EXECUTIVE SUMMARY

Functional Additives to Enhance PFAS-Free Fire Suppressants

Danielle Nachman
Hadas Elazar-Mittelman
Mary Yates
Johns Hopkins University Applied Physics Laboratory

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ACRONYMS AND ABBREVIATIONS

a.b.u.	arbitrary unit(s)
AFFF	aqueous film forming foam(s)
cm^3	cubic centimeter(s)
COTS	commercial-off-the-shelf
cSt	centistokes
DoD	U.S. Department of Defense
g/cm^3	gram(s) per cubic centimeter
GFFF	GreenFire FireFighting Foam
JHU/APL	Johns Hopkins University Applied Physics Laboratory
NF	National Foam
NRL-CBD	Naval Research Laboratory – Chesapeake Bay Detachment
PFAS	per- and polyfluoroalkyl substances
PFPE	perfluoropolyether
s	second(s)
SERDP	Strategic Environmental Research and Development Program
sq ft	square foot
U.S.	United States
wt%	weight percent

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Finally, thank you to the Weapons Systems and Platforms (WP) support team at Strategic Environmental Research and Development Program (SERDP) for providing guidance as to the project requirements, program needs, and helping to execute an extremely successful limited-scope effort.

1.0 INTRODUCTION

Aqueous film forming foams (AFFF) have traditionally been utilized for suppression of Class B fuel fires, such as gasoline, oil, and jet-fuel, in a variety of applications, but specifically by the U.S. Department of Defense (DoD) on military installations. AFFF are composed of a hydrocarbon-based surfactants and fluorinated surfactants classified as per- and polyfluoroalkyl substances (PFAS). PFAS are extremely effective as surfactants in AFFF for firefighting, as the strong C-F bonds are exceptionally strong, resulting in high heat capacity, resistance to degradation, and high chemical stability. Additionally, their oleophobicity, or lack of affinity for oils, promotes formation of a continuous film over the fuel surface to aid in vapor suppression while their high temperature stability allows for continued performance at high operating temperatures.

Recent studies, however, have determined PFAS to be hazardous to human health and are an environmental chemical of concern. Due to their resilience to degradation, PFAS are considered to be “forever chemicals,” as they persist in environmental systems for very long periods of time. This property allows PFAS to bioaccumulate and remain present in waters that may eventually be used for drinking. Due to the increasing health concerns associated with PFAS, the National Defense Authorization Act has ordered the transition away from PFAS containing AFFF by October 2024.

Several PFAS-free foam formulations have been developed as alternatives to PFAS containing AFFF for fire suppression. While many of these emerging ‘green’ PFAS-free foam formulations on the market show a great deal of promise, there are no PFAS-free firefighting foams that meet the MIL-PRF-24385 for chemical and physical properties, and fire-fighting performance. Due to the urgency of the upcoming transition to only PFAS-free foams by the DoD, it is imperative to find functional additives that can improve the performance of existing PFAS-free formulations. Through this Limited Scope Strategic Environmental Research and Development Program (SERDP) effort, Johns Hopkins University Applied Physics Laboratory (JHU/APL) focused on a time-sensitive approach to identifying commercial-off-the-shelf (COTS) functional additives that could be added to existing PFAS-free foams in order to improve their firefighting performance and provide the DoD with an immediate solution to urgent firefighting needs.

2.0 OBJECTIVES

The goal of the work presented in this report was to identify functional additives to increase the capabilities of commercially available PFAS-free fire-fighting foams with the ultimate objective of matching the capabilities of the legacy AFFF. In accordance with the Statement of Need, the intent was to identify and test functional additives in mature and emerging existing PFAS-free fire suppressants to enhance fire-suppression performance for military use. Due to the urgent need to discover and provide new firefighting foam solutions for the DoD, JHU/APL focused on promising combinations of COTS compounds and additives. JHU/APL, in collaboration with co-performers at Jensen Hughes, assessed the performance, stability, and storability of these foam-additive mixtures to identify combinations with the potential to significantly improve fire suppression. This assessment is a critical step in identifying and prioritizing PFAS-free fire suppression technologies that maintain performance requirements while meeting environmental regulations.

