

FINAL REPORT

Functional Additives to Enhance PFAS-Free Fire Suppressants

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April 2023

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|--|-------------|--------------------------------------|-------------------------------|--|---|--|
| REPORT DOCUMENTATION PAGE | | | | | Form Approved OMB No. 0704-0188 | |
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| 1. REPORT DATE (DD-MM-YYYY) 28/04/2023 | | 2. REPORT TYPE SERDP Final Report | | | 3. DATES COVERED (From - To) 4/28/2022 - 4/28/2025 | |
| 4. TITLE AND SUBTITLE Functional Additives to Enhance PFAS-Free Fire Suppressants | | | | 5a. CONTRACT NUMBER 22-P-0049 | | |
| | | | | 5b. GRANT NUMBER | | |
| | | | | 5c. PROGRAM ELEMENT NUMBER | | |
| 6. AUTHOR(S) Danielle Schlesinger Hadas Elazar-Mittelman Mary Yates | | | | 5d. PROJECT NUMBER WP22-3284 | | |
| | | | | 5e. TASK NUMBER | | |
| | | | | 5f. WORK UNIT NUMBER | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Johns Hopkins University Applied Physics Lab Office 21-N220 Laurel, MD 20723 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER WP22-3284 | | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of the Deputy Assistant Secretary of Defense (Energy Resilience & Optimization) 3500 Defense Pentagon, RM 5C646 Washington, DC 20301-3500 | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) SERDP | | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) WP22-3284 | | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited. | | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | | |
| 14. ABSTRACT The objective of the work described in this report was to identify and experimentally test functional additives for per- and polyfluoroalkyl substance (PFAS)-free fire-fighting foams in order to improve the physical properties and fire-fighting capabilities of the foam. PFAS are a common ingredient in aqueous film-forming foams (AFFF) due to their oleophobic properties and stability at elevated temperatures, but are being banned due to both environmental and health concerns. The National Defense Authorization Act (NDAA) has ordered the phaseout of PFAS containing AFFF at U.S military facilities by 2024, however, none of the currently available PFAS-free formulations can meet the requirements laid out in the MIL-PRF-24385. To this end, the Johns Hopkins University Applied Physics Laboratory (JHU/APL) worked to determine readily-available additives that can act to enhance the firefighting capabilities of mature (i.e., commercially available) and emerging PFAS-free fire suppressants for military use. | | | | | | |
| 15. SUBJECT TERMS Per/Polyfluoroalkyl substances, aqueous film forming foams, firefighting foams, PFAS-free firefighting foams, functional additives, fire suppression, green chemical | | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON | |
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Danielle Schlesinger | |
| UNCLASS | UNCLASS | UNCLASS | UNCLASS | 59 | 19b. TELEPHONE NUMBER (Include area code) 240-592-5243 | |

Table of Contents

| | |
|---|-----|
| List of Tables | ii |
| List of Figures | iii |
| List of Acronyms | v |
| Keywords | vi |
| Acknowledgements..... | vii |
| 1 Abstract | 1 |
| 2 Executive Summary | 2 |
| 3 Objective | 12 |
| 4 Background | 13 |
| 5 Materials and Methods..... | 14 |
| 6 Results and Discussion | 19 |
| 7 Conclusions and Implications for Future Research | 34 |
| Literature Cited | 38 |
| Appendix A – Surface Tension Data | 43 |
| Appendix B – Foam Expansion Ratio Data | 45 |
| Appendix C – Viscosity Data | 47 |
| Appendix D – JHU/APL Transmittal Letter..... | 48 |

List of Tables

Executive Summary

| | |
|---|-------|
| Table 1: List of potential additives for PFAS-free foam concentrates. | pp. 5 |
| Table 2: Time to extinguish and burnback time for GFFF in small-scale fire tests. | pp. 8 |
| Table 3: Time to extinguish and burnback time for NF in small-scale fire tests. | pp. 9 |
| Table 4: Time to extinguish and burnback time determined for larger-scale fire tests. | pp. 9 |

Full Report

| | |
|--|-----------|
| Table 1: Categories of additive with potential compounds of interest based on preliminary literature review | pp. 19-20 |
| Table 2: List of potential additives for PFAS-free foam concentrates. | pp. 20-21 |
| Table 3: Base values for surface tension, foam expansion ratio, and viscosity for the two PFAS-free foams with no additives. | pp. 21 |
| Table 4: Time to extinguish and burnback time for GFFF in small-scale fire tests | pp. 26-27 |
| Table 5: Time to extinguish and burnback time for NF in small-scale fire tests. | pp. 27 |
| Table 6: Time to extinguish and burnback time determined for larger-scale fire tests. | pp. 28 |

