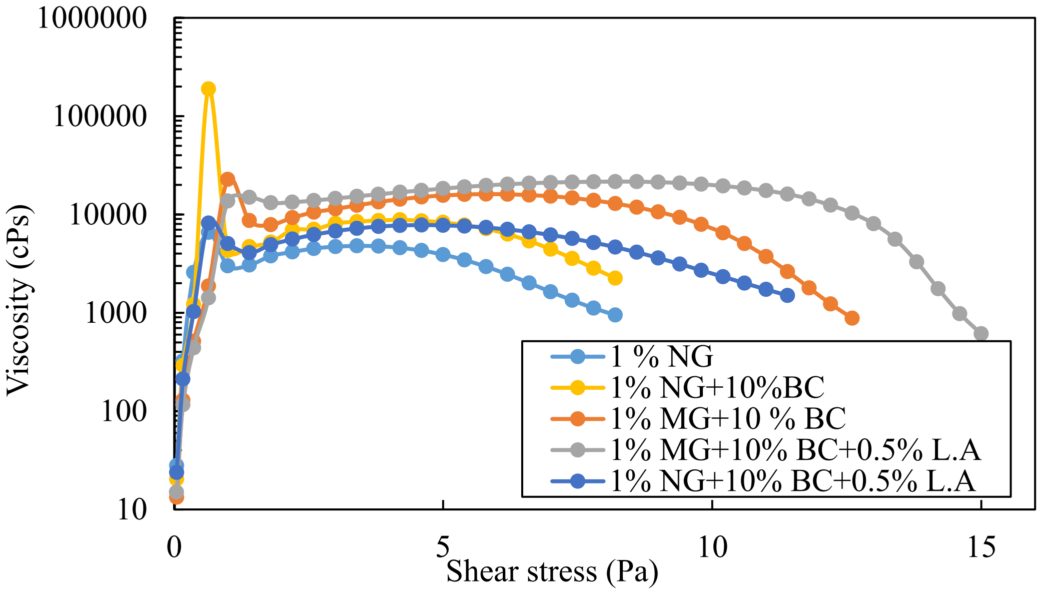


Figure 6.17. Dynamic yield stress of foams containing solvent and lauric acid.

6.4.2. Fire testing of foams containing secondary surfactants

The effect of increasing the yield stress and foam viscosity on the large scale fire performance was investigated using the promising formulations and are seen in Table 6.26.

Polymer	**Solvent**	**Fatty acid**	**Expansion ratio**	**Drainage time (min:sec)**	**Extinguishment time / s**	**Burnback**
NG1	None	None	6.26	>30 min	48	8:58
	10%	None	6.99	> 30 min	72	7.32
	1%	None	8.09	35:00	53	8:00
	10%	0.5 % LA	6.63	16.10	56	7.00
	1%	0.2% LA	7.95	16:28	55	6:00
	1%	0.2% SA	8.48	21:05	50	8:20

Polymer	Solvent	Fatty acid	Expansion ratio	Drainage time (min:sec)	Extinguishment time / s	Burnback
	None	0.2% LA	5.47	18:25	65	8:10
	None	0.5 % L.A	6.00	>30	70	8:12
	None	0.2% SA	6.08	28:17	58	8:22
	None	0.5 % S.A	6.01	>30	55	9:38
MG1	10%	0.5 % L.A	6.50	10.03	52	8.10

Table 6.26. MIL- PRF 24385F 28 ft^2 fire tests performed on heptane using fresh water in the presence of small alcohol and acid molecules.

From the large scale fire tests, the addition of small molecules slowed down extinguishment times, however less reopening of the foam blanket was observed, both these effects are due to an increase in the foam viscosity, slowing down the ability of the foam to spread rapidly over the fuel surface, however larger fatty acid species increased the burnback time. Alternative small molecules will be investigated that improve the foam stability and minimize reopening of the foam blanket, without affecting the rheological flow properties.

6.4.3. Effects of small molecules on the foam properties in sea water

The foam properties in the presence of fatty alcohol and fatty acid in sea water were investigated using base surfactant formulation and 10 % solvent with two polymers. (Table 6.27.)

[small molecule] / %	**Polymer**	**Ex ratio**		**Drainage time (25%)**		**Ext. Time (95 cm^2 pan/120 mL foam)**	
		Tap water	**Sea water**	**Tap water**	**Sea water**	**Tap water**	**Sea water**
0.5 % Fatty alcohol	1% NG	9.24	7.84	>30:00	32:54	No ext (foam too viscous)	10 s /10 s
	1% MG3	9.21	7.56	6:08	5:51	No ext (foam too viscous)	15 s /16 s
0 % Fatty acid	1% NG	8.78	8.55	31'42"	25'00"	16’’/-	11’’/14’’
	1% MG3	8.87	8.47	5'17"	5'20"	16’’/17’’	14’’/15’’
0.5 % Fatty acid	1% NG,	8.89	8.54	20'24"	39"28"	16’’/13’’	No ext./20’’
	1% MG3	8.83	8.52	7'08"	8'40"	13’’/14’’	15’’/14’’

Table 6.27. Foam properties and lab fire tests in salt water.

The effect of sea water on the foam properties is significantly more pronounced in the presence of fatty alcohol, probably due to the low solubility.

An alternative promising formulation pathway under investigation containing polypeptide polymer has concentrated on increasing foam stability primarily through the addition of fatty compounds. Increases in alkyl chain length and head group size produces foams that have higher yield stresses and are better able to resist coarsening. These measurements have been positively correlated with fire test data from the 28 ft^2 protocol and show promise as a means of predicting fire performance from key rheological characteristics.

Substituting lauryl alcohol with small acid molecules in the formulation, has reduced the 90 % and 99 % control times on gasoline to 26 s and 42 s respectively. (Table 6.28) It has also been possible with this formulation to extinguish the 28ft^2 gasoline fire in sea water in a time of 75 s.

	Lauryl alcohol	Alternative small molecule	Sea water
Expansion ratio	9.28	6.33	5.58
Drainage time (s)	5’36”	4’31	7’25”
90 % Control	42	27	29
99% Control	71	42	62
Extinguishment time (s)	77	56	75
Burnback time (m:s)	3’45”	6’25	4’46”

Table 6.28. MIL-PRF 24385F 28 ft^2 fire test result on gasoline.

6.4.4. Conclusions

Secondary small molecules that co-adsorb at the air / water interface have a significant effect on foam properties. A closely packed monolayer give better stability to fuel destruction, and would be expected to form a stronger barrier to vapor diffusion. High concentrations of secondary surfactant can stiffen the foam to the extent that spreading is slow, and fire control and extinguishment times are long.

6.5. Statistical Optimization

6.5.1. Optimization process

The formulation that gave the fastest extinguishing time on MIL- PRF 24385F 28 ft^2 pan in fresh water, has undergone statistical optimization to see what changes can achieve the best performance without the need to perform hundreds of tests. The MIL- PRF 24385F test extinguishment time is a difficult parameter to perform optimization on as the results have ± 5 s error on each result due to the human fire fighter variation and external including final flickers. A large concentration range for each component is needed to ensure that the differences due to the formulation changes are greater than the experimental variation. The statistical process can then find the optimal formulation.

The base formulation contained a primary surfactant, secondary polymeric surfactant, natural gum polymer and water. This formulation in the 28ft^2 test extinguished a heptane fire in 46 seconds and was the best formulation tested.

The use of the polymer gives insight into how the concentration affects re-opening of the foam blanket. This is linked to foam yield stress – too low and the foam blanket opens up, too stiff and the foam does not spread rapidly. The polymeric surfactant improves foam stability and has a synergy with the polymer which reduces the re-opening; the wide concentration range should show which formulations become too sticky and find that optimal yield stress. Upper (+) and lower (-) limits were set for each component, with the midpoint designated the zero (0) concentration.

6.5.2. Test program

The test program was performed on 28 ft^2 MIL- PRF 24385F pan under standard conditions with heptane. 12 tests were conducted due to three variable components, and one zero test which is the middle

concentration between each variable component:

Formulation	Surfactant	Polymeric surfactant	Polymer
0	0	0	0
1	+	+	+
2	+	+	-
3	+	-	+
4	+	-	-
5	-	+	+
6	-	+	-
7	-	-	+
8	-	-	-
9	0	0	0
10	0	0	+
11	+	0	0
12	0	-	0

Table 6.30. Statistical test program.

The extreme formulations were tested initially in order to set the boundaries and ensure a significant difference between formulations. It can be predicted that Formulation 8 would give the longest extinguishment time and shortest burnback, whereas formulations with a high concentration of polymer may make the foam too rigid and slow down extinguishment. Table 6.31 summarizes the results for each formulation.

Test number	**Expansion ratio**	**25% drainage / s**	**90 % control / s**	**99 % control / s**	**Extinguishment / s**	**BB (25%) / s**	**Comments**
0	7.02	2518	24	35	46	426	Less re-opening
1	6.24	19237	29	41	48	826	Solid stable blanket
2	8.75	2913	29	35	44	217	Poor foam properties
3	7.48	7117	25	32	37	765	Windy
4	8.49	819	29	36	41	238	Re-opening
5	3.37	3953	45	63	84	427	Re-opening
6	3.46	384	100	150	175	0	Runny foam
7	5.83	5714	40	57	98	444	Runny foam
8	4.74	302	39	77	79	56	Flash over
9	7.13	8640	31	37	39	515	
10	6.06	21600	24	37	44	1011	
11	7.04	6302	26	38	42	547	
12	6.58	6948	34	36	39	576	

Table 6.31. 28 ft^2 MIL- PRF 24385F fire tests on heptane under standard conditions.

The results were uploaded into the statistical software, JMP, and optimized by comparing expansion ratio, drainage, 90% and 99% control, extinguishment and burnback times. Figure 6.18 shows the optimized results where X1, X2 and X3 correspond to the concentrations of the three components. The black line is the statistically calculated value and the grey boundaries illustrate the error in the values and the trend that the values are showing. The red dotted line is the optimized value and the red figures the optimum formulation. The optimization and fire tests highlighted four key findings.

- Biggest impact on extinguishment time was the surfactant ratio where the lower surfactant concentrations struggled to control and burnback was weaker as a result.
- Polymeric surfactant in high amounts is detrimental to performance with low surfactant concentration (acts as an anti-foam)
- Polymer is the biggest contributor to burnback times.
- There is synergy between the polymer and surfactants and an anti-synergy between polymer and polymeric surfactant.

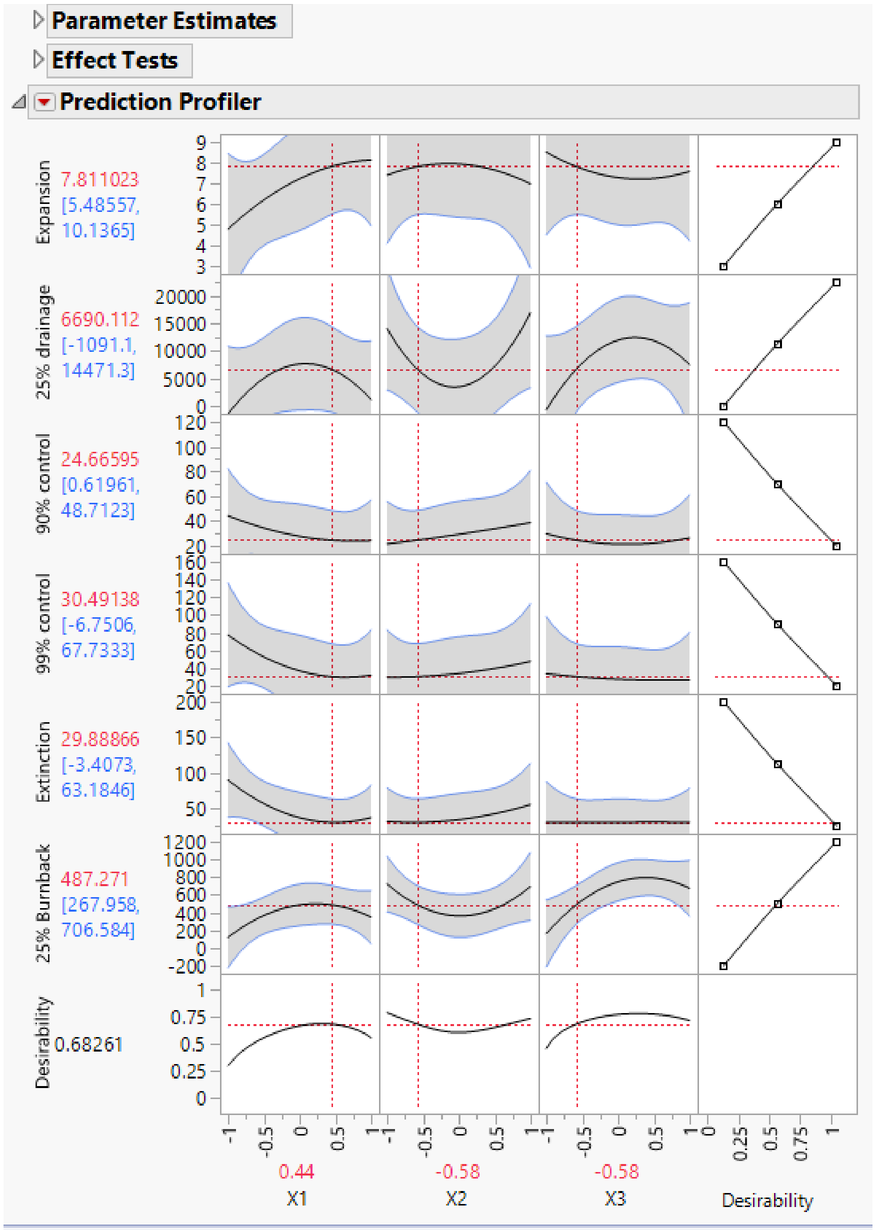


Figure 6.18. Optimization of foam properties and fire performance.

The minimum extinguishment time is 30 s and gives a burnback of 487 s (~8 minutes) which exceeds the values required from the MIL- PRF 24385F specification.

The problem with using this statistical optimization on a MIL- PRF 24385F fire test there is a high degree of variability ±10 s because of external factors. The 99 % control and the extinguishment times are often very close which have sometimes led to predictions where the extinguishment time is quicker than the 99 % control time. Two further optimizations were investigated:

A was optimized to give the quickest extinguishment time that can be made into a practical formulation.

B was optimized to balance the parameters and get a sub 35 s extinguishment time.

Table 6.32 shows the calculated and actual test results.

	A Predicted	**A Actual**	**B Predicted**	**B Actual**
Expansion ratio	7.81	7.90	7.06	7.21
Drainage time (s)	1’53’30”	46’44”	2’43’11”	2’00’27
90 % Control	25	19	25	31
99% Control	30	31	34	40
Extinguishment time (s)	30	36	35	44
Burnback time (m:s)	8’07”	7’57”	11’56”	9’52”
Comments	-	Good control, persistent final flickers	-	Some interference with the pipe across pan

Table 6.32. Predicted and actual test results of optimized formulations A and B.

The actual results obtained were slightly higher than the model predicted. This is attributed to the uncertainties involved in the actual test. Formulation A gave the best performance which was quicker than the predicted 90 % control time by 6 s but was 6 s slower than predicted on the extinguishment time.

At lower values of polymer, the model has strong agreement with the burnback times but at higher levels there is more discrepancy, which could be due to a smaller amount of initial tests conducted at the higher levels, hence a greater level of error.

6.5.3. Lean and rich proportioning

The MIL- PRF 24385F specification requires the formulation to be proportioned at lean (×0.5) and rich (×5) levels. The statistical model was used to estimate the performance of formulation A at variable proportioning levels, minimizing the requirement to conduct many large scale tests. The prediction at half strength is shown in Table 6.32. This method will enable further predictions and optimizations to be made, reducing the requirement of large scale fire tests.

	A **Predicted**	**A** **Half strength predicted**
Expansion ratio (test site)	7.81	6.71
Drainage time (s)-test site	1’53’30”	1’18’20”
90 % Control	25	26
99% Control	30	33
Extinguishment time (s)	30	33
Burnback time (m:s)	8’07”	6’21”

Table 6.33. Forecast fire performance of MIL-PRF 24385F 28 ft^2 test with heptane at lean proportioning.

6.5.4. Conclusions

Statistical processing has allowed a formulation to be optimized for fire performance. Actual fire testing gave a 90% control in 19 seconds and an extinguishment time on heptane in fresh water of 36 seconds, the fastest achieved in the project.

The model also predicts that at lean proportioning, extinguishment time would be 3 seconds slower, and burnback almost two minutes shorter.

7. Life Cycle Analysis

7.1. Introduction

7.1.1. Background to the study

This life cycle assessment (LCA) study was conducted by National Foam Inc. within the Foam Research and Development team as part of a project to enable the development of high-performance environmentally responsible firefighting foam products.

The intended audience for this LCA are primarily the internal decision makers. An abridged version may later be released for use as an informative and promotional tool targeted towards sustainability managers and supplier-chain officers representing foam-purchasing companies, specialist industry groups, LCA practitioners and experts involved in sustainability and energy, and other stakeholders interested in the environmental performance of different fire-fighting foam products.

7.1.2. Life cycle assessment

Life cycle assessment (LCA) is defined as a way of quantifying potential environmental impacts for the lifecycle of a product. This can help improve the understanding of the potential environmental impacts of a product from the raw material acquisition through production, use, and final disposal (ISO 14040, 2006).

Heightened awareness of sustainability and environmental protection associated with product manufacture and use has led to increasing implementation of LCA methodology. LCA may serve as an effective tool for the identification of potential areas where environmental impact reduction measures may be exercised within the product life cycle.

To the best of the author's knowledge, this represents the first cradle-to-grave life cycle analysis conducted for a firefighting foam product.

7.1.3. LCA methodologies

This LCA study was conducted following the ISO 14040 – 14044 (2006) guidelines and used the ReCiPe method for conducting life cycle impact assessment (LCIA). LCA is a systematic set of procedures for compiling and examining the inputs and outputs of materials and energy and the associated environmental impacts directly attributable to the functioning or use of a product or service system throughout its life cycle. The ReCiPe method translates the emissions and resource extractions into a limited number of environmental impact scores by means of characterization factors.

The data used within this study were gathered from a range of sources including manufacturers, peer-reviewed articles, and user survey. Wherever possible, steps have been taken to ensure that the data are compliant with ISO guidelines. Wherever data deviate from the ISO guidelines, a detailed explanation is provided within the appropriate sections of this report.

7.1.4. Structure and format of this report

This LCA study was conducted following the ISO 14040 – 14044 (2006) methodology. Consistent with the ISO standard, this LCA report is structured and formatted based on four fundamental stages of LCA: (1) Goal and scope definition, (2) inventory analysis, (3) impact assessment, and (4) interpretation.

7.1.5. Value choices

The LCA methodology employed for this study was ReCiPe (2016), which allows for the selection of an appropriate level of uncertainty within the calculations through offering three perspectives, which group similar types of assumptions and choices. These are individualistic (short-term, 20-years), hierarchist (mid-term, 100-years), and egalitarian (long-term, 1000-years), a detailed overview of these perspectives is provided in the ReCiPe guidelines.[2] (Huijbregts, *et al.,* 2016).

7.1.6. Impact pathways

Ecosystem quality, human health and resource scarcity are the three endpoints used for analysis within this study. Figure 7.1 shows all midpoint (impact) categories and linking damage pathways for the three endpoints as outlined in the ReCiPe method.[2] (Huijbregts et al., 2016).