3.0 TECHNICAL APPROACH

The work presented in this report was accomplished through a series of tasks originally outlined in the proposed technical narrative and are as follows:

- Task 1: Identify and enhance PFAS-free concentrate through the introduction of oleophobic compounds.
- Task 2: Identify and characterize selected additive and foam mixtures.
- Task 3: Test small-scale foam extinguishing performance.
- Task 4: Test large-scale fire-fighting performance at Jensen Hughes.
- Task 5: Evaluate storability and compatibility of chemical additives with COTS PFAS-free fire suppressant foam concentrate.

Through Task 1, a literature search was conducted with a focus on (a) identifying existing PFAS-free concentrates for use in testing, and (b) identifying and down-selecting additives for PFAS-free foams to enhance their firefighting ability. Two 'green' PFAS-free foams were ultimately selected for chemical property testing based on expertise from collaborators at Jensen Hughes. These were: GreenFire FireFighting Foam (GFFF) and National Foam (NF) Avio G3 Green KHC. Both the GFFF and NF products are recognized for having reasonable performance by industry standards and had been previously subjected to testing through external and government partners. Both concentrates are designed for use at 3% (i.e., 97% water and 3% concentrate). Additionally, a number of additives were identified for testing based on literature review focusing on previous uses in fire suppression activities, toxicity reports, ease of access to the material, and cost.

In Task 2, additives were tested at various mixtures (i.e., percent by weight of concentrate) in PFAS-free foam solutions to determine their influence on three critical chemical and physical properties that play an important role in overall fire suppression performance: surface tension (spreading coefficient), foam expansion ratio, and viscosity. In addition, these three parameters are laid out in the MIL-PRF-24385 for performance requirements for the firefighting foams. The goal of surface tension measurements was to observe a potential decrease in surface tension with additives present, as this would ultimately indicate an increase in spreading coefficient (a critical value in determining the fire-fighting success of the foam mixture, and based on the equation: $S_{ab} = \gamma_b - \gamma_a - \gamma_i$, where γ_b is the surface tension of the fuel, γ_a is the surface tension of the foam solution, and γ_i is the interfacial tension between the two liquids).

Foam expansion ratio was measured as the volume of a discharged foam relative to the starting liquid volume of the foam solution. Foam was leveled off at the top of a jar, and the mass of the jar plus foam was compared to the mass of the empty jar for the expansion ratio calculation as follows:

$$Foam\ expansion\ ratio = \frac{V\rho}{m_{f-}\ m_i}$$

where V = jar volume (cm^3), ρ = solution density (assumed to be approximately 1 g/cm^3 due to large volume of water), m_f = mass jar + foam, and m_i = mass empty jar. The MIL-PRF 24385 recommends that foam expansion ratio fall above 5, while feedback from co-performers at Jensen Hughes have recommended 7–10 as the ideal range.

Viscosity was measured utilizing capillary viscometers as described in ASTM D445-74. The goal for viscosity, based on the MIL-PRF-24385, was to achieve a value of >3 centistokes (cSt) at temperatures around 25ºC, to enable use by firefighting equipment.

Based on the results from Task 2, additives were down-selected for small-scale fire extinguishing tests in Task 3. The selected additive foam mixtures with GFFF and NF were evaluated for their fire-fighting performance in small-scale testing (Figure ES-1). This testing was accomplished utilizing an outdoor set up with a 9-inch pan. Each foam-additive mixture was prepared by diluting with water to a 3% type solution, and a drill whisk was utilized to create the foam. Both time to extinguish and burnback time were determined for each foam-additive mixture.