List of Figures

Executive Summary

| | |
|---|-------|
| Figure 1: Small-scale fire testing | pp. 4 |
| Figure 2: Ignited fuel in 28 sq ft pan and application of foam-additive mixture | pp. 4 |
| Figure 3: Extinguished fire | pp. 5 |
| Figure 4: Surface tension measurements for GFFF and NF at 3% with various additives | pp. 6 |
| Figure 5: Foam expansion ratio measurements for GFFF at 3% with various additives. | pp. 7 |
| Figure 6: Viscosity measurements for GFFF at 3% with various additives | pp. 8 |

Full Report

| | |
|--|--------|
| Figure 1: Structures of PFOS and PFOA | pp. 13 |
| Figure 2: Kibron Aqua Pi Tensiometer | pp. 14 |
| Figure 3: Foam expansion ratio testing | pp. 15 |
| Figure 4: Capillary viscometer used for viscosity measurements | pp. 15 |
| Figure 5: Small-scale fire testing | pp. 16 |
| Figure 6: Preparation of the foam solution | pp. 17 |
| Figure 7: Ignited fuel in 28 sq ft pan and application of foam-additive mixture | pp. 17 |
| Figure 8: Extinguished fire | pp. 18 |
| Figure 9: Burnback testing | pp. 18 |
| Figure 10: Surface tension measurements for GFFF at 3% with various additives | pp. 22 |
| Figure 11: Surface tension measurements for NF at 3% with various additives | pp. 23 |
| Figure 12: Foam expansion ratio measurements for GFFF at 3% with various additives | pp. 24 |
| Figure 13: Foam expansion ratio measurements for NF at 3% with various additives | pp. 24 |
| Figure 14: Viscosity measurements for GFFF at 3% with various additives | pp. 25 |

| | |
|--|--------|
| Figure 15: Viscosity measurements for NF at 3% with various additives | pp. 26 |
| Figure 16: Comparison of surface tension in GFFF pre-stability testing and post-stability testing | pp. 29 |
| Figure 17: Comparison of surface tension in NF pre-stability testing and post-stability testing | pp. 30 |
| Figure 18: Comparison of foam expansion ratio in GFFF pre-stability testing and post-stability testing | pp. 30 |
| Figure 19: Comparison of foam expansion ratio in NF pre-stability testing and post-stability testing | pp. 31 |
| Figure 20: Comparison of viscosity in GFFF pre-stability testing and post-stability testing | pp. 32 |
| Figure 21: Comparison of viscosity in GFFF pre-stability testing and post-stability testing | pp. 32 |

List of Acronyms

| | |
|---------|--|
| a.b.u. | Arbitrary units |
| AFFF | Aqueous Film Forming Foam |
| CAS | Chemical Abstracts Service |
| CBD | Chesapeake Bay Detachment |
| COTS | Commercial-Off-The-Shelf |
| cSt | Centistokes |
| DoD | Department of Defense |
| FTIR | Fourier-Transform Infrared |
| GFFF | Greenfire Firefighting Foam |
| HRMS | High-Resolution Mass Spectrometry |
| JHU/APL | Johns Hopkins University Applied Physics Laboratory |
| L | Liter |
| NDAA | National Defense Authorization Act |
| NF | National Foams |
| NMR | Nuclear Magnetic Resonance |
| NRL | Naval Research Laboratory |
| PFAS | Per/Polyfluoroalkyl substances |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctanesulfonic acid |
| RDP | Resorcinol bis(diphenyl phosphate) |
| SERDP | Strategic Environmental Research and Development Program |
| SDS | Safety Data Sheet |
| SON | Statement of Need |
| wt % | Weight Percent |

Keywords

Per/Polyfluoroalkyl substances, aqueous film forming foams, firefighting foams, PFAS-free firefighting foams, functional additives, fire suppression, green chemical

Acknowledgements

The work presented in this report was largely conducted by JHU/APL staff members: Matthew Sweeney, Collin McDermott, and Melanie Kowalski. Thank you to all three of them for their immensely hard work and enthusiasm for the objectives and critical challenges associated with this effort. Thank you to the program team at JHU/APL, including Marisa Hughes, Sarah Herman, Sarah Christoff, and Taylor Long, for executing the programmatic needs of this project, providing constructive support, and monitoring of finances.

Thank you, additionally, to our collaborator and subcontractor, Jerry Back with Jensen Hughes, for providing immensely useful feedback throughout the performance period and for putting together the larger-scale fire testing efforts.

Thank you to the team at NRL-CBD, including John Farley and Stan Karwoski, for implementing our foam-additive mixtures in larger-scale fire testing, helping to collect important data, and providing abundant expertise in firefighting performance.

Finally, thank you to the WP support team at SERDP for providing guidance as to the project requirements, program needs, and helping to execute an extremely successful limited scope effort!