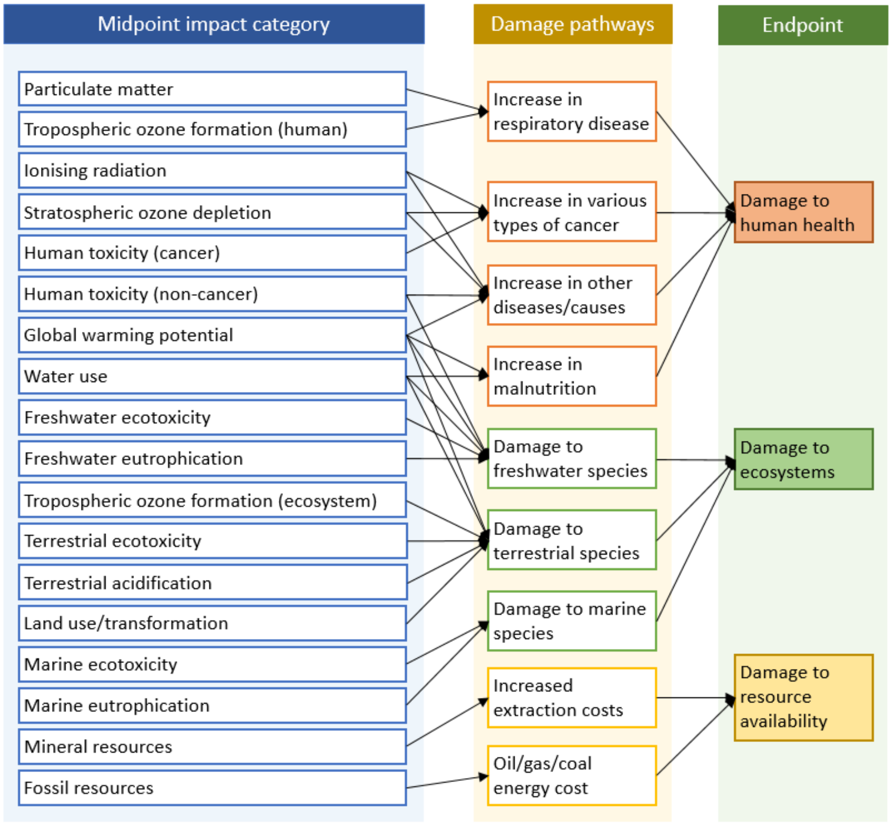


Figure 7.1. Overview of the impact categories and their relation to the areas of protection as outlined in the ReCiPe2016 methodology.[2]

7.2. Firefighting foams

Aqueous film-forming foam (AFFF) is deployed as a means of rapidly extinguishing and securing hydrocarbon liquid fuel fires and spills. Firefighting foam products are manufactured as a concentrate which, prior to use, is diluted in water at 1, 3 or 6 % dependent on the product.

This study focuses on the comparison of two fluorinated and two fluorine-free firefighting foam products produced by Angus International Safety Group, the production of which is geographically varied depending on the technical production requirements and the target market for the product.

Early AFFFs contained long-chain (>C8) per- and polyfluorinated compounds (e.g. PFOS and PFOA), however, modern firefighting foams use only short-chain (C6) telomer-based fluorocarbons as the active ingredients. Telomer-based fluorocarbons degrade via intermediates to a fluorotelomer sulfonate (FTS) and then to a perfluorocarboxylic acid end product, (e.g. 6:2 telomers go via 6:2 FTS to PFHxA).

Fluorine-free firefighting (F3) foams represent a relatively new technology which comprise of compounds which are both readily biodegradable and non-persistent. The development of these products requires the command of complex chemistries, a simple substitution of a fluorinated surfactant for a non-fluorinated surfactant is ineffective. Therefore, the formulation and manufacture of high-performance fluorine-free foams requires a complete rework of formulation constituents.

Due to their highly certified performance capabilities and proven efficacy in emergency response deployment, AFFF products remain the product of choice for high risk scenarios. However, recent developments in fluorine-free foam technology have yielded products which are increasingly capable of matching AFFF performance, as evidenced by increasing certification of fluorine-free products.

7.3. Goal

The goal of this study is to identify the relative life cycle impact of different AFFF and F3 foam formulations for key characterization factors relevant to environmental quality, human health, and resource depletion.

This study compares four foam formulations with different levels of certification:

AFFF-1 = MIL-PRF 24385F approved C6 fluorocarbon foam
AFFF-2 = ICAO B approved C6 fluorocarbon foam
F3-1 = UL 162 approved fluorine-free
F3-2 = ICAO B approved Newtonian fluorine-free

These are commercial foam concentrates manufactured by National Foam Inc. The exact formulation details are proprietary and are not disclosed in this report.

The study assessed the potential environmental impacts for the full life cycle for each foam product, taking a cradle-to-grave approach. This means that the following stages were assessed:

1. Raw material acquisition;
2. Foam product manufacture;
3. Foam product use;

4. Foam product disposal.

7.4. Scope

The scope of this LCA is cradle-to-grave. Impacts linked to the manufacture and end-of-life use and disposal of fire-fighting foam are assessed. The geographical and technological scope of manufacture are dictated by the differences in production location and volume.

This report will focus on four firefighting foam products: two fluorinated (AFFF) foams - AFFF-1, AFFF-2; and two fluorine-free foams – F3-1 and F3-2.

7.5. Functions of firefighting foam products

Firefighting foam products are used as a means of rapidly extinguishing and securing hydrocarbon liquid fuel fires and spills. All foam products within this study are sold and manufactured as a liquid concentrate. Prior to deployment, the user dilutes the foam concentrate, to 3 % — using any readily available water supply — to make the foam solution (3 parts foam concentrate to 97 parts water). The foam solution is aspirated to produce the foam, which is then deployed to fight the fire.

7.5.1. Fluorinated foams

7.5.1.1. AFFF 1

AFFF 1 is a high-performance, aqueous film-forming foam (AFFF), it has passed the MIL-PRF-24385F (SH) specification and as such is included on the qualified products list (QPL-24385) for use by the US military and US civil aviation authorities.

7.5.1.2.AFFF 2

AFFF-2 is a high-performance synthetic AFFF product. It is a C6 fluorocarbon surfactant-based foam and has been independently tested and certified to EN1568:2008 part 3, ICAO level B, UL 162, and IMO MSC1/Circ 1312.

7.5.2. Fluorine-free foams

7.5.2.1.F3-1

F3-1 is a high-performance F3 product. F3-1 has met the specification for EN1568 part 3 and part 4 on both fresh and sea water on all fuel types; IMO MSC 1/Circ. 1312; UL162; and Lastfire for use in both fresh and sea water. The manufacture is conducted on a fluorine-free production line

7.5.2.2.F3-2

F3-2 represents the World's first film-forming fluorine-free foam for use on aviation fuels. It has ICAO level B certification and has demonstrated 100 % biodegradation (OECD 301) and is produced on a fluorine-free production line.

7.6. Functional unit

The functional unit represents a quantity of the investigated product(s) and is chosen as the basis on which an LCA scaled.

The nature of firefighting foam products means that their intended use is in response to emergencies where the product will be used in excess until control or extinguishment is achieved. Use is therefore unplanned and un-restricted. This makes it inappropriate to base the selection of a functional unit on user practices. The functional unit was, therefore, defined as the quantity of foam solution required to extinguish a 10 m^2 aviation turbine fuel (Avtur) fire for 1 hour. This represents a normative value in terms of fire response, however, it does allow for direct comparison based on fire performance parameters. This will therefore enable future comparison with additional foam products.

This study focuses on the life cycle comparison of the two F3 (F3-1 and F3-2) and two AFFF (AFFF-1 and AFFF-2) foams, examining a range of impact categories. The comparison of these four products requires a normalized value, which, for this study, is the amount of foam required to extinguish and control a 10 m^2 fire for 1 hour. The quantity of each foam product required for this has been derived via the extrapolation of extinction (time for flames to be extinguished), burnback (time for 25 % re-ignition after initial extinction) times determined for each foam product by testing on a 0.25 m^2 test pan according to the DEF 42-40 performance specification (UK Ministry of Defence, 2002. Functional unit values are reported in Table 7.1.

Table 7.1 shows fire testing performance results and product and calculated water usage volumes for the F3 and AFFF foam products. A comparative performance test of extinction and burnback following the DEF 42-40 specification was performed for each product in a 0.25 m^2 test pan using 9L Aviation turbine fuel (avtur) for the extinction and 0.5 L avgas for the burnback. Results from the DEF 42-40 test were extrapolated for a larger scale fire (10 m^2) assuming a flow rate representative of a handheld nozzle (500 L min^{-1}).

			0.25 m^2 test pan and 0.75				**Extrapolated for 10 m^2 fire and 500 L min^{-1} nozzle**			
		Units	**F3-1**	**F3-2**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**	**AFFF-1**	**AFFF-2**
Single application	Extinction	s	65	51	23	44	65	51	23	44
	Expansion		6.4	8.4	9	7.4	6.4	8.4	9	7.4
	Flow rate	L min^{-1}	4.93	6.13	6.66	5.62	500	500	500	500
	Flow rate	kg min^{-1}	0.77	0.73	0.74	0.76	78.1	59.5	55.6	67.6
	Volume used	kg	0.83	0.62	0.28	0.56	84.6	50.6	21.3	49.6
Burnback time		s	1530	735	1496	1089				
1 hour response	Applications needed		2.35	4.90	2.41	3.31				
	Rounded		3	5	3	4				
	Foam solution	kg					254	253	63.9	198
Functional unit	**Foam concentrate**	**kg**					**7.62**	**7.59**	**1.92**	**5.95**
	Water	**kg**					**246**	**245**	**62.0**	**192**

Table 7.1 Fire testing performance results for the F3 and AFFF foam products.

7.7. System boundaries

The LCA examines the inputs and outputs of the foam manufacture process from cradle-to-grave. The system boundaries are outlined in Figure 7.2. However, this does not account for the energy used to heat and light the manufacturing facility, or water used in the production of electricity because these were considered independent to the foam manufacture process.

The LCI database has been constructed in a series of steps:

1) The LCI of the product constituent manufacturing processes have been combined based on their respective levels in x kg of product.
2) The LCI datasets of product constituents are added, where the constituent represented greater than 1 % of the formulation (for environmental analysis, all constituents are considered).
3) The consumption of energy, raw materials and environmental emissions associated with fire foam usage are calculated based on the foam usage scenarios outlined in functional unit.

The reference flow is the quantified amount of the product, including product parts, required for a specific product system to deliver the performance or outcome outlined by the functional unit. A generic reference flow diagram is shown in Figure 7.2, with product-specific flow diagrams shown in Figures 7.3-7.6.

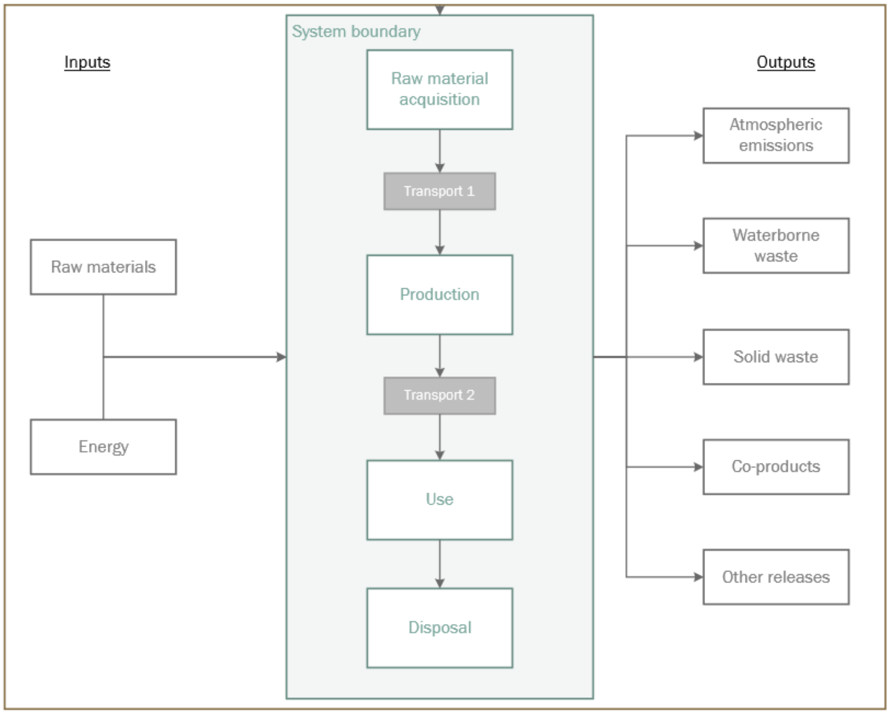


Figure 7.2. Summary diagram of the system boundaries applied.

The life cycle steps included within the system boundaries (as shown in Figure 7.2):

- Raw material extraction and production (e.g. surfactants, solvents, polymers);
- Conversion of raw materials to foam product;
- Use of foam product;
- End of life management - disposal of foam product via advised methods (incineration or waste water treatment);
- Production and disposal of materials and chemicals consumed at each stage;
- Production of fuels and electricity consumed by the processes.

Excluded from the system boundaries were:

- Product wastage throughout the supply chain and by end users – due to a lack of information;
- Transport of raw materials to the manufacturing sites – the raw material supply chain is a dynamic system with many of the raw materials purchased from various locations on a price-driven basis.

- Product transportation to the end users – as this varies significantly depending on the location of the end users.
- Packaging – the type of packaging used for foams products is quantity dependent, however, this is consistent between all products considered within this study.

The life cycle stages included within the system boundaries are described in more detail below.

7.7.1. Raw material acquisition

Production of raw materials such as surfactants (fluorocarbon and hydrocarbon), solvents, polymers, and other additives were included within the study. Extraction of non-renewable resources, cultivation of renewable resources and their processing was included. This covers both material and energy resources and also emissions of substances to air, water, soil, and waste. Where specific data were not available for a raw material, proxy constituents or processes were used (as contained within the Ecoinvent life cycle inventory database), instances where this was performed are detailed within the Section 7.10 (life cycle inventory) of this report.

7.7.2. Product manufacture

Conversion of the raw materials to firefighting foam concentrate. Energy inputs required by mixing and heating equipment. Where specific data were not available for electricity consumption by factory running demands, generic data for comparable equipment were used (as contained within the Ecoinvent life cycle inventory database).

7.7.3. Product use

Product use is assumed to have been performed using accurately proportioning foam deployment equipment where the foam concentrate is diluted at 3 % in mains water (97 %). Water was assumed to have been supplied from a municipal source and the attributed energy consumption was based on this. As outlined in Section 7.6 (functional unit), product use was determined based on the quantity of foam required to extinguish and suppress a 10 m^2 for 1 hour.

7.7.4. Product disposal

End of life for a foam product may occur as a result of either deployment in incident response or training scenarios, or when a product reaches the end of its shelf-life. Presently recommended that foam products are, wherever possible, captured for disposal by incineration. This LCA study assumes the full capture of all firefighting foam products, however, it is acknowledged that full foam capture is not always possible, particularly following incident response scenarios, where conditions such as volume and location of deployment are uncontrolled. The impacts of environmental fate will be considered in alternative studies.

7.7.5. Geography

The data used within this study have, wherever possible, been for global geographies. Whilst AFFF-1 is produced in the US and F3-1 produced in France, it is intended for this study to be used for comparison with other foam products, the manufacture of which occurs across a range of countries. To allow full comparison between the foam types, the use of global data was considered appropriate for the constituent and packaging manufacture, transport, usage, and disposal stages.

7.7.6. System boundary restrictions

7.7.6.1.Packaging

AFFF-1 and F3-1 are both supplied in 1000 L intermediate bulk containers (IBC) from a common source, therefore the production, use and disposal of the IBCs has been excluded from the scope of this LCA.

7.7.6.2.Transportation

As both AFFF-1 and F3-1 are subject to potentially global transportation dependent on need, transport of the foam product transportation has been excluded from this study.

7.7.6.3.Time scale

Time was not a factor considered within the scope of this study and datasets do not cover any particular time period.

7.7.6.4.Infrastructure and machinery maintenance

Infrastructure (construction and maintenance of buildings) and machinery (all lubricating oils, spare parts, and general maintenance) were not included within the system boundaries. This is because buildings and machinery are used for the production of multiple types of foam concentrate, over multiple years and thus the contribution from these is negligible compared to the flows (e.g. mass of materials, consumption of fuels and energy) included within the system boundaries in the time frame of the functional unit.

7.7.7. Allocation

An example of where allocation may be is used where a single manufacturing process may generate multiple products, of which only one is used as a constituent for the product that is the subject of the LCA. Where this occurs the emissions and energy demands of that product must be distributed proportionately between the multiple products.

The ISO standards on LCA suggest a procedure for allocation of material and energy flows and environmental emissions. Preferably, allocation should be avoided through increasing the level of detail or system expansion (adding processes to distribute the environmental loads). This is not always a viable option, in which case, the ISO recommendation is to perform allocation on the basis of mass.

An example for allocation used within this LCA would be for the manufacture of solvent molecules, through a process which also produces co-products which are useful in the manufacture of other products. Here the proportion (by weight) of the final product represented by a glycol solvent is used to calculate the proportion of the energy and raw material inputs and waste material outputs.

7.7.8. Assumptions

Some data categories are generated from only one data source, which assumes that there is no deviation in process technology and materials used in the manufacturing of these products. In order to address this, data sources from industry reviewed databases or peer-reviewed articles have been selected wherever possible.

All foam products examined within this study are readily proportioned using conventional air aspirating and non-air aspirating discharge devices. This study will assume that all foams are deployed under the same application conditions.

7.7.9. Limitations

This study is a comparative assessment of 4 firefighting foam products: 2 AFFF and 2 F3. Results from this study are given to provide an insight into:

- The type of impacts that the different foams studied have on the environment;
- The magnitude of selected environmental impacts for the different foam products studied;
- Areas where knowledge of different foam products is lacking:
    - Environmental fate;
    - Ecotoxicity;
    - Human toxicity.

The aim of this study was to generate information for use by stakeholders to inform and facilitate the transition process from AFFF to F3 foam products.

The results of this study are limited by data availability and the assumptions made where data gaps were encountered, and the systems assessed. Data gaps were evident for the fluorocarbon surfactant production systems and also for energy and water usage during the foam manufacturing process, for which estimates and proxy values were used. The use of estimates is limited to judging the significance of these life cycle stages in the context of the full life cycle.

It was intended that the environmental impacts of uncaptured foam released by product users would be incorporated into the scope of the study. However, only limited data was available to the project team, and, as a consequence, environmental toxicity and human toxicity midpoints were excluded from the study.

7.8. Identification of relevant impact categories

Life cycle assessment characterizes the use of resources in the manufacture of a product. The type of resources may be categorized by their nature depending on their renewability:

- **Stock resources** exist as a finite, fixed amount in the natural environment, with no possibility of regrowth, or renewal rates are too large compared to the human rate of consumption (e.g. oil, metals, and minerals).
- **Fund resources** can be depleted at a rate dependent on a ratio of extraction to regrowth or renewal rate. Both permanent depletion and an expansion of the fund are possible (e.g. a wood supply may be replenished through planting trees, however if the rate of consumption is greater than the rate of planting the resource will become depleted).
- **Flow resources** cannot be depleted, although there might be local or temporal non-availability (e.g. surface freshwater dependent on precipitation, solar or wind energy). Renewability of flow resources is relatively instantaneous.

Land use cannot be characterized as stock, fund or flow, and is reported in terms of area.

7.9. Data sources and quality

Data quality requirements as set out at the initiation of this project as defined in Table 7.2 and are based on the ISO standard (ISO 14044:2006).

Parameter	Description	Requirement
Time-related coverage	Desired age of the data and the minimum length of time over which data should be collected.	Data should represent the situation in 2018/19. General data and data from databases should represent the situation in 2018/19.
Geographical coverage	Area from which data for unit process should be collected.	Data should be representative of the situation in which a product is produced and deployed and should be consistent between products.
Technology coverage	Technology mix.	Data should be representative of the situation in which a product is produced and deployed.
Precision	Measure of the variability of the data values for each data category expressed.	No defined requirement in study scope.
Completeness	Assessment of whether all relevant input and output data are included for a certain dataset.	Specific datasets should be assessed and, where concerns arise, be compared with literature data and databases.
Representativeness	Degree to which the data represents the identified time-related, geographical and technological scope.	The data should fulfil the defined time-related, geographical and technological scope.
Consistency	The consistency with which the study method has been	The study method should be applied to all components of analysis.

Parameter	Description	Requirement
	applied to different components of the analysis.	
Reproducibility	Assessment of the method and data and whether an independent practitioner will be able to reproduce the results.	The information about the method and the data values should allow an independent practitioner to reproduce the results.
Sources of data	Assessment of data sources used.	Data should be derived from credible sources and databases.

Table 7.2. Data quality requirements.

Data for this investigation were obtained from a range of sources (Table 7.3).