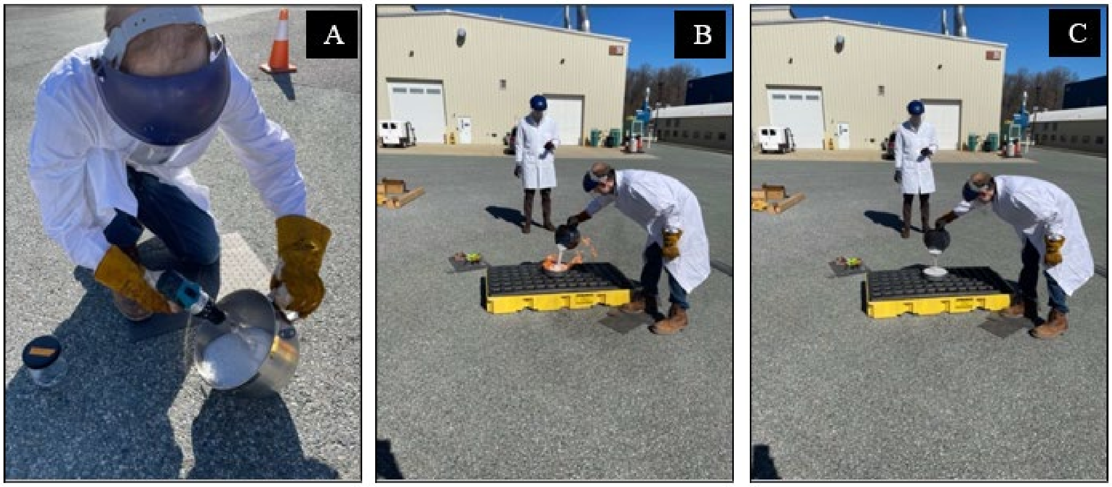

Figure ES-1. Small-scale Fire Testing: (A) Preparation of Foam Mixture, (B) Pouring Foam Mixture Over Fire and Collection of Time to Extinguish, (C) Fire Completely Extinguished by Foam Mixture

Results from small-scale fire testing allowed for further down-selection for Task 4, where fire suppression was evaluated at a larger scale in a 28 square foot (sq ft) pool in collaboration with Jensen Hughes and the Naval Research Laboratory – Chesapeake Bay Detachment (NRL-CBD) facility (Figures ES-2 and ES-3). Six foam-additive mixtures were chosen for larger-scale testing along with the two control tests for GFFF and NF. All were assessed for time to extinguish and burnback time required for reintroduced fire to spread over the extinguished pan, defined per military standards.

Figure ES-2. Ignited Fuel in 28 sq ft Pan and Application of Foam-additive Mixture

Figure ES-3. Extinguished Fire

Finally, in Task 5, the additive foam mixtures that were selected for larger-scale fire testing were assessed for their storability and compatibility in order to determine the stability of the foam-additive if they are to be stored over longer periods of time. Stability testing was performed as described in the MIL-PRF-24385 by placing the foam-additive mixtures in a vacuum oven set at 65ºC for a period of 10 days. Following this accelerated aging period, the foams were re-assessed for surface tension, foam expansion ratio, and viscosity as previously described.

4.0 RESULTS AND DISCUSSION

A number of additives were identified for potential testing (Table ES-1) based on their typical uses and previous use in fire suppression activities. The additives were categorized as high (green), medium (yellow), and low (red) priority based on toxicity reports, ease of access to the material, and cost.

Table ES-1. List of Potential Additives for PFAS-free Foam Concentrates

	Uses/Reasoning
Non-Fluorinated Analogues*	
🟩 1-dodecanol	Foaming agent, emulsifier
🟩 1-octanol	Viscosity controller
🟨 Octanoic acid	Hydrophobic, film forming
🟨 Octane-1-sulfonic acid	Foaming agent
🟨 Dodecanoic acid	Freezing point depressor, surface active agent
🟨 Dodecane-1-sulfonic acid	Ion-associating reagent
Green Alternatives	
🟩 Biochars[1–4]	Edge testing, research indicates as good fire retardant, phosphorus research shows that production of char suffocates fire
🟨 Baking soda (sodium bicarbonate)[5–8]	Large quantity needed to put out larger scale fires; has been shown to improve extinguishing efficiency in powder form
🟩 Siloxanes[9–12]	Promising results when used in AFFF as PFAS replacement
🟩 Silica aerogels[13–15]	Phenolic silica aerogels are great fire retardants: low thermal degradation, low heat release rate, retain structure for extended time periods at >1000ºC temperatures
🟩 Phosphates[16–18]	RDP; super-effective flame-retardant additive
🟥 Betaine compounds	Insufficient information found
🟥 Oleophobic coatings[19,20]	Most oleophobic coatings contain PFAS, PFPE (surfactis, aculon)
🟩 Magnesium oxide (dolomite)[21–23]	Has been used as a flame retardant and smoke suppressor

*Information on Non-Fluorinated Analogues collected from SDS.