1 Abstract

Introduction and Objectives. The objective of the work described in this report was to identify and experimentally test functional additives for per- and polyfluoroalkyl substance (PFAS)-free fire-fighting foams in order to improve the physical properties and fire-fighting capabilities of the foam. PFAS are a common ingredient in aqueous film-forming foams (AFFF) due to their oleophobic properties and stability at elevated temperatures, but are being banned due to both environmental and health concerns. The National Defense Authorization Act (NDAA) has ordered the phaseout of PFAS containing AFFF at U.S military facilities by 2024, however, none of the currently available PFAS-free formulations can meet the requirements laid out in the MIL-PRF-24385. To this end, the Johns Hopkins University Applied Physics Laboratory (JHU/APL) worked to determine readily-available additives that can act to enhance the firefighting capabilities of mature (i.e., commercially available) and emerging PFAS-free fire suppressants for military use.

Technical Approach. Functional additives were selected based on an extensive literature review to assess their potential to improve physical properties critical to fire-fighting performance, including surface tension, foam expansion ratio, and viscosity. Key criteria were utilized to further down-select additives for testing, including prior use in fire-fighting formulations, cost, reduced toxicity, and environmental hazard. Physical property testing was conducted at various mixtures of additives and PFAS-free fire-fighting concentrates. Those with the most significant improvement on surface tension and viscosity were selected for fire-suppression testing. Small-scale fire suppression testing was conducted at JHU/APL to assess extinguish and burnback times in comparison with the PFAS-free foams with no additives. The foam-additive mixtures with the best performance were selected for larger -scale 28 ft² fire suppression testing conducted in collaboration with Jensen Hughes.

Results. For the two PFAS-free firefighting foams tested in this study, Greenfire GFFF and National Foam (NF) Avio F3 Green KHC, it was determined that four of the functional additives consistently altered and improved the foam solution physical properties most critical to fire suppression performance. These four additives were octanol, biochar, octanoic acid, and dodecanol. In particular, octanol was found to be the best performing additive, capable of both reducing surface tension of the foam solution and controlling viscosity. Results of the small-scale and larger-scale fire testing indicated an improvement in fire-fighting performance by both octanol and biochar in GFFF and NF, respectively, for both time to extinguish and burnback time, improving to nearly the requirements set out in the MIL-PRF-24385. Octanol added at 5% by weight ultimately improved time to extinguish in GFFF by 25 seconds and improved burnback time by 141 seconds, and biochar at 10 % by weight improved NF time to extinguish by 7 seconds and burnback time by 30 seconds. It was also observed that some additives, such as octanoic acid, completely destroyed the foam solution's fire suppression ability, indicating that molecular scale interactions of additives in the foam solutions can have a dramatic effect on fire suppression capability. More work can be done to better characterize these interactions and produce better performing firefighting foams.

Benefits. The work conducted in this study provides a basis for further development and assessment of additives to enhance performance of commercially available PFAS-free foams with the ultimate object of equaling the capabilities of legacy AFFF. Additional work to further characterize the successful additives tested, and related modified additives based on these results, is a critical next step in understanding the molecular basis for why these additives improve fire suppression and to optimize foam solution mixture ratios for military performance requirements. Building on this exploration, JHU/APL's industry partners can help to conduct further testing and assess scalable production methods in order to transition to use of novel additive mixtures that can supplant PFAS containing AFFF. This transition is essential due to the identified risks of PFAS, including persistence in the environment, bioaccumulation, and toxic human health effects.

2 Executive Summary

Introduction Section. 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 US Department of Defense (DoD) on military installations. AFFF are composed of a hydrocarbon-based surfactants and fluorinated surfactants classified as per/poly-fluoroalkyl 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 contaminant. 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 NDAA 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, 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.

Objectives Section. 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 (SON), 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 commercial-off-the-shelf (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.

Technical Approach Section. 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: PFAS-free concentrate identification and enhancement through the introduction of oleophobic compounds

Task 2: Identify and characterize selected additive and foam mixtures

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Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

Task 3: Small-scale testing of foam extinguishing performance

Task 4: Fire-fighting performance large scale testing 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 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 will 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:

$$\text{Foam expansion ratio} = \frac{V\rho}{m_f - m_i}$$

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 25°C , 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 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,

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Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
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and a drill whisk was utilized to create the foam. Both time to extinguish and burnback time were determined for each foam-additive mixture.