Component	Data description	Data source
	Foreground data	
Raw material acquisition	Energy and land area needed for raw material acquisition.	LCI databases and literature
Constituent manufacturing process	Energy and quantity of raw materials needed for manufacture	LCI databases and literature
Transportation of raw materials to manufacturing plant	Transport mode, quantity, and distance	LCA database
	Fuel consumption	
Foam manufacturing process	Energy and constituents needed for manufacture.	Factory records
Emission to air	Total volume of waste discharged	LCI databases and literature

Component	Data description	Data source
	Concentration of COD, BOD, and chemical composition.	
Emission to water	Total volume of waste discharged	LCI databases and literature
	Concentration of COD, BOD, and chemical composition.	
Transport to customer	Transport mode, quantity, and distance	LCI databases and literature
	Fuel consumption	
Foam deployment	Volume, scenario, and environmental conditions of foam deployment	Consumer habits research and supplier recommendations.
	Disposal procedures for deployed/expired foam.	
Background data - Utilities		
Public treated water	Treatment of water supply	LCI databases and literature
Electricity	Electricity generation and consumption	LCI databases and literature
Fuel	Fuel production and consumption	LCI databases and literature

Table 7.3. Data sources and components.

There was no cut-off criteria for default input or output data. All known inputs and emissions from processes included within the system boundaries, regardless of their importance, were included in the LCA model. Where the contribution of an environmental indicator was found to be insignificant, no further refinement was undertaken. Refinement and sensitivity analyses were carried out for the variables of highest environmental significance.

7.10. Inventory analysis

Inventory analysis involves data collection and calculation procedures to quantify relevant inputs and outputs for the product system. For each firefighting foam product assessed, inventories of significant environmental flows to and from the environment, and internal material and energy flows were produced.

The inventories generated provided data for numerous internal and elemental flows for each foam product production system. As such, only summary inventory flows for each product are included in this final report:

- Raw material use;
- Water use;
- Energy use;
- Product manufacture;
- Airborne emissions;
- Waterborne emissions;
- Solid waste.

Water use was included due to global environmental and political concerns relating to water use. Energy use is presented as a cumulative energy value. The Ecoinvent database was used as a primary source of input and output data. The inventory analysis was conducted using Microsoft Excel software.

7.11. Impact assessment

The impact assessment phase of the LCA served to assign the results of the inventory to different impact categories. The potential contributions of each firefighting foam product to the impact categories listed in Table 7.4 have been assessed.

Impact category	**Indicator**	**Unit**	**Characterization factor CF_m**	**Abbreviation**	**Unit**
Climate change	Infra-red radiative forcing increase	W x yr/m^2	Global warming potential	GWP	kg CO_2 to air
Ozone depletion	Stratospheric ozone decrease	ppt x yr	Ozone depletion potential	ODP	kg CFC-11 to air
Ionizing radiation	Absorbed dose increase	man x Sv	Ionizing radiation potential	IRP	kBq Co-60 to air
Fine particulate matter formation	PM2.5 population intake increase	kg	Particulate matter formation potential	PMFP	kg PM2.5 to air
Photochemical ozone formation: ecosystem quality	Troposphere ozone increase (AOT40)	ppb.yr	Photochemical ozone formation potential: ecosystems	EOFP	kg NOx to air
Photochemical ozone formation: human health	Tropospheric ozone population intake increase (M6M)	kg	Photochemical ozone formation potential: humans	HOFP	kg NOx to air
Terrestrial acidification	Proton increase in natural soils	yr x m^2 x mol/L	Terrestrial acidification potential	TAP	kg SO_2 to air

Freshwater eutrophication	Phosphorus increase in fresh water	yr x m^3	Freshwater eutrophication potential	FEP	kg P to freshwater
Marine eutrophication	Dissolved inorganic nitrogen increase in marine water	yr.kg O_2/kg N	Marine eutrophication potential	MEP	kg N to marine water
Human toxicity: cancer	Risk increase of cancer disease incidence		Human toxicity potential	HTPc	kg 1,4-DCB to urban air
Human toxicity: non-cancer	Risk increase of non-cancer disease incidence		Human toxicity potential	HTPnc	kg 1,4-DCB to urban air
Terrestrial ecotoxicity	Hazard-weighted increase in natural soils	yr x m^3	Terrestrial ecotoxicity potential	TETP	kg 1,4-DCB to industrial soil
Freshwater ecotoxicity	Hazard-weighted increase in freshwaters	yr x m^3	Freshwater ecotoxicity potential	FETP	kg 1,4-DCB to freshwater
Marine ecotoxicity	Hazard-weighted increase in marine water	yr x m^3	Marine ecotoxicity potential	METP	kg 1,4-DCB to marine water
Land use	Occupation and time-	yr x m^2	Agricultural land occupation potential	LOP	m^2 x yr annual crop land

	integrated transformation				
Water use	Increase in water consumed	m^3	Water consumption potential	WCP	m^3 water consumed
Mineral resource scarcity	Ore grade decrease	kg	Surplus ore potential	SOP	kg Cu
Fossil resource scarcity	Upper heating value	MJ	Fossil fuel potential	FFP	kg oil

Table 7.4. Overview of all characterization factors as outlined in ReCiPe report.[2] Impact categories listed in orange are outside the scope of this study.

The impact categories used for this LCA relate to potential impacts, meaning that they express what might happen if the cause-effect relationship is enacted. The impact assessment approach used within this study follow the ReCiPe method (2016).

7.12. Endpoint analysis

Human health, ecosystem quality and resource scarcity represent three areas of protection (Goedkoop *et al.,* 2016; Table 7.5). 1) Human health represents the years that are lost or that a person is disabled due to disease or accident, measured in DALY (disability-adjusted life years). 2) Ecosystem quality is the local species loss integrated over time (species year). 3) Resource scarcity represents the extra costs involved for future mineral and fossil resource extraction ($).

Area of protection	Endpoint	Abbreviation	Name	Unit
Human health	Damage to human health	HH	Disability-adjusted loss of life years	Year
Natural environment	Damage to ecosystem quality	ED	Time-integrated species loss	Species x yr
Resource scarcity	Damage to resource availability	RA	Surplus cost	Dollar

Table 7.5. Overview of the endpoint categories, indicators and characterization factors.

7.13. Reporting

In accordance with ISO standards, when the results of an LCA are to be communicated to a third party, an appropriate report should be prepared.

7.14. Firefighting foam product inventory analysis

7.14.1. Product formulations

Foam constituents are produced at supplier facilities and are processes over which National Foam exercises limited control. Raw material data were obtained from several inventories related to the production of chemicals. Where specific data were not available, proxy data were gathered for comparable materials with the details given below.

The fluorinated foam formulations comprise of a blend of solvents, fluorosurfactants, hydrocarbon surfactants, and a number of additives such as pH buffer and corrosion inhibitor. Fluorine-free foams are comprised of a blend of solvents, hydrocarbon surfactants, biopolymers, and a number of additives.

7.14.2 Raw material manufacture

Foam constituents are produced at supplier facilities and therefore are not processes over which National Foam exercises control. Some of the constituent production processes are proprietary; these are identified as such within the relevant section. Where specific data were not available, proxy data were gathered for comparable materials with the details given below.

7.14.3 Fluorinated foam

7.14.3.1 AFFF-1 raw materials

7.14.3.1.1 Solvents

Water. The production of 1 kg clean water, requires the use of 1.129 kg water, this has been factored into the calculations.

Solvents A and B are products of the same chemical production process and are therefore grouped together for the purpose of life cycle inventory (Figure 7.3). Briefly, they are produced using a multi-tubular reactor, followed by a hydrolysis to form the final solvent product.

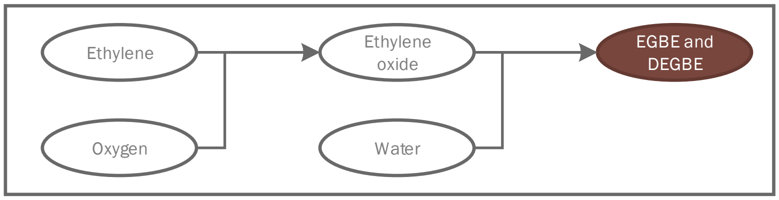


Figure 7.3 Production process flow for ethylene glycol (EGBE) and diethylene glycol (DEGBE).

7.14.3.1.2 Hydrocarbon surfactants

Non-ionic surfactant

Nonionic surfactants are derived from natural resources and manufactured in a two stage synthesis. An example is derived from maize that is refined as shown in the flow diagram then converted to the raw surfactant molecule.[42] The calculations presented within this study are based on LCA data obtained from the Ecoinvent database (v3.0) with some exclusions which were very low energy usage with > 95 % yield in the preparation.

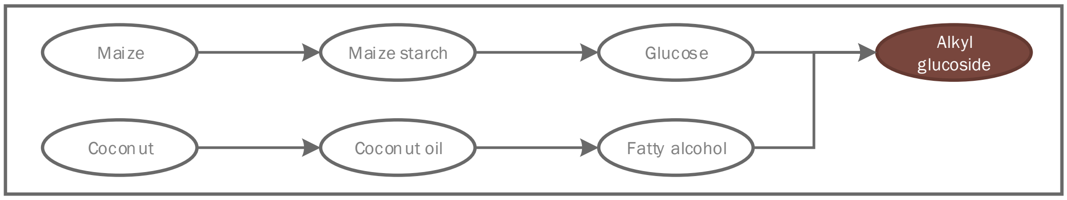


Figure 7.4. Production process flow for nonionic hydrocarbon surfactant .

Anionic surfactant

Anionic hydrocarbon surfactant is manufactured through the treatment of a fatty alcohol and oleum to produce the active species.

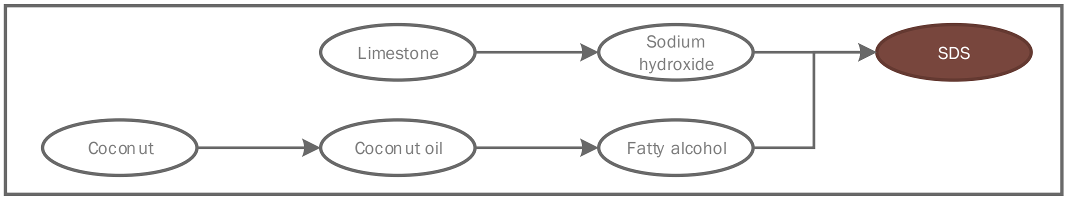


Figure 7.5. Anionic hydrocarbon surfactant production process flow.

7.14.3.1.3 Fluorosurfactants

Information detailing the manufacturing processes for the fluorosurfactants used within this formulation are not readily available. Therefore, the manufacturing process has been derived through observation of the molecular structure and estimation of the synthesis process through which they may be produced. Therefore the data included for the fluorosurfactants serves as an approximation, which will be revisited in future iterations should any further details become available (Figure 7.6).

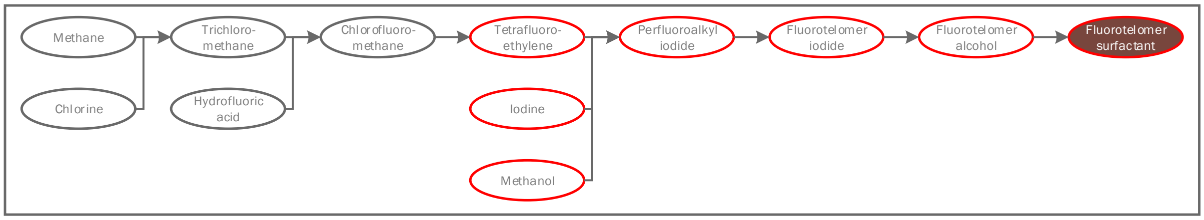


Figure 7.6. Production process flow for fluorotelomer surfactants. Constituents with a red outline show where production data is unavailable and proxy processes were used.

7.14.3.2 AFFF-2 raw materials

7.14.3.2.1 Solvents

Water. The production of 1 kg clean water requires 1.129 kg water total.

Solvents A and B Further detail for the manufacture of the solvents are detailed in Section 7.14.3.1.1 of this report.

7.14.3.2.2 Hydrocarbon surfactants

Amphoteric surfactant

LCI information detailing the manufacturing processes for the amphoteric hydrocarbon surfactant are not readily available. Therefore, the manufacturing process has been derived through calculation based on the molecular masses, allowing for the estimation of the final stage of product preparation. Therefore the data included for the production process serves as an approximation, which will be revisited in future iterations should any further details become available (Figure 7.7).

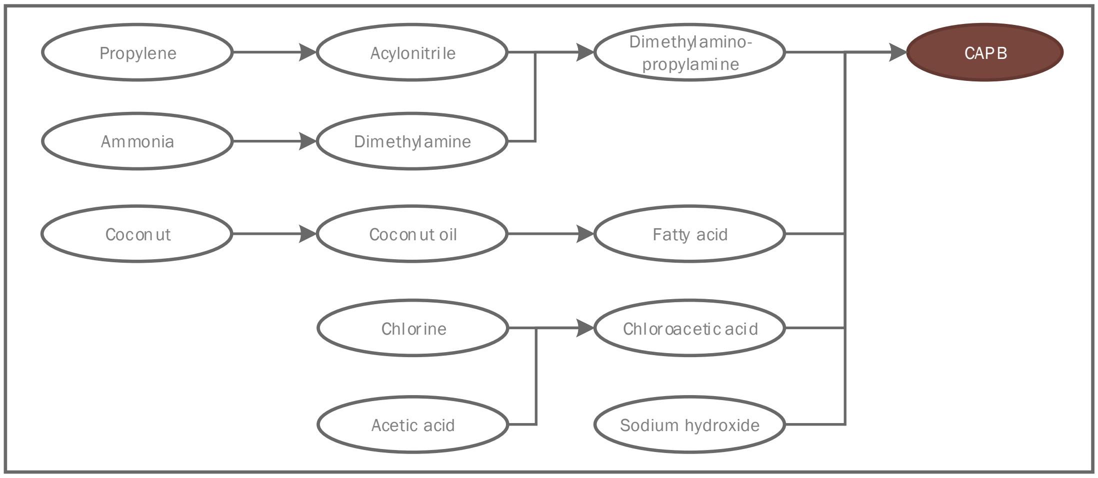


Figure 7.7. Production flow for amphoteric surfactant.

Anionic hydrocarbon surfactant

Further detail for the manufacture is detailed in Figure 7.5.

7.14.4 Fluorine-free foams

7.14.4.1 F3-1 raw materials

Raw material data were obtained from several inventories related to the production of chemicals.

7.14.4.1.1 Solvents

Water. The production of 1 kg clean water requires 1.129 kg water total.

The linear alcohol source for this constituent is petrochemical derived. Figure 7.8 shows the basic process through which the linear alcohol may be produced.

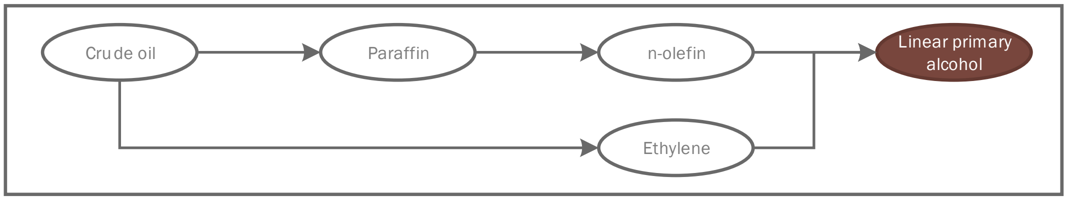


Figure 7.8. Basic linear primary alcohol manufacture process flow.

Solvent C is an organic solvent, manufactured in a closed continuous system. This study draws on data from the manufacture of a similar molecule as a proxy for solvent C.

Solvent D is an organic solvent, and the production involves a hydration process requiring a catalyst.

7.14.4.1.2 Hydrocarbon surfactants

Anionic

The anionic surfactant was prepared by ethoxylation of an alcohol. (Figure 7.9).

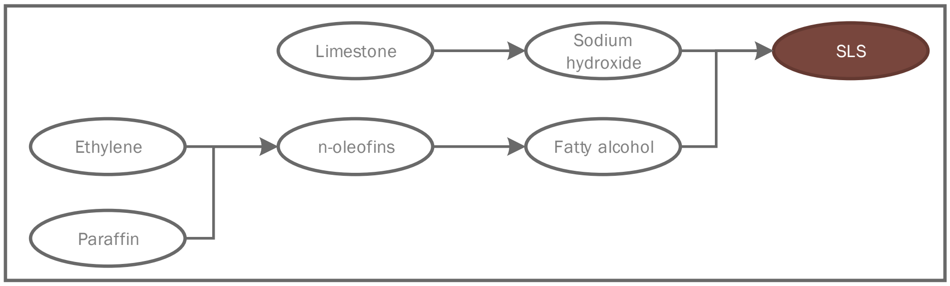


Figure 7.9. Sodium alkyl sulfate production process.

Life cycle inventory data for the manufacturing process are presently unavailable within the literature, however, it is reported that there are similarities between other anionic hydrocarbon surfactants, thus, a petrochemical-derived surfactant was used as a proxy within this LCA. Further detail for the manufacturing process detailed in Section 4.2.1.1.2. (Figure 7.10).

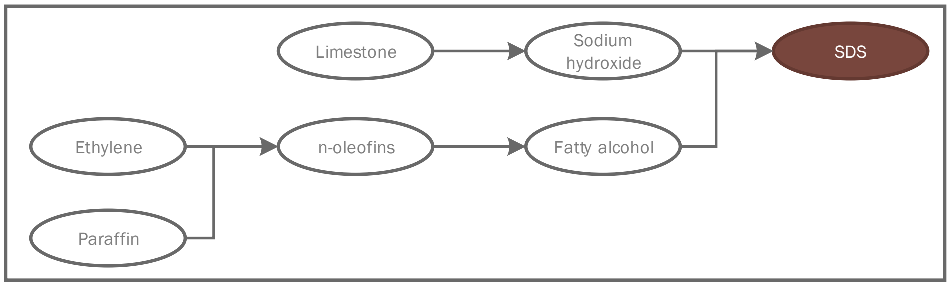


Figure 7.10. Sodium alkyl sulfate production process.

Short chain anionic hydrocarbon (SAS). There is limited information availability for the production of SAS and thus the procedure for SDS manufacture has been used as a proxy (Figure 7.10), as described previously.

Non-ionic hydrocarbon surfactant is produced in a two stage process in the presence of a catalyst at 393 K.[42]

The process of production is outlined in Figure 7.11, the calculations presented within this study are based on LCA data obtained from the Ecoinvent database (v3.0) with some exclusions which were very low energy usage with > 95 % yield in the preparation.[43]

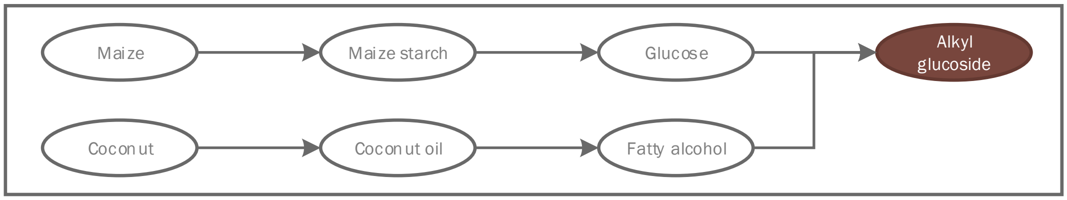


Figure 7.11. Basic production process for nonionic surfactant.

7.14.4.1.3 Other constituents

A biopolymer was used to modify the viscosity of the foam formulation. It is synthesized from a fermentation process and is conducted under agitation and aeration conditions. Details for the production of a starch biopolymer have been used as a proxy.

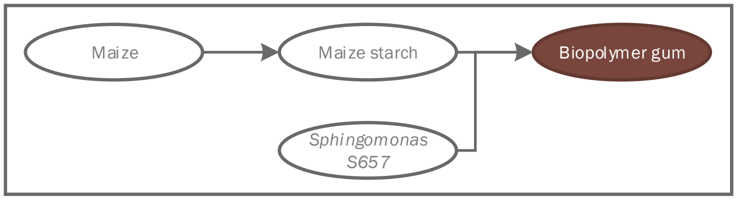


Figure 7.12. Biopolymer production process.

7.14.4.2 F3-2 raw materials

7.14.4.2.1 Solvents

Water. The production of 1 kg clean water requires 1.129 kg water total.

Solvent A. Further detail for the manufacture of the solvent is detailed in Section 3.2.1.1.1 of this report.