The following chemicals were obtained for testing as functional additives for the PFAS-free foams: 1-dodecanol, 1-octanol, octanoic acid, octane-1-sulfonic acid, dodecanoic acid, dodecane-1-sulfonic acid, siloxane, RDP, biochar, magnesium oxide, and baking soda (sodium bicarbonate).

In Task 2, the observations for surface tension indicated that several additives improved surface tension of the GFFF solution by lowering the surface tension value calculated (e.g., dodecanoic acid, biochar, octanoic acid, and octanol), while some additives had no improvement or displayed worse performance (e.g., dodecanol, baking soda, dodecanesulfonic acid, RDP, and magnesium oxide). In general, liquid additives performed better in improving surface tension than solid additives, which may be a result of more homogenous mixing with the liquid additives and the difficulty of some solid additives to completely dissolve in solution. Additionally, in almost all cases, 1 weight percent (wt%) loading of additive was not significant enough to impact surface tension values. The surface tension results for the best performing mixtures are shown in Figure ES-4.

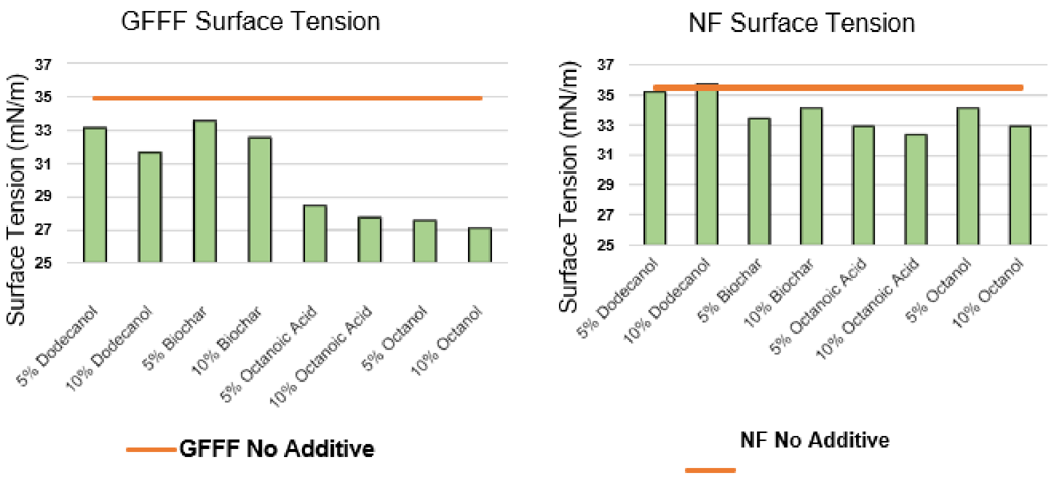

Figure ES-4. Surface Tension Measurements for GFFF and NF at 3% With Various Additives

Overall, dodecanol, biochar, octanoic acid, and octanol showed the most promising results with various wt% additive mixtures for GFFF, with octanoic acid and octanol showing the best performance in reducing surface tension. This was similarly the case for NF, however, dodecanol did not improve surface tension measurements. Additionally, all additives that improved surface tension had a more significant impact on GFFF when compared with NF, with a higher percentage decrease in surface tension value. These were also the additive mixtures down-selected for small-scale fire testing.

In the case of foam expansion ratio results, several additives increased the foam expansion ratio with increasing wt% additive in solution. The foam expansion ratio results for the best performing mixtures are shown in Figure ES-5.