7.14.4.2.2 Hydrocarbon surfactants

Amphoteric hydrocarbon surfactant. The product is reported to be derived from plant, animal and marine sources, however, this provides only limited specificity with regard to the source of the raw materials.

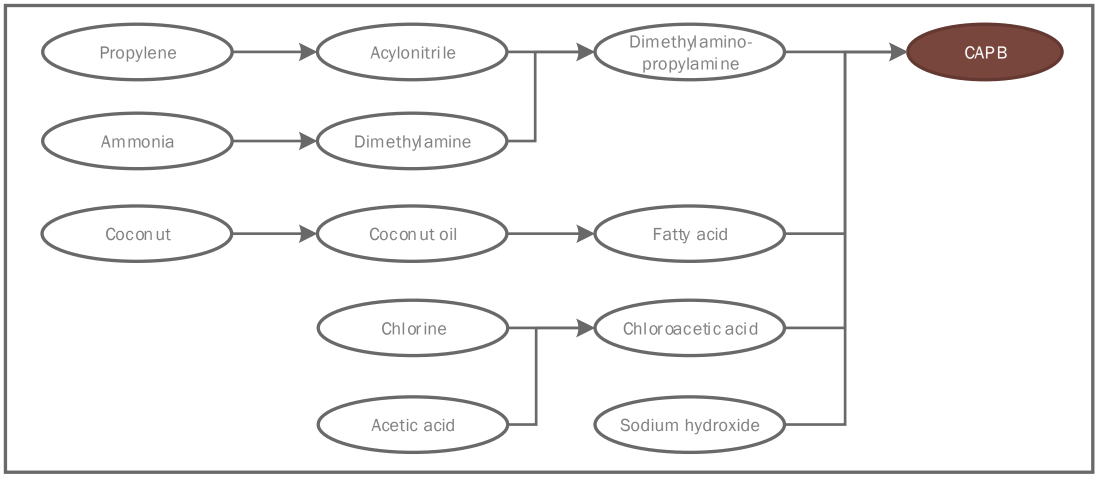


Figure 7.13. Production flow for amphoteric surfactant.

Anionic hydrocarbon surfactant.

Further detail for the manufacture is detailed in Section **4.2.1.1.2**

7.14.4.2.3 Corrosion inhibitor

The corrosion inhibitor is a mixture of components, only the large components in the mixture were used for this LCA.

7.15. Product use - Foam deployment

All foams assessed within this report are deployed at 3 % concentration in mains water. The quantity of foam deployed is incident specific, however, in order to generate a normative comparison between the four foams on which this report is focused, the functional unit is employed.

Foam Product	Volumes required to extinguish and control a 10 m^2 aviation turbine fuel fire for 1 hour		
	Total foam solution (L)	**Foam concentrate (L)**	**Water (L)**
AFFF-1	63.89	1.92	61.97
AFFF-2	198.2	5.95	192.3
F3-1	253.9	7.52	246.3
F3-2	253.0	7.59	245.4

Table 7.6. Volume of each foam product estimated to be required to extinguish a 10 m^2 aviation turbine fuel (Avtur) fire for 1 hour.

7.16. Disposal – End of life

This study performed two end-of-life scenario comparisons.

Scenario 1 assumes that all foam product is disposed of as advised by the manufacturer or local authority. Presently, it is recommended that foam products are, wherever possible, captured for disposal by incineration and thus, this study is based on this assumption.

Incineration values were derived from the Ecoinvent (v2.0) database. The AFFF foam products are assumed to have been disposed of following hazardous material incineration practices, whilst the fluorine-free foam products were assumed to follow general materials incineration practices.

Scenario 2 assesses the impact of non-containment of deployed fluorine-free foam, whilst maintaining that all fluorinated foams are collected for incineration. This is based on the readily biodegradable nature of the two fluorine-free foam products within this study, as per OECD guidelines (OECD 301, 1992).

An assumption is made that the foam deployment takes place in to a large and dynamic water course, whereby sufficient dilution is achieved to ensure negligible adverse environmental impacts.

7.17. Results and discussion

Each firefighting foam product has been assessed for its potential environmental impact for the following impact categories.

- Global warming potential– gases contributing to the greenhouse gas effect are aggregated according to their impact on radiative warming compared to a carbon dioxide (CO_2) reference. Impacts are expressed in kg CO_2 equivalents.
- Photochemical ozone formation – Ozone is formed as a result of photochemical reactions of NO_x and non-methane volatile organic compounds (NMVOCs). Impacts are expressed as kg NO_x equivalents.
- Terrestrial acidification – Atmospheric deposition of inorganic substances, such as, sulfates, nitrates, and phosphates, cause a change in soil acidity. This can have harmful implications for plant growth and soil organisms, with a knock-on effect across an ecosystem. Impacts are expressed as kg SO_2^- equivalents.
- Freshwater eutrophication – phosphorus and nitrogen release to freshwater may have significant environmental impacts relating to loss of species. The impact is expressed as kg P equivalents.
- Marine eutrophication – phosphorus and nitrogen release to freshwater may have significant environmental impacts relating to loss of species. It is assumed that N is limiting within marine waters, and thus, the impact is expressed as kg N equivalents.
- Land use – Land use covers the processes of land transformation, land occupation and land relaxation, which each have a different level of environmental impact. Impacts are expressed as m^2 annual crop equivalent.
- Water use – Water consumption is the use of water in such a way that the water is evaporated, incorporated into products, transferred to other watersheds, or disposed into the sea. Impacts are expressed as m^3 consumed.
- Minerals resource scarcity – The primary extraction of a mineral resource leads to an overall decrease in ore grade, meaning that the concentration of that resource in orders worldwide is decreased. Impacts are expressed as USD2013 kg^{-1} Cu equivalents.
- Fossil resource scarcity – An increase in fossil fuel extraction causes an increase in costs due to a reduction in the total remaining supply. Impacts are expressed as USD2013 kg^{-1} for crude oil, hard coal, brown coal, and peat; and as USD2013 m^2 for natural gas.

- Ozone depletion – Emission of ozone depleting substances (ODSs) ultimately leads to damage to human health due to increased UVB-radiation. Chemicals which deplete ozone are relatively persistent and have chlorine or bromine groups in their molecules. Impacts are expressed as kg CFC-11 equivalents.
- Fine particulate matter – Emission of NO_x, NH_3, SO_2 or primary PM2.5 may result in damage to human health. Impacts are expressed as kg PM2.5 eq.

A detailed description and analysis for each impact category is provided in the ReCiPe framework (2016). Firefighting foam is a tool utilized on a worldwide basis, and thus, wherever appropriate, calculations use world weighted average values as provided by the ReCiPe (2016) framework.

7.18. Product impact assessment

7.18.1 Environmental impact

The impact assessment results are presented for the four foam products per the functional unit and also per liter of foam on individualist, hierarchist, and egalitarian bases. The impact assessment results for the four firefighting foam products are presented for Scenario 2 for the functional unit and per liter of foam in Tables 7.7 and 7.8 respectively.

Global warming (terrestrial) represents the predominant impact category for all foam products on all timescales. On a per liter-basis AFFF-1 is, for most midpoint categories, the highest contributor to environmental quality impact, however, on a functional unit basis, the AFFF-2 product has the greatest impact and the AFFF-1 the lowest (Table 7.7).

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Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Individualist					
Global warming (terrestrial)	kg CO_2 eq.	6.76×10^{-8}	3.75×10^{-7}	2.03×10^{-7}	1.13×10^{-7}
Global warming (freshwater)	kg CO_2 eq.	1.84×10^{-9}	1.02×10^{-11}	5.53×10^{-12}	3.07×10^{-12}
Photochemical ozone formation	kg NO_2 eq.	3.95×10^{-9}	3.20×10^{-9}	1.47×10^{-9}	4.32×10^{-9}
Acidification	kg SO_2 eq.	1.52×10^{-9}	5.52×10^{-9}	1.91×10^{-9}	7.17×10^{-9}

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Water consumption (terrestrial)	m^3 consumed	-	-	-	-
Water consumption (freshwater)	m^3 consumed	3.77×10^{-12}	8.04×10^{-12}	3.39×10^{-12}	8.92×10^{-12}
Land use – occupation	Annual crop eq.	8.14×10^{-9}	2.67×10^{-9}	2.93×10^{-8}	1.43×10^{-9}
Eutrophication (freshwater)	kg P eq.	5.22×10^{-9}	5.82×10^{-9}	6.14×10^{-11}	2.92×10^{-12}
Eutrophication (marine water)	kg N eq.	8.60×10^{-9}	3.49×10^{-8}	1.30×10^{-11}	1.98×10^{-14}
Hierarchist					
Global warming (terrestrial)	kg CO_2 eq.	3.69×10^{-7}	1.21×10^{-6}	1.14×10^{-6}	5.37×10^{-7}
Global warming (freshwater)	kg CO_2 eq.	3.95×10^{-9}	3.20×10^{-9}	1.47×10^{-9}	4.32×10^{-9}
Photochemical ozone formation	kg NO_2 eq.	3.95×10^{-9}	3.20×10^{-9}	1.47×10^{-9}	4.32×10^{-9}
Acidification	kg SO_2 eq.	1.52×10^{-9}	5.52×10^{-9}	1.91×10^{-9}	7.17×10^{-9}
Water consumption (terrestrial)	m^3 consumed	7.98×10^{-8}	1.71×10^{-7}	7.36×10^{-8}	1.90×10^{-7}
Water consumption (freshwater)	m^3 consumed	3.57×10^{-12}	7.65×10^{-12}	3.29×10^{-12}	8.50×10^{-12}
Land use – occupation	Annual crop eq.	8.14×10^{-9}	2.67×10^{-9}	2.93×10^{-8}	1.43×10^{-9}
Eutrophication (freshwater)	kg P eq.	5.22×10^{-9}	5.82×10^{-9}	6.14×10^{-11}	2.92×10^{-12}
Eutrophication (marine water)	kg N eq.	8.60×10^{-9}	3.49×10^{-8}	1.30×10^{-11}	1.98×10^{-14}
Egalitarian					
Global warming (terrestrial)	kg CO_2 eq.	1.95×10^{-6}	7.01×10^{-6}	6.06×10^{-6}	3.52×10^{-6}

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Global warming (freshwater)	kg CO_2 eq.	5.32×10^{-8}	1.91×10^{-10}	1.65×10^{-10}	9.59×10^{-11}
Photochemical ozone formation	kg NO_2 eq.	3.93×10^{-9}	3.09×10^{-9}	1.18×10^{-9}	4.04×10^{-9}
Acidification	kg SO_2 eq.	1.51×10^{-9}	5.43×10^{-9}	1.73×10^{-9}	6.99×10^{-9}
Water consumption (terrestrial)	m^3 consumed	7.98×10^{-8}	1.71×10^{-7}	7.36×10^{-8}	1.90×10^{-7}
Water consumption (freshwater)	m^3 consumed	3.57×10^{-12}	7.64×10^{-12}	3.29×10^{-12}	8.50×10^{-12}
Land use – occupation	Annual crop eq.	8.14×10^{-9}	2.67×10^{-9}	2.93×10^{-8}	1.43×10^{-9}
Eutrophication (freshwater)	kg P eq.	5.22×10^{-9}	5.82×10^{-9}	6.14×10^{-11}	2.92×10^{-12}
Eutrophication (marine water)	kg N eq.	8.60×10^{-9}	3.49×10^{-8}	1.30×10^{-11}	1.98×10^{-14}

Table 7.7. Impact assessment midpoint results of each firefighting foam product as per the functional unit for Scenario 2 on each time scale basis.

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Individualist					
Global warming (terrestrial)	kg CO_2 eq.	3.53×10^{-8}	6.30×10^{-8}	2.67×10^{-8}	1.49×10^{-8}
Global warming (freshwater)	kg CO_2 eq.	9.58×10^{-10}	1.72×10^{-12}	7.27×10^{-13}	4.05×10^{-13}
Photochemical ozone formation	kg NO_2 eq.	2.06×10^{-9}	5.38×10^{-10}	1.93×10^{-10}	5.70×10^{-10}
Acidification	kg SO_2 eq.	7.93×10^{-10}	9.27×10^{-10}	2.51×10^{-10}	9.45×10^{-10}

Impact category	Unit	AFFF-1	AFFF-2	F3-1	F3-2
Water consumption (terrestrial)	m^3 consumed	-	-	-	-
Water consumption (freshwater)	m^3 consumed	1.98×10^{-12}	1.37×10^{-12}	4.59×10^{-13}	1.19×10^{-12}
Land use – occupation	Annual crop eq.	4.24×10^{-9}	4.48×10^{-10}	3.84×10^{-9}	1.88×10^{-10}
Eutrophication (freshwater)	kg P eq.	2.72×10^{-9}	9.78×10^{-10}	8.06×10^{-12}	3.84×10^{-13}
Eutrophication (marine water)	kg N eq.	4.48×10^{-9}	5.87×10^{-9}	1.70×10^{-12}	2.60×10^{-15}
Hierarchist					
Global warming (terrestrial)	kg CO_2 eq.	1.92×10^{-7}	2.03×10^{-7}	1.49×10^{-7}	7.07×10^{-8}
Global warming (freshwater)	kg CO_2 eq.	5.23×10^{-9}	5.56×10^{-12}	4.08×10^{-12}	1.93×10^{-12}
Photochemical ozone formation	kg NO_2 eq.	2.06×10^{-9}	5.38×10^{-10}	1.93×10^{-10}	5.70×10^{-10}
Acidification	kg SO_2 eq.	7.93E-10	9.27×10^{-10}	2.51×10^{-10}	$9.45E\times10^{-10}$
Water consumption (terrestrial)	m^3 consumed	4.16×10^{-8}	2.87×10^{-8}	9.66×10^{-9}	2.50×10^{-8}
Water consumption (freshwater)	m^3 consumed	1.86×10^{-12}	1.29×10^{-12}	4.32×10^{-13}	1.12×10^{-12}
Land use – occupation	Annual crop eq.	4.24×10^{-9}	4.48×10^{-10}	3.84×10^{-9}	$1.88E\times10^{-10}$
Eutrophication (freshwater)	kg P eq.	2.72×10^{-9}	9.78×10^{-10}	8.06×10^{-12}	3.84×10^{-13}
Eutrophication (marine water)	kg N eq.	4.48×10^{-9}	5.87×10^{-9}	1.70×10^{-12}	2.60×10^{-15}

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Egalitarian					
Global warming (terrestrial)	kg CO_2 eq.	1.02×10^{-6}	1.18×10^{-6}	7.96×10^{-7}	4.64×10^{-7}
Global warming (freshwater)	kg CO_2 eq.	2.77×10^{-8}	3.22×10^{-11}	2.17×10^{-11}	1.27×10^{-11}
Photochemical ozone formation	kg NO_2 eq.	2.06×10^{-9}	5.38×10^{-10}	1.93×10^{-10}	5.70×10^{-10}
Acidification	kg SO_2 eq.	7.93×10^{-10}	9.27×10^{-10}	2.51×10^{-10}	9.45×10^{-10}
Water consumption (terrestrial)	m^3 consumed	4.16×10^{-8}	2.87×10^{-8}	9.66×10^{-9}	2.50×10^{-8}
Water consumption (freshwater)	m^3 consumed	1.86×10^{-12}	1.29×10^{-12}	4.32×10^{-13}	1.12×10^{-12}
Land use – occupation	Annual crop eq.	4.24×10^{-9}	4.48×10^{-10}	3.84×10^{-9}	1.88×10^{-10}
Eutrophication (freshwater)	kg P eq.	2.72×10^{-9}	9.78×10^{-10}	8.06×10^{-12}	3.84×10^{-13}
Eutrophication (marine water)	kg N eq.	4.48×10^{-9}	5.87×10^{-9}	1.70×10^{-12}	2.60×10^{-15}

Table 7.8. Impact assessment results of each firefighting foam product for Scenario 2, per 1 liter of foam product.

The results for the foam products show the constituent acquisition life cycle stage to represent the major contributor to environmental impact for all foam products across all characterized midpoint categories (Table 7.9). The impact caused by raw material acquisition stage ranged from 76 to 100 % for Scenario 1 and 95 – 100 % for Scenario 2 across all impact category midpoints. When compared to the constituent acquisition phase; the manufacture, use, and disposal phases had minor contributions towards the total environmental impact of firefighting foam products.

The surfactants modelled in the study were of varied origins (i.e. both oleo chemical origin – palm and coconut resources; and petrochemical), the fraction of oleo chemicals drives the impact categories for natural land transformation and agricultural land occupation (land use).

Table 7.9 shows the characterised midpoint results for each product life cycle stage as a percentage of the total foam life cycle per functional unit on a hierarchist basis for both scenario 1 (disposal by incineration for all products) and scenario 2 (Disposal by incineration of AFFF products and non-containment of F3 products). GWP = climate change, EOFP = photochemical ozone formation, TAP = terrestrial acidification, WCP = water consumption, LOP = land use, ETP = eutrophication.

			Ecosystem quality total	**Terrestrial**					**Freshwater**			**Marine**
				GWP	EOFP	TAP	WCP	LOP	GWP	ETP	WCP	ETP
Scenario 1												
Characterized results (%)	AFFF-1	Constituents	99.59	99.67	98.84	97.48	99.14	100.0	100.0	100.0	99.14	100.00
		Manufacture	0.00	0.00	0.03	0.25	0.00		0.00		0.00	
		Use	0.23	0.13			0.77		0.00		0.77	
		Disposal	0.18	0.20	1.13	2.27	0.09		0.00		0.09	
	AFFF-2	Constituents	99.57	99.68	95.55	97.85	98.75	100.0	99.68	100.0	98.75	100.00
		Manufacture	0.01	0.00	0.11	0.22	0.01		0.00		0.01	
		Use	0.24	0.13			1.11		0.13		1.11	
		Disposal	0.19	0.19	4.34	1.94	0.13		0.19		0.13	
	F3-1	Constituents	99.37	99.59	76.18	85.71	96.54	100.0	99.59	100.0	96.54	100.00
		Manufacture	0.03	0.02	1.31	3.32	0.07		0.02		0.07	
		Use	0.35	0.17			3.29		0.17		3.29	
		Disposal	0.25	0.21	22.51	10.97	0.09		0.21		0.09	
	F3-2	Constituents	99.00	99.18	92.37	97.07	98.69	100.0	99.18	100.0	98.69	100.00
		Manufacture	0.00	0.00	0.01	0.02	0.00		0.00		0.00	
		Use	0.59	0.36			1.27		0.36		1.27	
		Disposal	0.41	0.45	7.61	2.91	0.04		0.45		0.04	
Scenario 2												
Characterized results (%)	AFFF-1	Constituents	99.59	99.67	98.84	97.48	99.14	100.0	100.0	100.00	99.14	100.00
		Manufacture	0.00	0.00	0.03	0.25	0.00		0.00		0.00	
		Use	0.23	0.13			0.77		0.00		0.77	
		Disposal	0.18	0.20	1.13	2.27	0.09		0.00		0.09	
	AFFF-2	Constituents	99.57	99.68	95.55	97.85	98.75	100.00	99.68	100.00	98.75	100.00
		Manufacture	0.01	0.00	0.11	0.22	0.01		0.00		0.01	
		Use	0.24	0.13			1.11		0.13		1.11	
		Disposal	0.19	0.19	4.34	1.94	0.13		0.19		0.13	
	F3-1	Constituents	99.62	99.81	98.31	96.27	96.63	100.00	99.81	100.00	96.63	100.00
		Manufacture	0.03	0.02	1.69	3.73	0.07		0.02		0.07	

			Ecosystem quality total	**Terrestrial**					**Freshwater**			**Marine**
				GWP	EOFP	TAP	WCP	LOP	GWP	ETP	WCP	ETP
		Use	0.35	0.17			3.30		0.17		3.30	
	F3-2	Constituents	99.62	99.81	98.31	96.27	96.63	100.00	99.81	100.00	96.63	100.00
		Manufacture	0.03	0.02	1.69	3.73	0.07		0.02		0.07	
		Use	0.35	0.17			3.30		0.17		3.30	

Table 7.9 Characterized midpoint results.

Environmental quality impact endpoint analysis (excluding environmental toxicology) for the functional unit demonstrates AFFF-1 has the lowest environmental impact over all time scales assessed within this study, whilst AFFF-2 represents the highest. The impacts of all foam products vary with time scale and are, predictably, highest over the egalitarian time scale (1000 years, Figure 7.14c).

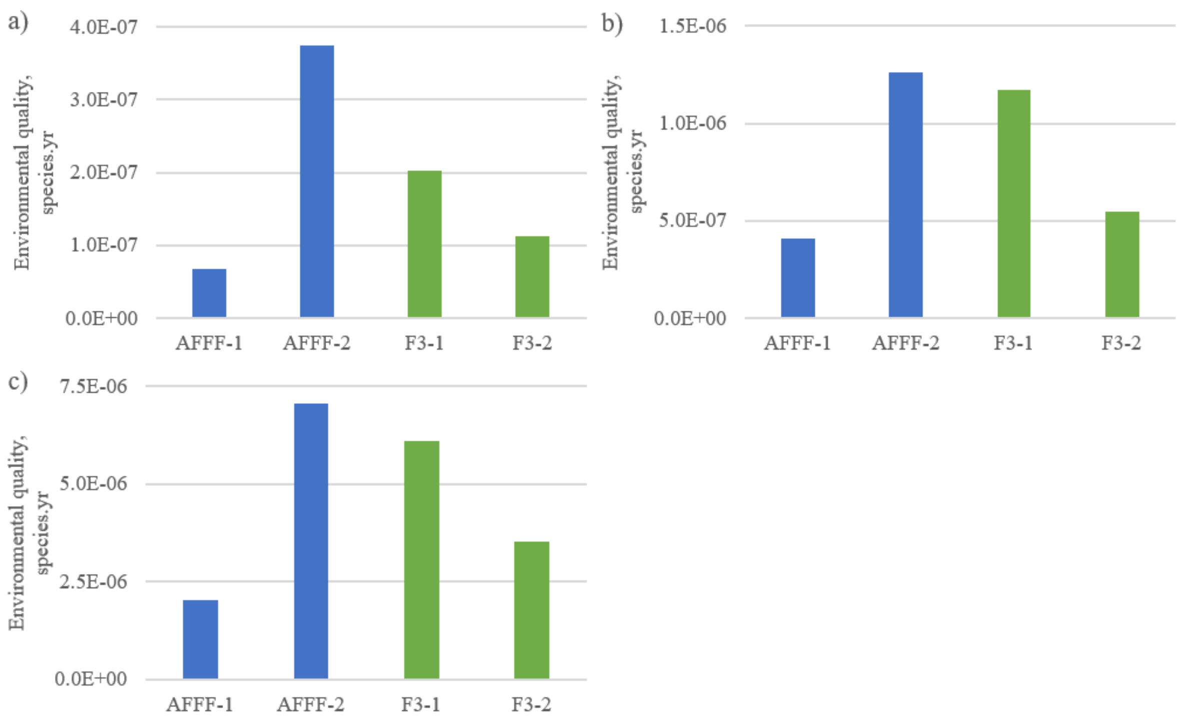

Figure 7.14. Endpoint characterization for the environmental quality impact for a) individualistic, b) hierarchist, and c) egalitarian time scales for Scenario 1 in species.yr.

Figures 7.15 and 7.16 illustrate the proportion of each midpoint category as its contribution to the environmental quality impact endpoint.

Results for the individualist model suggests terrestrial climate change represents the predominant contributor to the impact categories assessed in this study for the constituent acquisition, use and disposal life cycle phases whilst terrestrial acidification was predominant for the manufacturing phase (Figure 7.17). The manufacture, use and disposal phases demonstrate a similar composition for all foam products, whilst there is greater variation between products for the constituent acquisition phase, which reflects the variation in constituent types and sources.

The hierarchist model suggests terrestrial climate change to be the predominant impact category for constituent acquisition, manufacture, and disposal life cycle phases for all foam products (Figure 7.16). Water consumption represents the predominant impact category for the use life cycle phase for all foam products.

The egalitarian model suggests climate change to be the predominant impact category for all foam products in all life cycle stages (Figure 7.17).

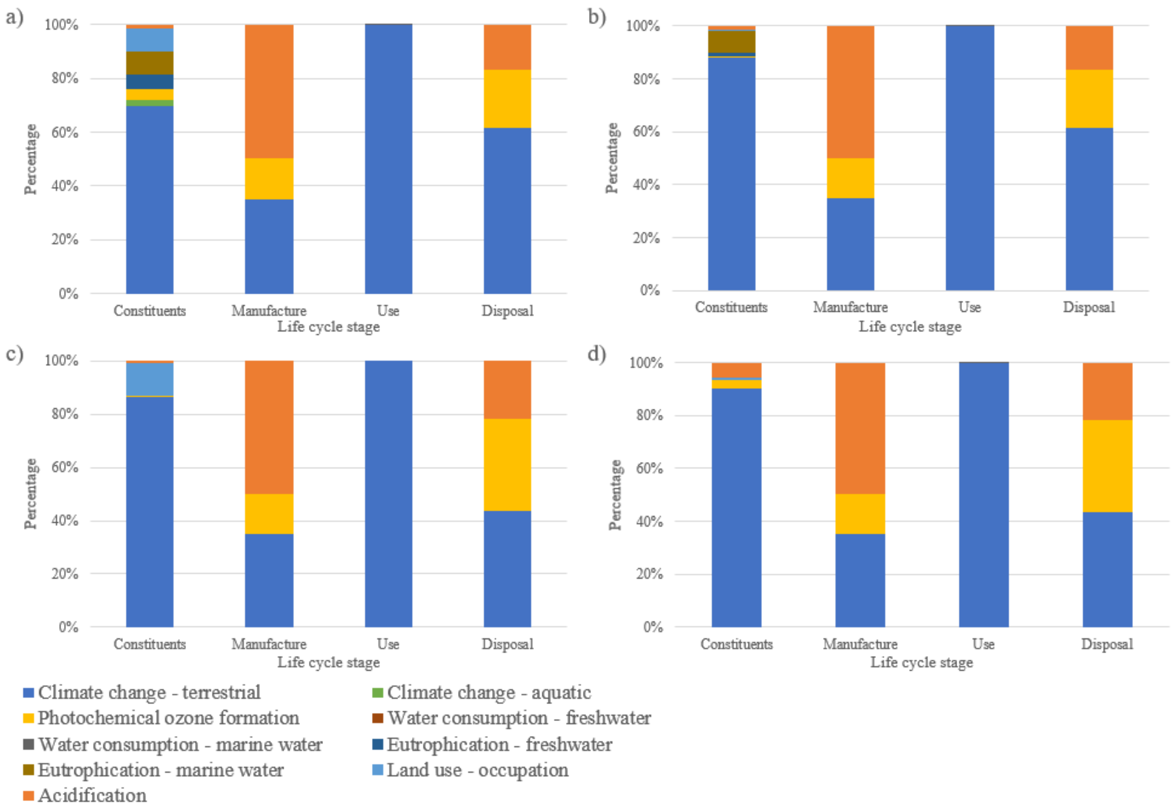

Figure 7,15. Environmental impact results associated with the different life cycle stages for a) AFFF-1, b) AFFF-2, c) F3-1, and d) F3-2 for Scenario 1 on an individualist timescale.

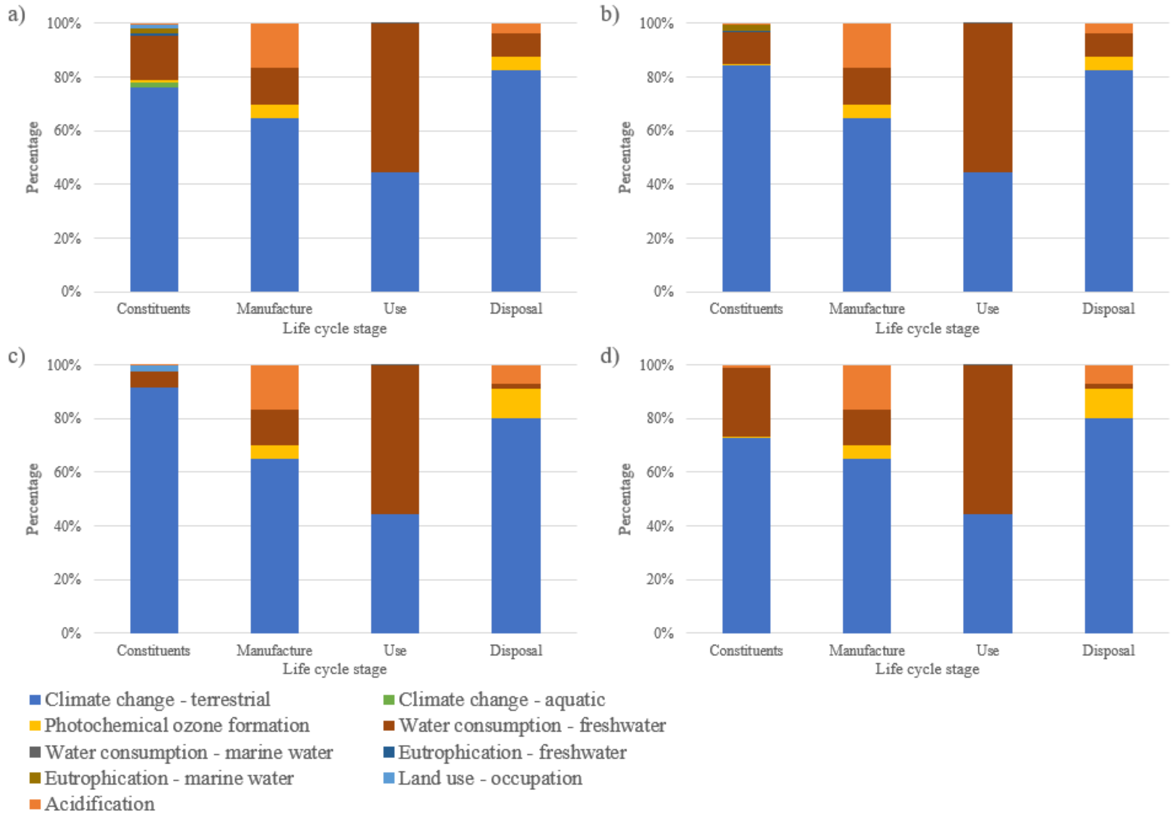

Figure 7.16. Environmental impact results associated with the different life cycle stages for a) AFFF-1, b) AFFF-2, c) F3-1, and d) F3-2 for Scenario 1 on a hierarchist timescale.

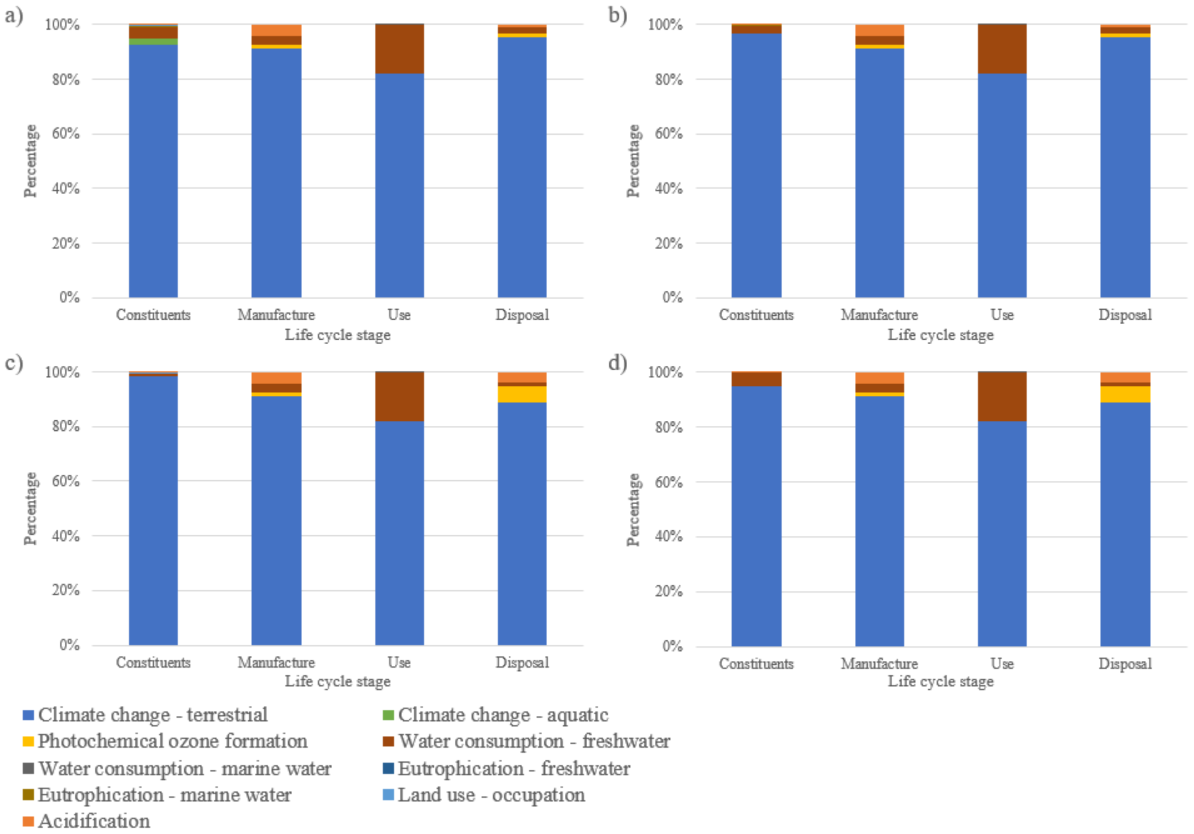

Figure 7.17. Environmental impact results associated with the different life cycle stages for a) AFFF-1, b) AFFF-2, c) F3-1, and d) F3-2 for Scenario 1 on an egalitarian timescale.

7.18.2. Human impact

The human health midpoint impact categories for this study are presented for the four foam products per the functional unit and also per liter of foam on individualist, hierarchist, and egalitarian bases for Scenario 2 (Tables 7.10 and 7.11, respectively).

Results suggest that global warming potential (climate change) and water consumption are the two dominant impact categories for all foam products, the impact of which are both greatest over the hierarchist time scale.

On a per liter basis, both AFFF products have greater impact than the F3 products, however, on a functional unit basis, AFFF-1 has the lowest impact in all categories (except individualist - water consumption and photochemical ozone formation), this is because the functional unit accounts for foam performance, and whilst the life cycle per liter of AFFF-1 has a relatively high human health impact value, this is offset by the reduced quantity of foam required to control and extinguish a fire.

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Individualist					
Global warming	kg CO_2 eq.	1.03×10^{-5}	5.72×10^{-5}	1.72×10^{-5}	3.08×10^{-5}
Stratospheric ozone depletion	kg CFC11 eq.	8.87×10^{-8}	1.36×10^{-6}	3.44×10^{-8}	2.37×10^{-7}
Fine particulate matter formation	kg PM2.5 eq.	4.34×10^{-7}	6.91×10^{-7}	6.21×10^{-7}	2.22×10^{-6}
Photochemical ozone formation	kg NOx eq.	1.75×10^{-6}	2.08×10^{-8}	2.47×10^{-8}	6.56×10^{-9}
Water consumption	m^3 consumed	1.95×10^{-5}	4.17×10^{-5}	4.65×10^{-5}	1.79×10^{-5}
Hierarchist					
Global warming	kg CO_2 eq.	$1.32\times10^{+2}$	$4.32\times10^{+2}$	$4.07\times10^{+2}$	$1.92\times10^{+2}$
Stratospheric ozone depletion	kg CFC11 eq.	4.62×10^{-4}	3.61×10^{-3}	1.60×10^{-3}	2.54×10^{-4}
Fine particulate matter formation	kg PM2.5 eq.	9.91×10^{-4}	8.703	6.29×10^{-3}	1.07×10^{-2}
Photochemical ozone formation	kg NOx eq.	2.94×10^{-2}	2.28×10^{-2}	1.00×10^{-2}	2.96×10^{-2}
Water consumption	m^3 consumed	5.91	$1.27\times10^{+1}$	5.45	$1.41\times10^{+1}$
Egalitarian					
Global warming	kg CO_2 eq.	9.78×10^{-4}	3.51×10^{-3}	1.77×10^{-3}	3.02×10^{-3}
Stratospheric ozone depletion	kg CFC11 eq.	8.77×10^{-7}	4.81×10^{-6}	4.73×10^{-7}	3.25×10^{-6}
Fine particulate matter formation	kg PM2.5 eq.	6.24×10^{-7}	5.47×10^{-6}	6.58×10^{-6}	3.73×10^{-6}

Impact category	Unit	AFFF-1	AFFF-2	F3-1	F3-2
Photochemical ozone formation	kg NOx eq.	1.75×10^{-6}	2.08×10^{-8}	2.47×10^{-8}	6.83×10^{-9}
Water consumption	m^3 consumed	1.31×10^{-5}	2.81×10^{-5}	3.14×10^{-5}	1.21×10^{-5}

Table 7.10. Impact assessment midpoint results of each firefighting foam product as per the functional unit for Scenario 2 on each time scale basis.

Impact category	Unit	AFFF-1	AFFF-2	F3-1	F3-2
Individualist					
Global warming	kg CO_2 eq.	5.38×10^{-6}	9.62×10^{-6}	4.07×10^{-6}	2.27×10^{-6}
Stratospheric ozone depletion	kg CFC11 eq.	4.62×10^{-8}	2.28×10^{-7}	3.17×10^{-8}	5.05×10^{-9}
Fine particulate matter formation	kg PM2.5 eq.	2.26×10^{-7}	1.16×10^{-7}	2.96×10^{-7}	8.53×10^{-8}
Photochemical ozone formation	kg NOx eq.	9.10×10^{-7}	3.49×10^{-9}	1.16×10^{-9}	3.54×10^{-9}
Water consumption	m^3 consumed	1.01×10^{-5}	7.01×10^{-6}	2.36×10^{-6}	6.11×10^{-6}
Hierarchist					
Global warming	kg CO_2 eq.	6.37×10^{-5}	6.74×10^{-5}	4.95×10^{-5}	2.34×10^{-5}
Stratospheric ozone depletion	kg CFC11 eq.	1.28×10^{-7}	3.22×10^{-7}	1.12×10^{-7}	1.78×10^{-8}
Fine particulate matter formation	kg PM2.5 eq.	3.25×10^{-7}	9.20×10^{-7}	5.19×10^{-7}	8.90×10^{-7}
Photochemical ozone formation	kg NOx eq.	9.10×10^{-7}	3.49×10^{-9}	1.20×10^{-9}	3.54×10^{-9}
Water consumption	m^3 consumed	6.84×10^{-6}	4.73×10^{-6}	1.59×10^{-6}	4.12×10^{-6}
Egalitarian					
Global warming	kg CO_2 eq.	5.09×10^{-4}	5.89×10^{-4}	3.98×10^{-4}	2.32×10^{-4}

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Stratospheric ozone depletion	kg CFC11 eq.	4.57×10^{-7}	8.09×10^{-7}	4.35×10^{-7}	6.93×10^{-8}
Fine particulate matter formation	kg PM2.5 eq.	3.25×10^{-7}	9.20×10^{-7}	5.19×10^{-7}	8.90×10^{-7}
Photochemical ozone formation	kg NOx eq.	9.10×10^{-7}	3.49×10^{-9}	1.20×10^{-9}	3.54×10^{-9}
Water consumption	m^3 consumed	6.84×10^{-6}	4.73×10^{-6}	1.59×10^{-6}	4.12×10^{-6}

Table 7.11 Impact assessment midpoint results of each firefighting foam product as per 1 L of product for Scenario 2 on each time scale basis.

The constituent acquisition represents the predominant contributor to human health impact for all foam products across all midpoint categories and the endpoint for human health impact for both Scenarios 1 and 2 (>99 % total human health impact, Table 7.12). When compared to the constituent acquisition phase; the manufacture, use, and disposal phases had minor contributions towards the total human health impact of firefighting foam products, however, it is important to acknowledge that the exclusion of human toxicity as an impact category from this study will have reduced the long-term human health impact resulting from foam use and disposal.

Table 7.12 gives the characterised midpoint results for each product life cycle stage as a percentage of the total foam life cycle per functional unit on a hierarchist basis for both scenario 1 (disposal by incineration for all products) and scenario 2 (disposal by incineration of AFFF products and non-containment of F3 products). GWP = climate change, ODP = stratospheric ozone depletion, PMFP = fine particulate matter formation, HPOF = human photochemical ozone formation, WCP = water consumption.