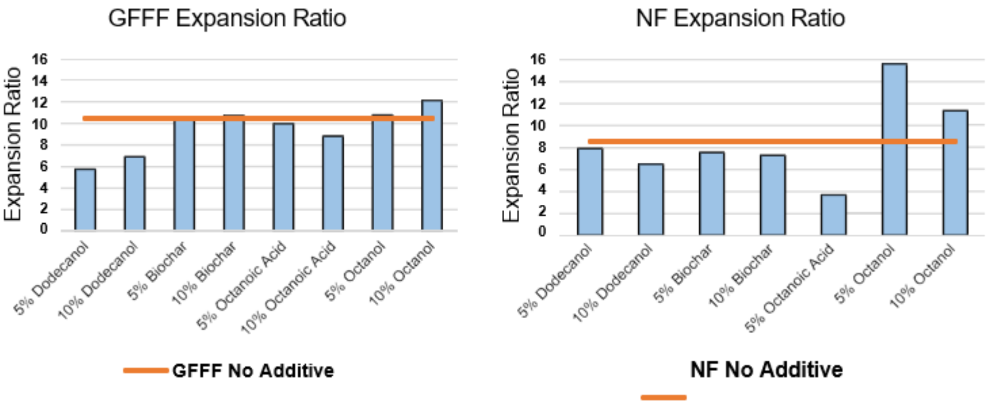

Figure ES-5. Foam Expansion Ratio Measurements for GFFF at 3% With Various Additives

For GFFF, most additives did not significantly influence foam expansion ratio and maintained foam expansion ratio near that of the baseline GFFF. The exception was dodecanol, which significantly reduced foam expansion ratio below the preferred performance range of 7–10 arbitrary units (a.b.u.) advised by Jensen Hughes (though all maintained above the MIL-PRF-24385 requirement of 5 a.b.u.). In the case of NF, dodecanol and biochar maintained the foam expansion ratio near that of the NF with no additive, however octanoic acid significantly reduced foam expansion ratio to below the MIL-PRF-24385 requirement. Additionally, octanol significantly increased the foam expansion ratio to well above 10 a.b.u.

Most additives did not have a significant influence on viscosity; however, octanol increased viscosity to nearly 2.5 cSt. The viscosity results for the best performing mixtures are shown in Figure ES-6.