			Human Health					
			Total	GWP	ODP	PMFP	HOFP	WCP
Scenario 1								
characterized results (%)	AFF F-1	Constituents	99.56	99.67	99.15	87.43	99.98	99.14
		Manufacture	0.01	0.00	0.02	0.57	0.00	0.00
		Use	0.19	0.13				0.77
		Disposal	0.24	0.20	0.83	12.01	0.02	0.09
	AFF F-2	Constituents	99.57	99.68	99.66	95.56	95.16	98.75
		Manufacture	0.01	0.00	0.01	0.20	0.12	0.01
		Use	0.19	0.13				1.11
		Disposal	0.23	0.19	0.33	4.24	4.72	0.13
	F3-1	Constituents	99.04	99.18	89.53	96.95	91.53	98.69
		Manufacture	0.00	0.00	0.02	0.02	0.01	0.00
		Use	0.48	0.36				1.27
		Disposal	0.48	0.45	10.45	3.03	8.45	0.04
	F3-2	Constituents	99.04	99.18	89.53	96.95	91.53	98.69
		Manufacture	0.00	0.00	0.02	0.02	0.01	0.00
		Use	0.48	0.36				1.27
		Disposal	0.48	0.45	10.45	3.03	8.45	0.04
Scenario 2								
characterized results (%)	AFF F-1	Constituents	99.56	99.67	99.15	87.43	99.98	99.14
		Manufacture	0.01	0.00	0.02	0.57	0.00	0.00
		Use	0.19	0.13				0.77
		Disposal	0.24	0.20	0.83	12.01	0.02	0.09
	AFF F-2	Constituents	99.57	99.68	99.66	95.56	95.16	98.75
		Manufacture	0.01	0.00	0.01	0.20	0.12	0.01
		Use	0.19	0.13				1.11
		Disposal	0.23	0.19	0.33	4.24	4.72	0.13
	F3-1	Constituents	99.51	99.64	99.98	99.98	99.99	98.73
		Manufacture	0.00	0.00	0.02	0.02	0.01	0.00

			Human Health					
			Total	GWP	ODP	PMFP	HOFP	WCP
		Use	0.48	0.36				1.27
	F3-2	Constituents	99.70	99.81	99.90	98.44	98.02	96.63
		Manufacture	0.04	0.02	0.10	1.56	1.98	0.07
		Use	0.27	0.17				3.30

Table 7.12. Characterized midpoint results.

Human health impact endpoint analysis (excluding human toxicology) for the functional unit demonstrates AFFF-1 shows the lowest human impact over all time scales assessed within this study, whilst AFFF-2 represents this highest (Figure 7. 18). The impacts of all foam products vary with time scale and are, predictably, highest over the egalitarian time scale (1000 years, Figure 7.18c). F3-1 has a lower human health impact than F3-2 for the individualist timescale, whilst this is reversed for the hierarchist and egalitarian timescales.

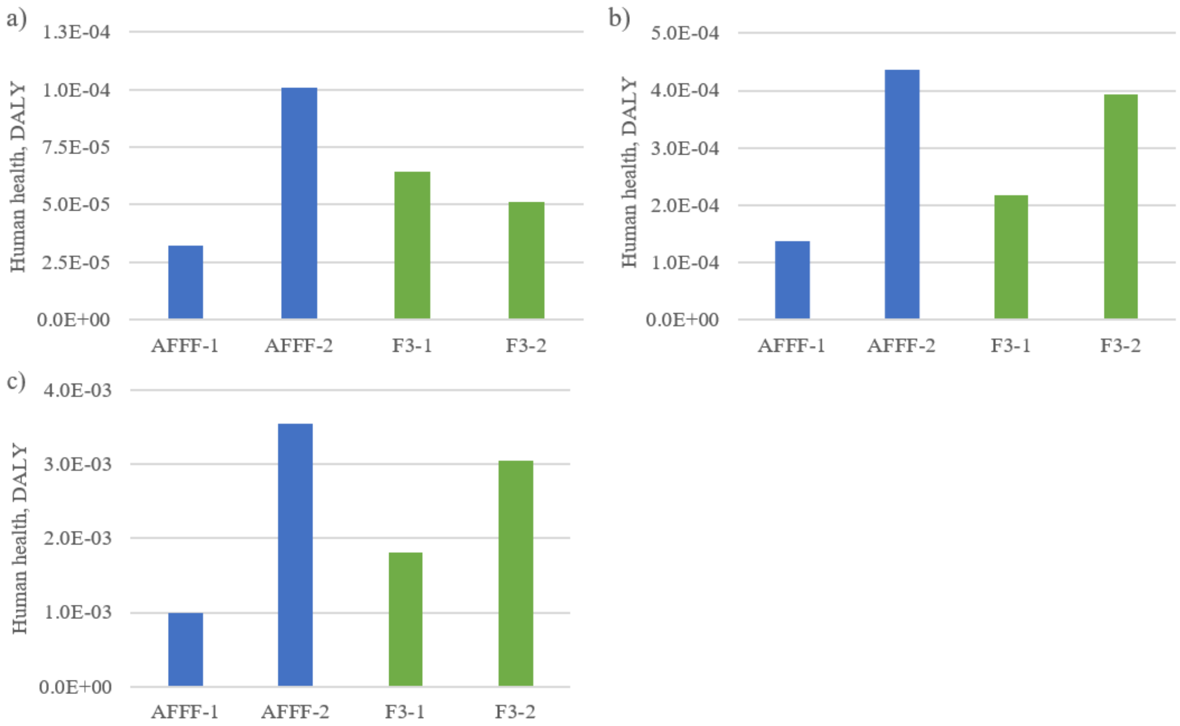

Figure 7.18. Endpoint characterization for the human health impact for a) individualistic, b) hierarchist, and c) egalitarian time scales for Scenario 1 in DALY.

Figures 7.19 – 7.21 illustrate the proportion of each midpoint category as its contribution to the human health impact endpoint.

Results for the individualist model suggests that water consumption and climate change are the major contributors to human health impact for the constituent acquisition, manufacture, and use life cycle stages for all foams. The major contributor to the disposal stage for AFFF-1 and AFFF-2 was fine particulate matter formation, which may be attributed to the incineration disposal method used for the AFFF products, Scenario 2 did not include incineration for F3 products.

The hierarchist model suggests climate change to be the major contributor to human health impact for all foams at all life cycle stages, with water consumption the secondary contributor for constituent acquisition and use stages; and fine particulate matter production for manufacturing and disposal phases (Figure 7.20).

The egalitarian model suggests climate change to be the predominant impact category for all foam products in all life cycle stages (Figure 7.21).

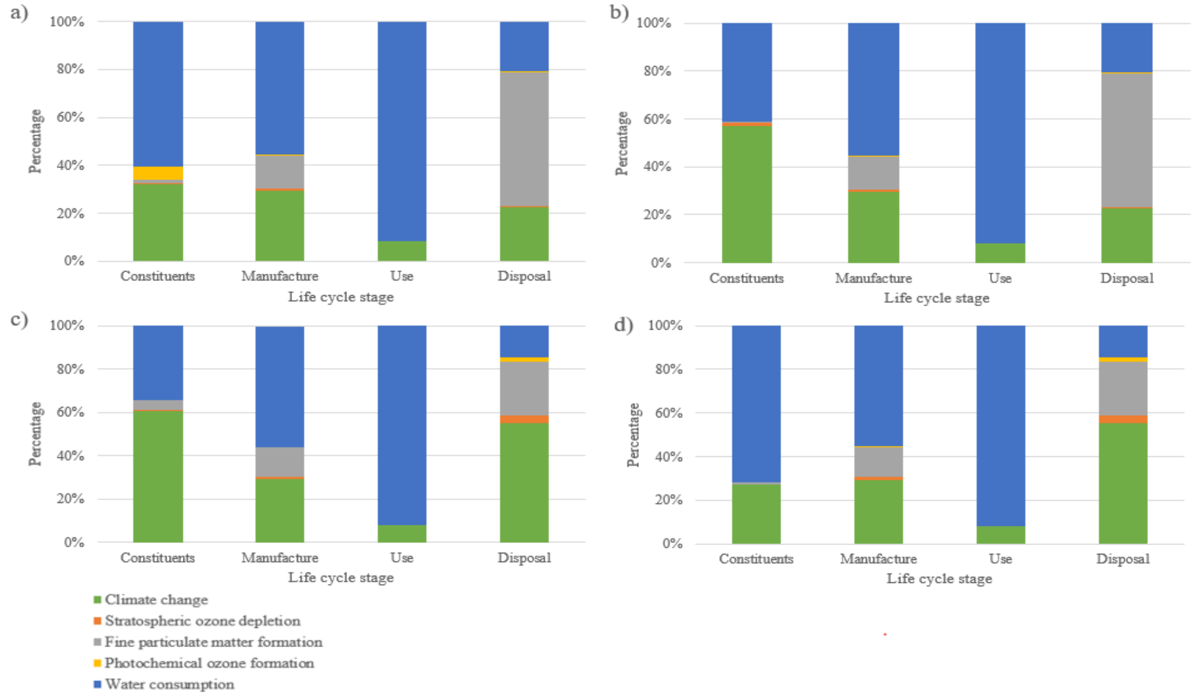

Figure 7.19. Human impact results associated with the different life cycle stages for a) AFFF-1, b) AFFF-2, c) F3-1, and d) F3-2 for Scenario 1 on an individualist timescale.

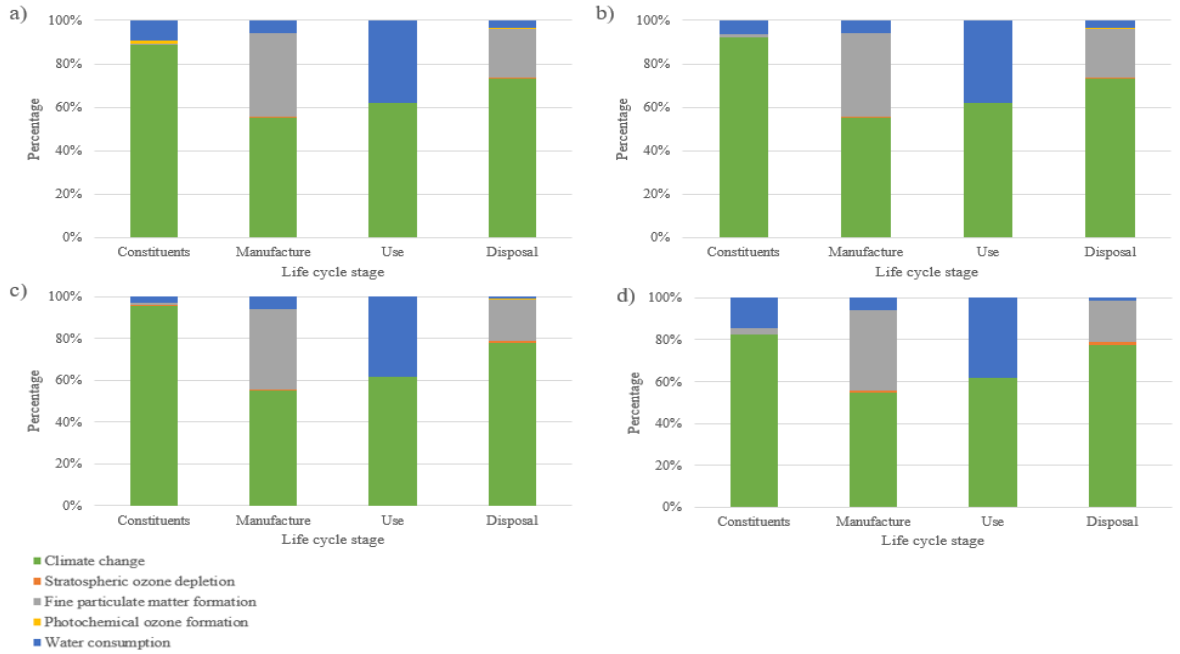

Figure 7.20. Human impact results associated with the different life cycle stages for a) AFFF-1, b) AFFF-2, c) F3-1, and d) F3-2 for Scenario 1 on a hierarchist timescale.

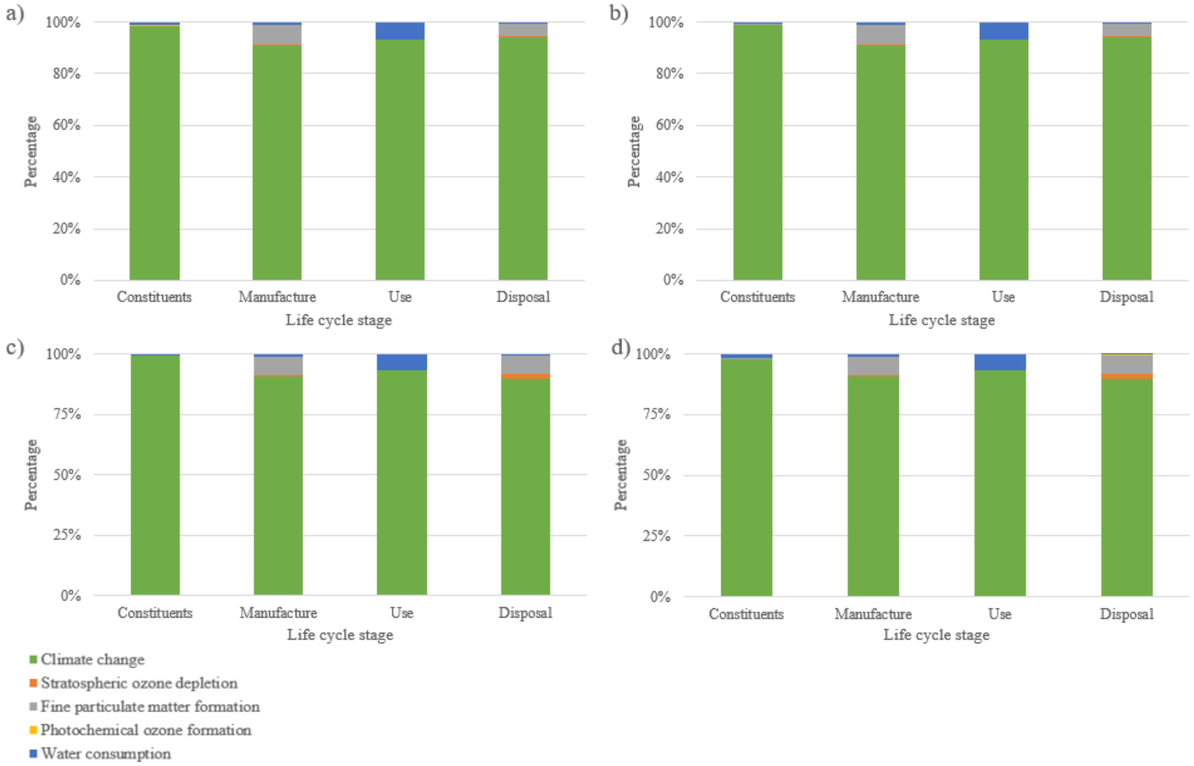

Figure 7.21. Human impact results associated with the different life cycle stages for a) AFFF-1, b) AFFF-2, c) F3-1, and d) F3-2 for Scenario 1 on an egalitarian timescale.

7.18.3. Resource depletion

The resource depletion midpoint impact categories for this study are presented for the four foam products per the functional unit and also per liter of foam on individualist, hierarchist, and egalitarian bases for Scenario 2 (Tables 7.13 and 7.14 respectively).

Results suggest that fossil resource use: crude oil and natural gas are the two dominant impact categories for all foam products, the impact of which are both greatest over the hierarchist and egalitarian time scale.

On a per liter basis, both AFFF products have greater impact than the F3 products, and unlike with environmental quality and human health endpoints, AFFF products also have a greater impact on a functional unit basis. It is suggested that this is due to the petrochemical source for a number of surfactants using within the AFFF products, whilst the F3 products use predominantly oleo-based surfactants.

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Individualist					
Mineral resource scarcity	kg Cu	0.1721	0.1921	0.0001	0.0002
Fossil resource scarcity					
- Crude oil	kg	0.8175	3.3810	3.1393	0.1766
- Hard coal	kg	0.0028	0.0099	0.0075	0.0152
- Natural gas	m^3	1.3940	0.5965	0.5105	0.0386
Hierarchist					
Mineral resource scarcity	kg Cu	0.2716	0.3032	0.0002	0.0004
Fossil resource scarcity					
Crude oil	kg	0.8175	3.3810	3.1393	0.2531
Hard coal	kg	0.0028	0.0099	0.0075	0.0220
Natural gas	m^3	1.3940	0.5965	0.5105	0.0559
Egalitarian					
Mineral resource scarcity	kg Cu	0.2716	0.3032	0.0002	0.0004

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Fossil resource scarcity					
Crude oil	kg	0.8175	3.3810	3.1393	0.2531
Hard coal	kg	0.0028	0.0099	0.0075	0.0220
Natural gas	m^3	1.3940	0.5965	0.5105	0.0559
Brown coal	kg				0.0000
Peat	kg	0.0000	0.0000	0.0000	0.0000

Table 7.13. Impact assessment midpoint results of each firefighting foam product as per the functional unit for Scenario 2 on each time scale basis.

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Individualist					
Mineral resource scarcity	kg Cu	0.0896	0.0323	2.46E-05	1.18E-05
Fossil resource scarcity					
- Crude oil	kg	0.4258	0.5682	0.0234	0.4120
- Hard coal	kg	0.0015	0.0017	0.001997	0.0010
- Natural gas	m^3	0.7260	0.1003	0.0051	0.06700
Hierarchist					
Mineral resource scarcity	kg Cu	0.1415	0.05097	5.43×10^{-5}	2.57×10^{-5}
Fossil resource scarcity					
Crude oil	kg	0.4258	0.5682	0.0333	0.4120
Hard coal	kg	0.0015	0.0017	0.0029	0.0010
Natural gas	m^3	0.7260	0.1003	0.0074	0.0670
Egalitarian					
Mineral resource scarcity	kg Cu	0.1415	0.0510	5.43×10^{-5}	2.58×10^{-5}
Fossil resource scarcity					
Crude oil	kg	0.4258	0.5682	0.0333	0.4120
Hard coal	kg	0.0015	0.0017	0.0029	0.0009

Impact category	**Unit**	**AFFF-1**	**AFFF-2**	**F3-1**	**F3-2**
Natural gas	m^3	0.7260	0.1003	0.0074	0.0670
Brown coal	kg			4.65×10^{-11}	
Peat	kg	2.58×10^{-6}	3.39×10^{-6}	2.06×10^{-6}	6.01038×10^{-19}

Table 7.14. Impact assessment midpoint results of each firefighting foam product as per 1 L of product unit for Scenario 2 on each time scale basis.

The resource depletion endpoint is predominantly contributed to by the constituent acquisition life cycle stage for all foam products across all midpoint categories and the endpoint for human health impact for both Scenarios 1 and 2 (98 – 100 % total human health impact, Table 7.10).

Table 7.15. shows characterised midpoint results for each product life cycle stage as a percentage of the total foam life cycle per functional unit on a hierarchist basis for both scenario 1 (disposal by incineration for all products) and scenario 2 (Disposal by incineration of AFFF products and non-containment of F3 products). MRS = mineral resource scarcity, CO = crude oil, HC = hard coal, NG = natural gas.

			Resource Depletion Total *		**Fossil resource scarcity**		
				MRS	**CO**	**HC**	**NG**
Scenario 1							
characterized results (%)	AFFF-1	Constituents	99.98	100.00	99.95	100.00	100.00
		Manufacture	0.02		0.05		
		Use	0.00				
		Disposal	0.00	0.00			
	AFFF-2	Constituents	99.97	99.99	99.96	100.00	100.00
		Manufacture	0.03		0.04		
		Use	0.00				
		Disposal	0.01	0.01			
	F3-1	Constituents	100.0	88.62	100.00	100.00	100.00
		Manufacture	0.00		0.00		
		Use	0.00				

		Disposal	0.00	11.38			
	F3-2	Constituents	98.09	94.61	97.51	100.00	100.00
		Manufacture	1.90		2.49		
		Use	0.00				
		Disposal	0.01	5.39			
Scenario 2							
characterized results (%)	AFFF-1	Constituents	99.98	100.00	99.95	100.00	100.00
		Manufacture	0.02		0.05		
		Use	0.00				
		Disposal	0.00	0.00			
	AFFF-2	Constituents	99.97	99.99	99.96	100.00	100.00
		Manufacture	0.03		0.04		
		Use	0.00				
		Disposal	0.00	0.01			
	F3-1	Constituents	100.0	100.00	100.00	100.00	100.00
		Manufacture	0.00		0.00		
		Use	0.00				
	F3-2	Constituents	98.1	100.00	97.51	100.00	100.00
		Manufacture	1.90		2.49		
		Use	0.00				

* Sum of total percentage may exceed 100 due to rounding.

Table 7.15. Characterized midpoint results

Resource depletion impact endpoint analysis for the functional unit demonstrates F3-2 to have the lowest resource depletion impact over all time scales assessed within this study, whilst AFFF-2 represents the highest (Figure 7.22). The impacts of all foam products vary with time scale and are, predictably, highest over the egalitarian time scale (1000 years, Figure 7.22c).

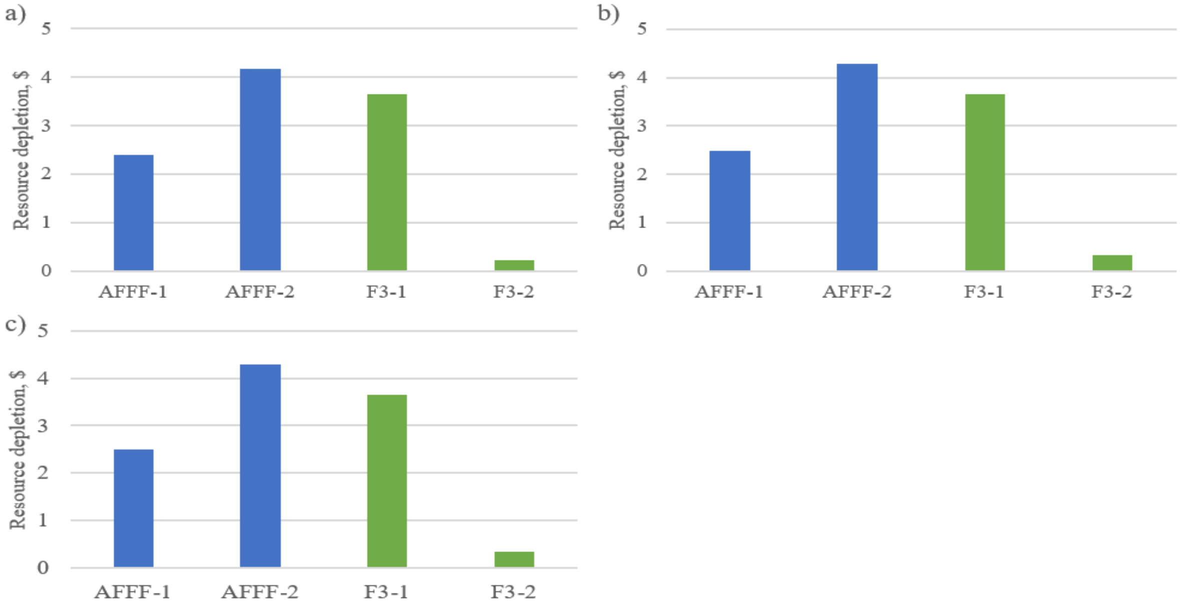

Figure 7.22. Endpoint characterisation for the resource depletion for a) individualistic, b) hierarchist, and c) egalitarian time scales for Scenario 1 in dollars ($).

7.18.4. Results synthesis

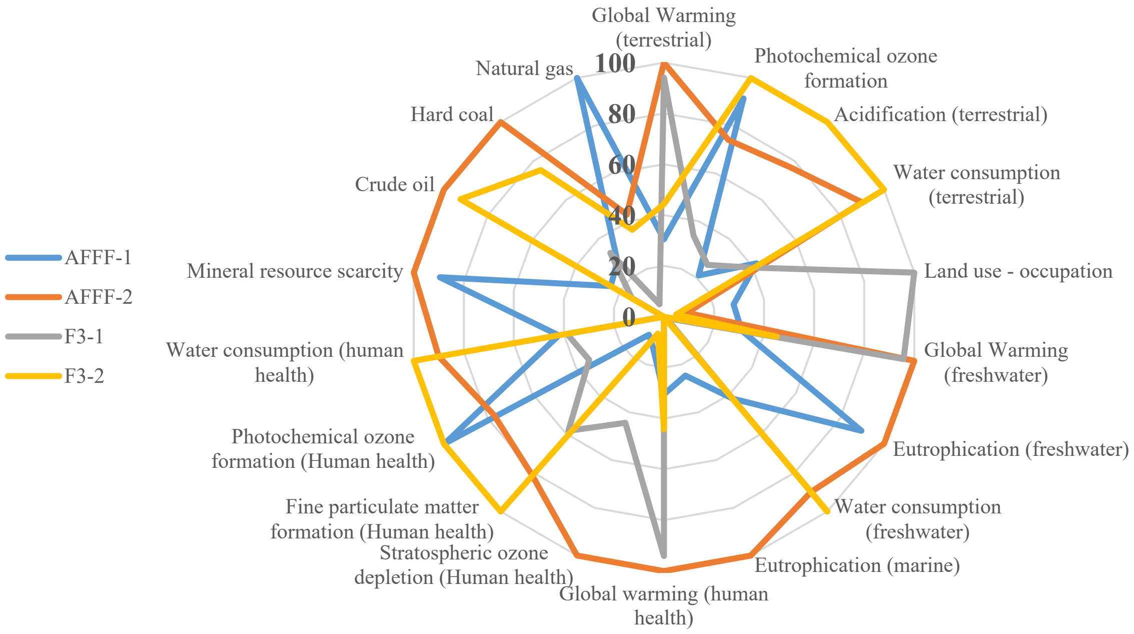

Figure 7.23. Relative midpoint categories for Scenario 2 using the hierarchist timescale.

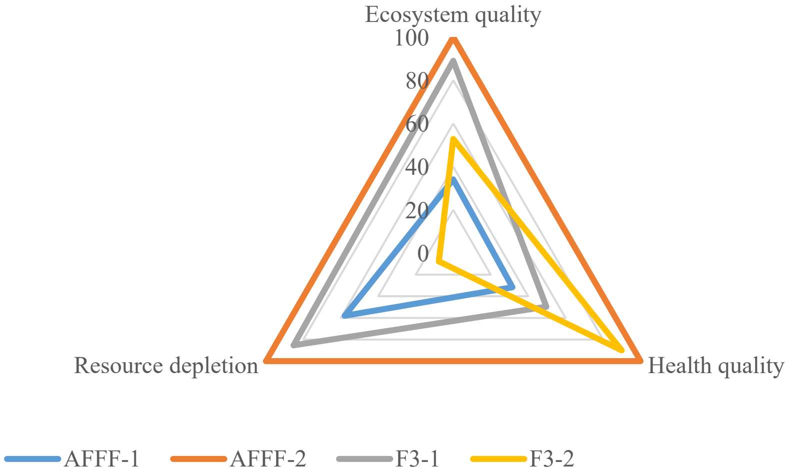

Figure 7.24. Relative endpoint categories for scenario 2 using the hierarchist timescale.

7.19. General discussion

Fluorinated firefighting foam (AFFF) products are subject to sustained scrutiny from regulatory and media bodies. This is owing to their reliance on PFAS (per- and polyfluoroalkyl substances) as active ingredients, which were added to Annex B of the Stockholm Convention as persistent organic pollutants (POPs). Fluorine free (F3) foams are being developed as an environmentally friendly alternative to the traditional AFFFs and as such are required to have comparable performance capabilities in terms of fire extinction and control, whilst having a lower environmental impact.

Whilst developments have been made towards establishing the environmental risk posed by PFAS compounds, the large catalogue of PFAS structures means that there remain significant uncertainties, although they have been widely demonstrated to be persistent and some PFAS are bioaccumulative. This means that the removal of PFAS from firefighting foam products would be a desirable outcome.

The compilation of life cycle studies in this report shows the environmental impacts of four firefighting foam products: two AFFF and two fluorine-free, with the exclusion of human and ecotoxicity impacts. The results are presented for comparison between AFFF and F3 foam products with the functional unit designed to reflect relative performance capabilities for each product.

7.19.2. Limitations

The environmental and human toxicity impacts were outside the scope of this study. It is accepted that AFFF products contain compounds which are reported to be persistent, and bioaccumulative, whilst F3 products contain only readily biodegradable compounds. This mode of examination was developed to enable the broader comparison of non-toxicity-related environmental impacts AFFF and F3 products.

Water use data associated with many inventories do not differentiate between different water sources or water quality. This should be remembered when interpreting the findings of the study.

The life cycle inventories for some surfactants were modelled using proxy substances to account for incomplete or unavailable datasets. Instances where proxy data were used are acknowledged within the appropriate in Section 7.14.2 (Raw material manufacture).

In all product LCAs, choices and assumptions were made that could affect the results and to determine the extent of this, a sensitivity analysis was performed. These were product disposal method and product quantity. The results of the sensitivity analysis did not reveal new insights.

Additionally, the functional unit determined for use in this study demonstrates differences in the performance of AFFF and F3 foam products with regard to rate of extinction and control for a standardized fire size. Whilst this has served as a means of deriving a suitable functional unit for this analysis, it should not be interpreted as a true measure of performance during fire response scenarios, with more appropriate fire testing specifications used to determine performance thresholds. Furthermore alternative fuels and pan sizes should come into consideration.

7.19.3. Sources of the environmental impacts

Based on the results of this study, it may be concluded that foam constituent (raw material) acquisition represented the major source of environmental impact for all firefighting foam products.

7.20. Conclusion

This study considered the environmental impacts of four firefighting products: two AFFF and two fluorine-free. This study excluded the human and ecotoxicity impact categories, which, whilst of significant concern, are a difficult point of comparison due to the structural variability within surfactant products and whilst it is widely accepted that PFAS are persistent within the environmental, information remains still limited regarding the extent of environmental impact. Contrastingly, F3 products are composed of entirely readily biodegradable compounds, thus making them non-persistent within the environment.

When examined on a per gallon basis, fluorine-containing fire-fighting foams have greater environmental burdens. This is partly explained by the energy required to form HF, a key intermediate in fluorocarbon synthesis, from its starting material fluorspar. When examined by functional unit, the differences between fluorine-containing and fluorine-free foams are reduced, since fluorine-free foams require greater initial amounts to extinguish the fire, and more frequent reapplication to prevent ignition. Therefore whilst F3 foams appear, in general, to require an increased quantity of product for extinguishment and control of a consistently sized fire, the environmental impact as a function of the functional unit remains comparable.

Thus, once the readily biodegradable status of the F3 product is considered in balance with the persistence of the PFAS contained within AFFF foams, it suggests that the detrimental environmental legacy of firefighting foam products will be significantly reduced.

As the performance of fluorine-free foams continues to improve, and extinguishment quantities reduce, the environmental impact will reduce further.

7.21 Drainage of fluorosurfactants from within an aqueous film-forming foam

To understand the fate of fluorocarbons applied to a hydrocarbon fire, a PFAS analysis method using HPLC-MS qToF has been developed. Control samples and exposed foam have been analyzed to understand which PFAS are formed from 6:2 FtSaB on exposure to fire. This will aid the life cycle analysis by improving our knowledge of the fate of fluorosurfactants used to extinguish a fire

The gravitational drainage dynamics within a simple model aqueous film-forming foam containing a single fluorocarbon surfactant (6:2 FTSaB) were examined through small-scale fire tests from which drainage solution was sampled over regular time intervals. Surfactant concentration within drainage solution was explored using three methodologies: 1) through HPLC-HRqToF-MS analysis of 6:2 FTSaB concentration; 2) analysis of dynamic surface tension; and 3) determination of refractive index.

An aqueous foam is a disordered system and, at the point of use, consists of polyhedral gas bubbles separated by thin liquid films or lamella which are applied to the surface of the burning fuel - forming a foam blanket. This system is out of equilibrium with spatial and temporal liquid distribution governed by fluid dynamics in the foam.[43] The stability of the foam blanket is complex with a number of mechanisms suggested to influence the foam drainage processes: 1) foam drainage by gravitational liquid flow; 2) shear stresses imparted by capillary pressure difference, inducing coarsening by diffusion of gas between bubbles; 3) bubble coalescence caused by the rupture of liquid films between neighboring bubbles. [44-47]

A simple model AFFF foam concentrate was formulated to pass an industry standard fire test (EN1568: Part 3, Figure 7.25) on a heptane fuel.

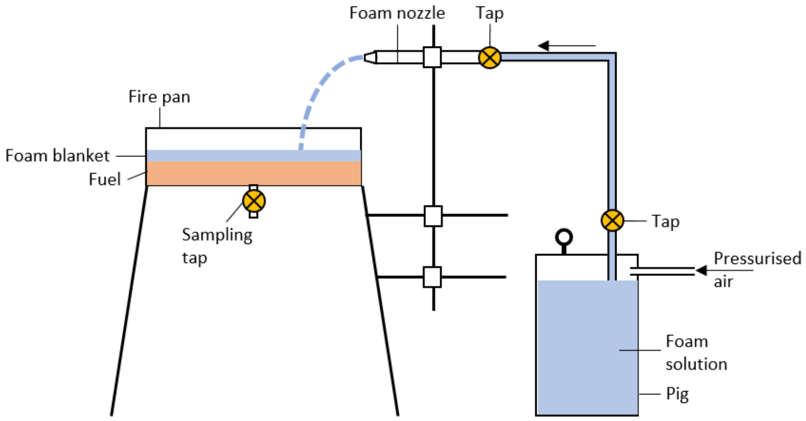

Figure 7.25. Schematic for fire test.

The foam solution was transferred to a steel pig and pressurized to 100 psi. Fire exposure was performed using an adapted EN1568: Part 3 fire test. Heptane fuel (9 L) was added to a 0.25 m^2 stainless steel pan with a conical base and a sampling tap in the center (Figure S1). The heptane fuel was ignited and allowed to burn for 60 seconds prior to beginning foam application. Foam application rate was 700 ± 20 g min^{-1} for 2 minutes 45 seconds.

Following the foam application, drainage solution was sampled from the base of the pan, with all available drainage solution collected at 4-minute intervals for 20 minutes, after which, further samples were collected at 30 and 60 minutes. The fire test was conducted in duplicate, with a further non-fire test performed to provide control values. All sample vessels were cleaned using HPLC-grade methanol; foam generation and capture equipment was cleaned using an acetone (20 %) solution and rinsed using HPW

The foam contained a single commercially-available fluorosurfactant, (6:2 FTSaB) the structure of which is shown in Figure 7.26, extensively used in AFFF products. The model foam also contained hydrocarbon surfactant, solvent and high purity water (18.2 MΩ.cm at 25 ºC) (Table 7.16.). The foam concentrate was proportioned at 3% in high purity water.

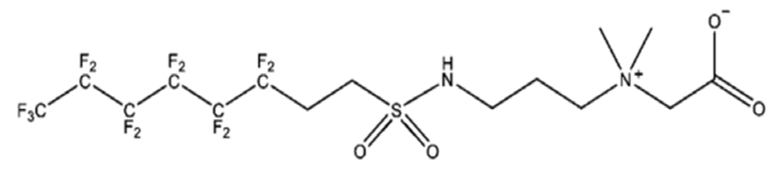

Figure 7.26. Structure of 6:2 FtSaB

Role	Compound	Activity	Conc. (g L^{-1})
Fluorosurfactant	6:2 Fluorotelomer (6:2 FTSaB)	27 %	25.75
Hydrocarbon surfactant	Anionic surfactant	28 %	53.10
Solvent	Glycol ether	-	95.36
Water	High purity water (18. 2 MΩ.cm at 25ºC)	-	825.0

Table 7.16. Composition of model foam concentrate.

The fire test was conducted in duplicate on lit heptane fuel, with a further control test performed on unlit heptane fuel. Foam was applied at a rate of 750 g min^{-1} for 2 min 45 s for all tests. Following the application period, foam was allowed to drain gravimetrically with all drainage solution collected through a tap at the base of the pan at 4 minute intervals for 20 minutes, then at 30 minutes and 60 minutes from the time of extinguishment.

Samples of foam drainage solution were analysed using HPLC-HRqToF-MS to determine the concentration of 6:2 FTSaB within the drainage samples. Any PFAS species found in the spent foam after exposure to fire can only have derived from the initial 6:2 FtSaB.

Prior to analysis, samples were filtered using polyester PET-20/15 15 mm, 0.2 µm pore size Chromofil^{TM} syringe filters and diluted by a factor of 333 using LC/MS grade methanol.

PFAS compounds analysis was conducted using HPLC-HRqToF-MS (instrumental settings are reported in Table 7.17 and an example of the raw data in Figure 7.27). The ESI was operated in both positive and negative instrument modes. Analysis was conducted in full scan mode MS mode.

Parameter		**Detail**
Columns	Guard:	Agilent Zorbex SIL (4.6 x 12.5 mm, 5 µm) and DIOL (4.6 x 12.5 mm, 5 µm)
	Main:	Agilent Zorbex Eclipse Plus C18 (4.6 x 12.5 mm, 5 µm)
Injection volume		20 µL
Mobile phase	Solution A:	Water with 10 mM ammonium acetate
	Solution B:	Methanol with 10 mM ammonium acetate
Elution period	0 to 10 min:	Solution A at 95 % : Solution B at 5 %
	10 – 17 min:	Solution A at 5 % : Solution B at 95 %
	17 – 25 min	Solution A at 95 % : Solution B at 5 %
Column temperature		30 °C
Instrument mode		Both positive and negative runs performed
Needle wash		30 seconds in acetone, directed to waste
Flow rate		0.35 mL min^{-1}

Sheath gas temperature	350 °C
Fragmentor voltage	80 V
VCAP	4000 V
MS-scanning	100 – 1000 m/z

Table 7.17. Operational instrumental parameters for HPLC-HRqToF-MS

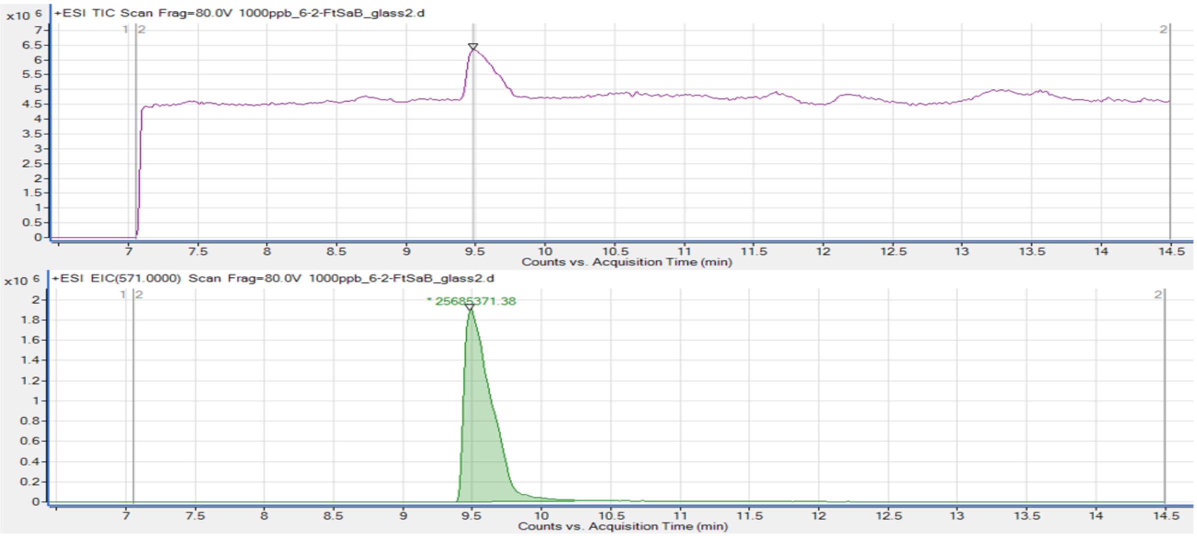

Figure 7.27. Raw HPLC-HRqToF-MS data for 6:2 FTSaB.

The PFAS concentration values for samples under the negative-mode run were determined by normalization against the mass-labelled 6:2 FTS internal standard (50 ng mL-1). All natives were calibrated against the Wellington Laboratories calibration solutions CS1-CS5 (2 – 1000 ng mL-1).

Due to the unavailability of an appropriate positive-mode PFAS calibration solutions, the PFAS concentration values determined using a calibration series prepared from a purified Capstone 1157 derived 6:2 FTSaB (0.1 – 1000 ng mL-1).