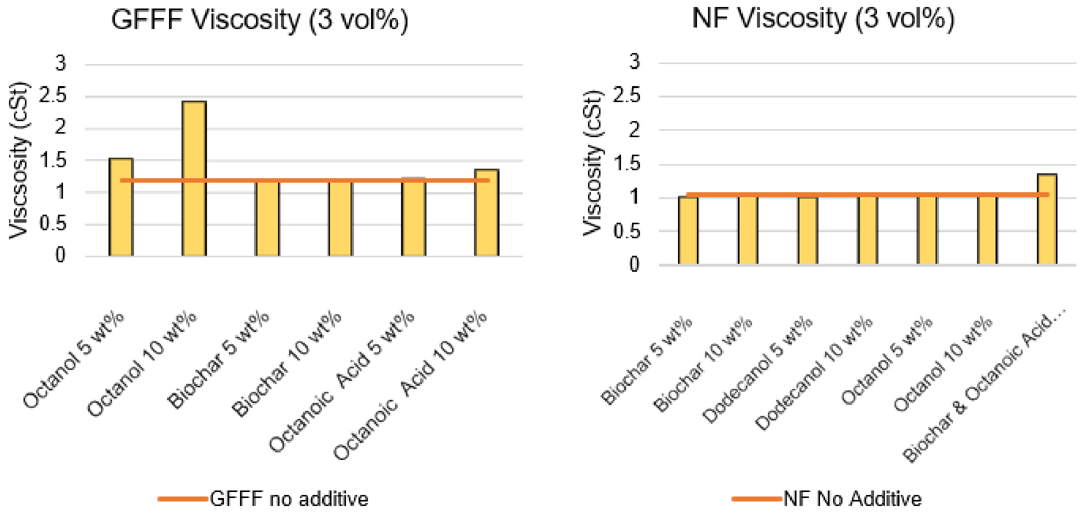

Figure ES-6. Viscosity Measurements for GFFF at 3% With Various Additives

Results of viscosity testing for GFFF indicated that octanol at either 5 or 10 wt% had the most profound impact on increasing the viscosity. In the case of 10 wt%, viscosity was increased to 2.43 cSt, which meets the requirements in the MIL-PRF-24385. Octanoic acid at 10 wt% also indicated some improvement for viscosity relative to the GFFF baseline, but viscosity remained consistent with the GFFF baseline in all other cases. Similarly, in the case of NF, most additives had no impact on viscosity, except in the case of the mixture of biochar and octanoic acid both at 5 wt%. This was intriguing, as it indicated that varied ratios of additives mixed together might have different influences on chemical and physical properties compared with single additive mixtures.

Based on results from Task 2, a number of foam additive mixtures were selected for small-scale fire testing. The most promising results of the small-scale fire-testing that were used for down-selection for larger-scale testing are presented in Tables ES-2 (GFFF) and ES-3 (NF):

Table ES-2. Time to Extinguish and Burnback Time for GFFF in Small-scale Fire Tests

Mixture	Time to Extinguish (seconds [s])	Burnback Time (s)
GFFF	13.0	107.5
GFFF	10.9	67.2
5% octanol	5.9	73.7
5% octanol	6.9	97.0
10% octanol	7.93	116.5
10% octanol	17.5	130.6
5% biochar, 5% octanol	10.5	89.1
10% biochar, 10% octanol	9.9	94.2

Table ES-3. Time to Extinguish and Burnback Time for NF in Small-scale Fire Tests

Mixture	Time to Extinguish (s)	Burnback Time (s)
NF 3%	2.7	199.1
NF 3%	3.2	129.4
5% biochar	7.4	199.9
5% biochar	4.0	129.4
10% biochar	5.8	124.6
10% biochar	4.8	199.1
5% biochar, 5% octanoic acid	5.6	206.8

Results of the small-scale fire testing indicated that in the case of GFFF, **only octanol improved time to extinguish significantly, reducing the time by nearly half**. All other additives had no effect of performance. Additionally, octanol improved the burnback time relative to the GFFF without additive. For this reason, this mixture was chosen for larger-scale testing. In the case of NF, the time to extinguish was already quite low for the NF without additives, however, a number of additives significantly improved the burnback time, including biochar and octanoic acid (5%) (and the mixture of these two additives). As such, these additives were also chosen for larger-scale fire testing. An interesting note was that octanoic acid at 10% in NF seemed to completely destroy the mixture's ability to create a foam. This mixture may be an interesting comparison for future work to look into molecular properties that may influence the firefighting performance and can provide insight as to chemical mixtures that do not work for firefighting compared with those that do.

Based on the results from Task 3, six foam-additive mixtures were chosen for larger-scale testing along with the two control tests for GFFF and NF. The results of the larger-scale fire testing are presented in Table ES-4.

Table ES-4. Time to Extinguish and Burnback Time for Larger-scale Fire Tests

Concentrate	Additive	Time to Extinguish (s)	Burnback Time (s)
GFFF	N/A	95	42
GFFF	5% Octanol	**70**	**183**
GFFF	10% Octanol	87	90
GFFF	5% Biochar 5% Octanol	88	46
NF	N/A	49	260
NF	5% Octanoic Acid	Did not extinguish	n/a
NF	5% Biochar	50	270
NF	10% Biochar	**43**	**300**

Results of the larger-scale fire testing confirmed that certain additive-foam mixtures improved the time to extinguish the fire and burnback time. The most notable influence on extinguishment time was the GFFF with 5% octanol. This mixture extinguishment time was 70 seconds (s), which was 25 s faster than GFFF alone. This is a significant improvement over the baseline of 95 s for GFFF. Additionally, this additive **improved the burnback time by more than four-fold**, from 42 s for the baseline GFFF to 183 s, which is much closer to approaching the required burnback time of 360 s in the MIL-PRF-24385. Interestingly, the 10% octanol solution in GFFF had a slight improvement for extinguishment time and a two-fold improvement in burnback time but did not achieve the same level of improvement observed with the 5% octanol solution in GFFF. Additionally, octanol was the additive that had the most significant improvement on both surface tension and viscosity values for GFFF, further indicating that there is a potential correlation between these properties and fire-fighting performance.