The concentration of 6:2 FTSaB within the gravimetrically-sampled drainage solution represents the concentration of fluorosurfactant constituent within the foam, from which the drainage dynamics may be observed (Figure 7.28). The initial rate of gravimetric drainage, approximately 0 to 8 minutes after foam application, was relatively constant for both the control and fire exposed tests, at this point the hydrostatic pressure at the bottom of the foam is greater than the external pressure, resulting in liquid flowing out of the foam. [48,49] From approximately 8 minutes after the foam application, the volume of drainage generated decreased rapidly, suggesting that the remaining foam may be close to a state of hydrostatic equilibrium[6], these findings are supported another study which observed the initial drainage rate for an AFFF to be more rapid.[49]

The 6:2 FTSaB concentration was lower in the initial samples (0 – 12 min) of drainage solution, increasing in concentration with increasing drainage time. This suggests that the fluorosurfactant compounds are retained within the foam blanket.

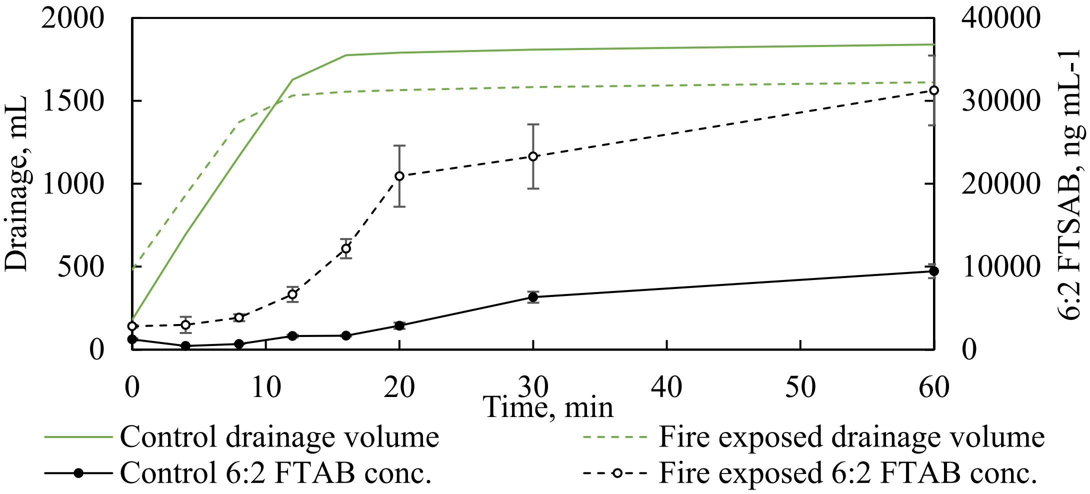

Figure 7.28. Left axis) Cumulative drainage volume for fire-exposed and control tests. **Right axis)** Concentration values of 6:2 FTSAB within time-series sampled foam drainage solution for fire-exposed and control tests. The 6:2 FTSAB analysis was performed using HPLC-HRqToF-MS analysis (n=4).

Fire exposure was observed to have a significant impact on this observation, with the 6:2 FTSAB concentration significantly higher in all. It is proposed that these differences have occurred as a result of increased temperature , which lowers the bulk viscosity of a liquid and has been observed to increase the rate of thinning within the vertical lamellae.[50] Thus, the proportion of foam drained over the 60 minute experimental duration was lower for the control test than the fire exposed test. To further support this, variation in the rates of dynamic surface tension evolution within the time series samples of drainage solution were compared (Figure 7.29). The dynamic surface tension was used as an indicator of surfactant concentration within the drainage samples. An inverse correlation was observed between the concentration of 6:2 FTSaB and the surface tension values at a set time point (20 s) for both the control (r = 0.90) and fire-exposed (r = 0.95) samples (Figure 7.30). This provides further support to show that surfactant concentration within the drainage solution was lower in the early drainage stages compared to later drainage stages.

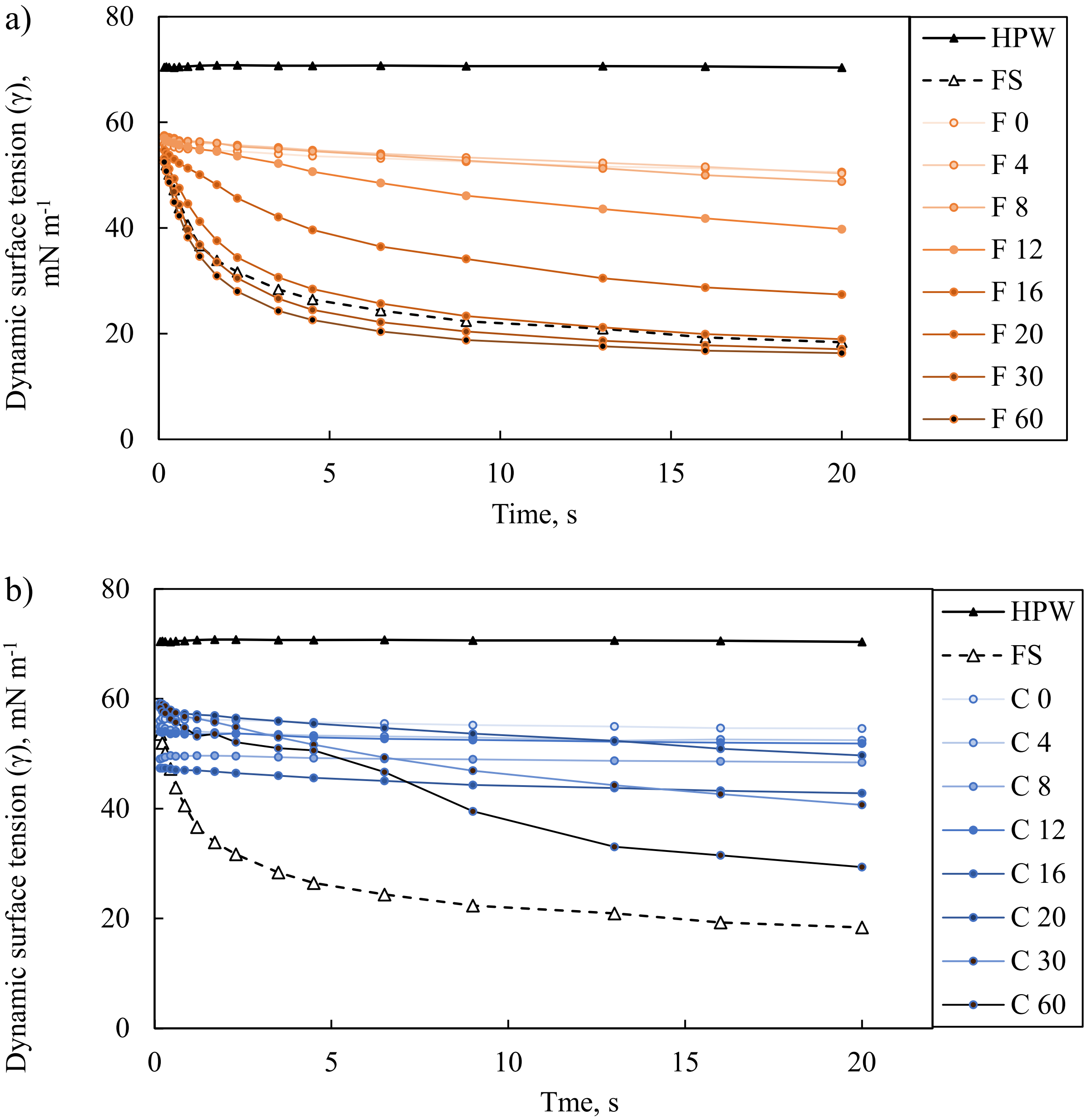

Figure 7.29. Comparison of the dynamic surface tension (γ) evolution for time-series sampled drainage solution taken for a) the fire-exposed foam (F= fire exposed; 0-60 = time sample taken following foam application) and b) the control (non-fire exposed) foam (C = control; 0-60 = time sample taken following foam application). Measurements were performed at 25 °C using a Sita –

Proline 115 bubble pressure tensiometer. FS = foam solution; HPW = high purity water (18.2 MΩ cm^{-1}).

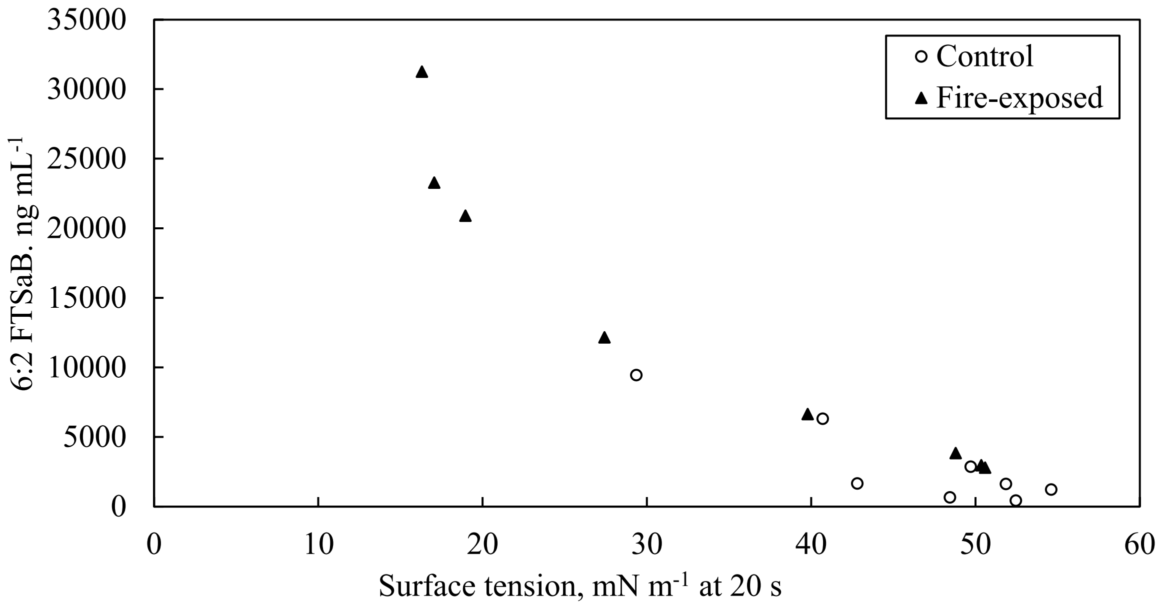

Figure 7.30. Correlation between 6:2 FTSaB concentrations and dynamic surface tension values recorded at 20 s for each drainage sample for the control (r = -0.90) and fire-exposed (r = -0.95) samples.

Whilst drainage of liquid films and foams, coarsening, and coalescence are recognized as the main processes which determine the longevity of a foam, due to the complexities of foam structure, their relative weighting and interactions are difficult to quantify.[47] The non-linear surfactant drainage dynamics exhibited within the presented data highlights a further complexity with regard to the behavior of surfactant foams. It is proposed that bubbles comprising the foam blanket do not have an equal probability of rupture.[50] Therefore, the rate of foam collapse decreases with time, as bubbles with lower stability burst, until those with a higher persistence and higher surfactant content remain.[46]

In terms of the surfactant drainage rate following deployment of a foam, these findings indicate that the retention of surfactant within the foam blanket may contribute to foam performance thereby improving incident response efficacy. Following deployment, the delayed drainage of the surfactant constituent of a foam may allow more time for containment of surfactants, potentially reducing the extent subsequent clean-up processes and lowering environmental impact.

7.22 Biodegradation of fluorine-free foam

The biodegradation of each component of a fluorine-free foam in waste water was measured. It was found that all are readily or inherently biodegradable, on a timescale that is too fast to make intermediate breakdown products a subject of concern.

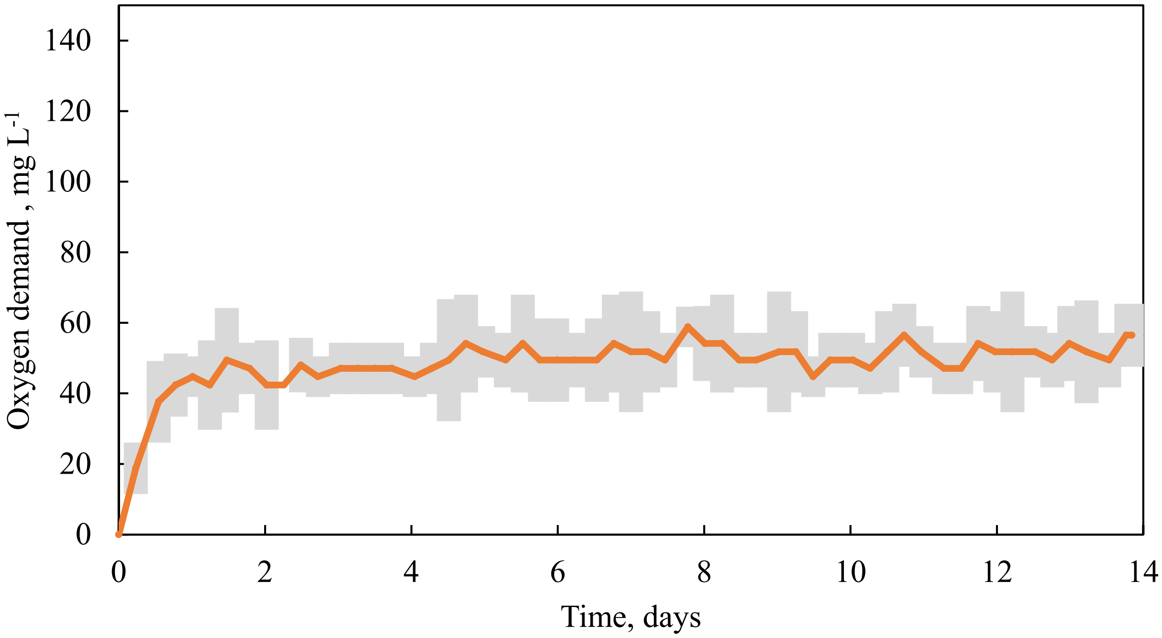

Figure .7.31. BOD for fluorine free formulation in waste water.

The BOD for the F3 foam solution (3%) rapidly reached equilibrium in <2 days, suggesting rapid biodegradation. No gaps in persistence data have been identified that would require additional toxicity testing.

8. Conclusions and Implications for Future Research / Implementation

This project has helped to increase understanding of how the components of a fire-fighting foam formulation determine the physical properties of the foam, and how they in turn affect fire performance. The behavior of surfactants at the air / water interface is critical, as is the role of polymers in the bulk foam solution. There is clearly more work to do in this area, but foam rheology, and foam stability to fuel have been identified as crucial to good fire performance.

Breaking the foam formulation into individual components, and identifying the role of each component has been successful. Primary surfactants generate the foam and contribute to fuel stability and vapor diffusion. Surfactants that diffuse rapidly to a newly formed air/water interface give a high expansion ratio, and close packing at the air/water interface improves foam stability. Secondary surfactants modify foam rheology and drainage rate, and improve fuel stability by adsorbing at the air / water interface more slowly, but giving a more elastic interface. Polymers increase the bulk viscosity of the foam solution, slowing drainage rates, and can also interact with the condensed layer of surfactants changing foam rheology. Foams that have too high a yield stress do not flow well, slowing control of the fire and extinguishment. Solvents improve foam expansion ratio in salt water but increase fuel emulsification.

The project demonstrates that fire-fighting foams developed without the use of fluorocarbon surfactants or polymers can give high levels of fire performance in the standard MIL-PRF 24385F 28 ft^2 fire tests in fresh water on heptane or gasoline fuels. Foam is generated using the standard 2 gallon per minute nozzle with spreader tip and delivered at the normal application rate. These foams can be formulated as 3 or 6 % foam concentrates with flowable characteristics, and can be proportioned using current proportioners. This means the new foams can be employed as drop-in replacements for AFFF without requiring any new or modified hardware.

Extinguishment times of experimental formulations are around 35 seconds on heptane and 65 seconds on gasoline, and further optimization of the formulations and fire-fighting method will reduce these times. Control of 90% of the fire was achieved in 18 seconds on heptane and 26 seconds on gasoline. Burnback times exceed the target of 6 minutes and do not require improvement.

Further research into performance in salt water is required to develop foams for use in sea-based operations. Optimization of performance on gasoline will be required should future specifications require gasoline as test fuel.

Large scale fire performance at lean and rich proportioning and after ageing has not yet been established, although lab scale fire tests suggests some loss of fire performance. Corrosion performance has not been measured, although addition of suitable iron and copper corrosion inhibitors generally satisfies this requirement.

The life cycle analysis has shown that fluorine-free foams can reduce the environmental burdens associated with foam manufacture, and as the performance of these foams continues to improve, this benefit will increase. Short chain fluorocarbons do not appear to transform into either longer or shorter fluorocarbons on exposure to fire. The water draining from fluorosurfactant-based foams is initially highly depleted in fluorocarbon compared to the initial foam solution.

Benefits

This project demonstrates that fire-fighting foams based on hydrocarbon surfactants can deliver fire performance in MIL- PRF 24385F 28ft^2 tests of a similar level to AFFF in fresh water. Foam concentrates can be deployed as drop in replacements for use in existing hardware. This gives confidence that a future MIL- PRF 24385F specification for fluorine-free fire-fighting foams will be deliverable with acceptable levels of fire protection, and that foams will be developed to satisfy that specification.

These new foams will continue to ensure the protection of DoD personnel and assets at airfields and other land-based operations without use of persistent materials and potential long term damage to the environment.

The use of existing components, already used in other industries, gives a rapid and low cost route to deployment without the need for new manufacturing assets or extensive testing of toxicological and environmental properties.

Supporting new formulations with life cycle assessments ensures that the environmental burdens associated with the manufacture and use of fire-fighting foams can be measured and controlled.

Future work

Further development will focus on alternative fuel tolerant additives and materials with vapor suppression characteristics. This will help to improve control of final flickers and final extinguishment time.

The fuel/water interface is worthy of study, and additives that can minimise fuel emulsification on vigorous application of foam to a hydrocarbon fire will be investigated. Prevention of foam destruction by fuel droplets, and retardation of fuel molecules diffusing across the foam interfaces are also required.

Foaming of high salinity aqueous solutions has not been widely reported, although the properties of saline surfactant solutions have been extensively studied for use in enhanced oil recovery to improve flooding of porous oil-bearing rocks. Important properties such as oil entering and spreading coefficients have been reported and give valuable direction to formulating a foam in sea water. Novel surfactants or small molecules that have a high tolerance to salt water will be investigated. Furthermore, work on protein based surfactants will continue as they have shown excellent properties in high salt conditions.

The life cycle analysis should be extended to cover environmental and human toxicology effects. This will also include examining the various metabolites used within each formulation and how they impact each category. Process Mass Intensity (PMI) will be explored as a possible route to monitor changes in formulation species throughout manufacturing and the lifecycle of the product.

Comparisons of the aspects of economic and social aspects of AFFF and F3 will be examined to highlight key differences in the life cycle of each foam type, including manufacturing, use volume, clean up and disposal costs.

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Appendices

Appendix A Supporting data

All relevant data have been included in the main body of the report

Appendix B Publications

SCI poster, A scientific approach to the development of fluorine-free fire-fighting foam, K. Shelbourne and J. Payne, London

Life cycle assessment of MIL-PRF 24385F fire-fighting foam part 1. Investigation of the environmental fate of fluorinated fire-fighting foams. Schofield, Shelbourne, Plant, Joslin, Regina, Payne SERDP Symposium 2017 Washington DC

Transformation of PFAS on exposure to fire in a single-surfactant model AFFF, Schofield, da Costa, Megson, Payne SERDP Symposium 2018, Washington DC

A fluorine-free fire fighting foam that meets the MIL-PRF 24385F fire performance standard. Richardson, Shelbourne, Tinker, Schofield, Joslin, Regina, da Costa, Payne SERDP Symposium 2019, Washington DC

The non-linear gravitational drainage dynamics of fluorinated surfactants within an aqueous film-forming foam, Schofield, da Costa, Megson, submitted for publication to Soft Matter, April 2020.

Appendix C Other

No patent applications have been filed arising from this project

Experimental protocols have been developed for:

- Rheology of foams
- Microscopy of foams in presence of emulsified fuel

These are detailed in Methods and Materials in the body of the report

No awards or honors have been gained