For NF, the 5% biochar NF mixture did not improve the extinguishment time, however, the 10% biochar NF mixture did improve extinguishment time by 6 s (43 s versus 49 s). Additionally, the 10% biochar improved the burnback time by 40 s from 260 s to 300 s. This indicates that biochar is a very promising additive for some PFAS-free foams and has the additional benefit of being a less toxic and more environmentally friendly alternative to some of the other additives tested. Biochar was also the additive that had one of the more significant impacts on surface tension and viscosity, again indicating a potential correlation between these properties and fire-fighting performance. The 5% octanoic acid NF mixture did not extinguish the fire and was observed in both the small- and larger-scale testing that octanoic acid in some cases destroyed the mixture's ability to foam.

The additive mixtures that were selected for larger-scale fire testing were also assessed for their long-term compatibility and storability under accelerated aging conditions. Results for GFFF indicated that for both 5 and 10 wt% octanol, foam-additive solutions were negatively affected by the aging process, resulting in an overall increase in surface tension, decrease in foam expansion ratio, and decrease in viscosity. This performance was in line with the control GFFF, where chemical and physical properties were negatively affected following accelerated aging. In the case of NF, however, biochar at both 5 and 10 wt% generally improved all the tested properties with little change or further decrease in surface tension, increase in foam expansion ratio, and little change or further increase in viscosity. These changes also followed trends observed in the control NF stock solution pre-and post-stability aging testing. This was significant, as it showed that biochar was particularly compatible with NF, and biochar did not affect long-term stability of the foam concentrate, showing that **biochar is an exceptionally promising additive** in PFAS-free foam solutions. Not only can biochar improve fire suppression, it is an eco-friendly, non-toxic alternative to PFAS for firefighting foams.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

The experimental effort described in this report demonstrated that the fire-fighting capabilities of PFAS-free foams can be enhanced by adding COTS chemicals. In particular, octanol and biochar were determined to improve overall firefighting performance in time to extinguish a gasoline fire and in burnback time of two different PFAS-free foams, GFFF and NF, respectively. Additionally, chemical and physical property testing often correlated well with fire suppression testing and could possibly be used to predict fire-fighting capabilities of future mixtures/formulations. These COTS additives, octanol and biochar, both provide a more eco-friendly, more easily degradable, and reduced toxicity alternative to PFAS[1–3] and may be a time-sensitive solution to respond to the urgent need by the DoD to procure PFAS-free firefighting foams that at least meet the requirements laid out in MIL-PRF-32725 and ideally meet the requirements in MIL-PRF-24385.

The experimentation and successful results of this study will help to identify a path forward for PFAS-free fire suppressants that maintain or improve the performance of current PFAS-free foams. To date, the PFAS-free foams available do not match the performance of legacy AFFF. The easily accessible, cost-effective, and more health friendly additives assessed in this study have the potential to narrow this gap while increasing the pool of candidates of MIL-PRF-32725.

The next steps for this work will involve utilization of JHU/APL expertise in molecular scale material and chemical properties modeling in order to assess and predict large scale firefighting performance in a wider variety of related additive analogues and PFAS-free firefighting foams. The objective of this work will be to utilize the successful experimental results gained during the Limited Scope portion of this work to determine an ideal additive mixture, which may involve multiple additives, that can achieve chemical and physical properties and superior fire suppression results.

The potential of this approach has been demonstrated, and the project team expects to achieve even greater performance in future efforts by assessing other chemical additives, optimizing capabilities/mixtures, performing parametric assessments to further understand the relation between physical properties and performance, and developing predictive tools using these parameters. Additional challenges to firefighting conditions such as fuel mixes, saltwater, and temperature could be considered. Partnerships with green foam developers could accelerate analysis and enable better targeting of solutions with the potential to scale and deploy rapidly.

The benefits of both the work to date and potential follow-on work is to demonstrate pathways for COTS additives and novel related analogues to be incorporated into future emerging PFAS-free firefighting foam formulations.

6.0 LITERATURE CITED

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