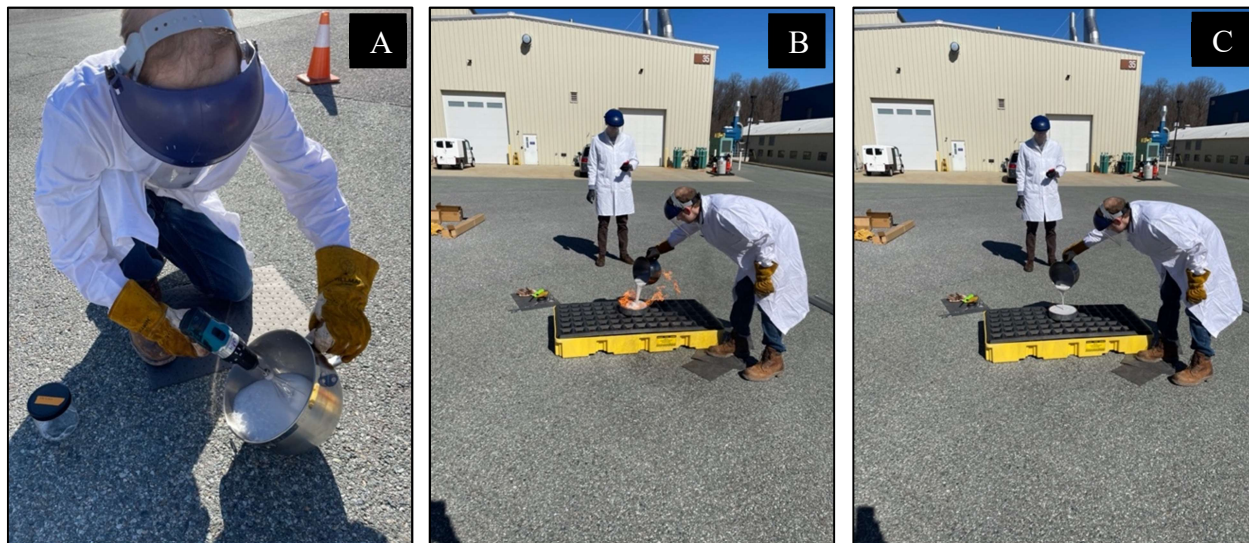


Figure 1: Small-scale fire testing: A) Preparation of foam mixture; B) Pouring foam mixture over fire and collection of time to extinguish; C) Fire completely extinguished by foam mixture.

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 ft² pool in collaboration with Jensen Hughes and the Naval Research Laboratory (NRL) – Chesapeake Bay Detachment (CBD) facility (Figures 2-3). 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 2: Ignited fuel in 28 sq ft pan and application of foam-additive mixture.

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Proposal #WP22-C2-3284



Figure 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 65°C 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.

Results and Discussion Section. A number of additives were identified for potential testing (Table 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 1: List of potential additives for PFAS-free foam concentrates.

| Non-Fluorinated Analogues* | Uses/Reasoning |
|---|--|
| 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 | Uses/Reasoning |
| 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 |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

| | |
|---|---|
| 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 >1000 deg C temps |
| 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 shown in Figure 4.

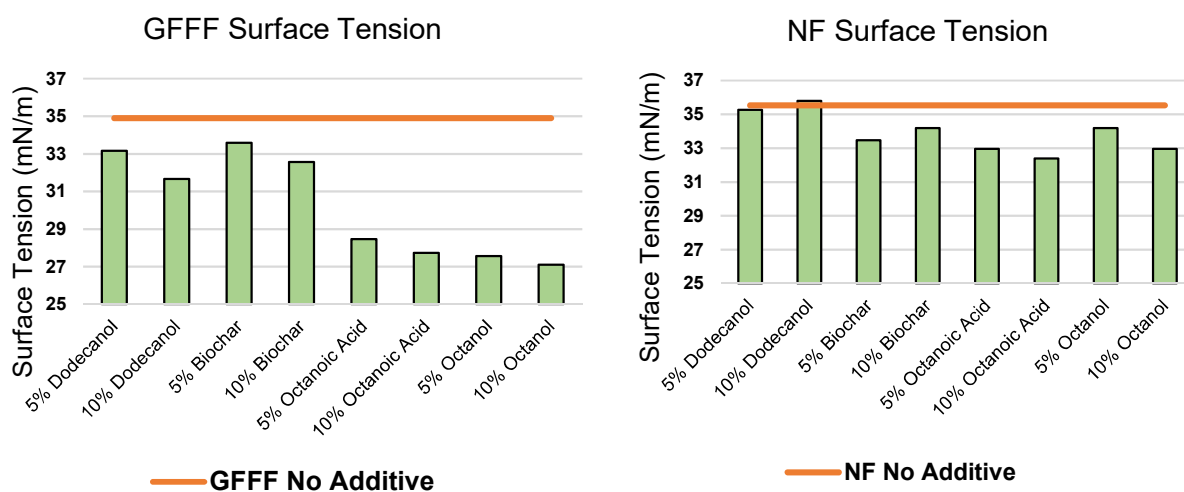


Figure 4: Surface tension measurements for GFFF and NF at 3% with various additives.

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

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 5.

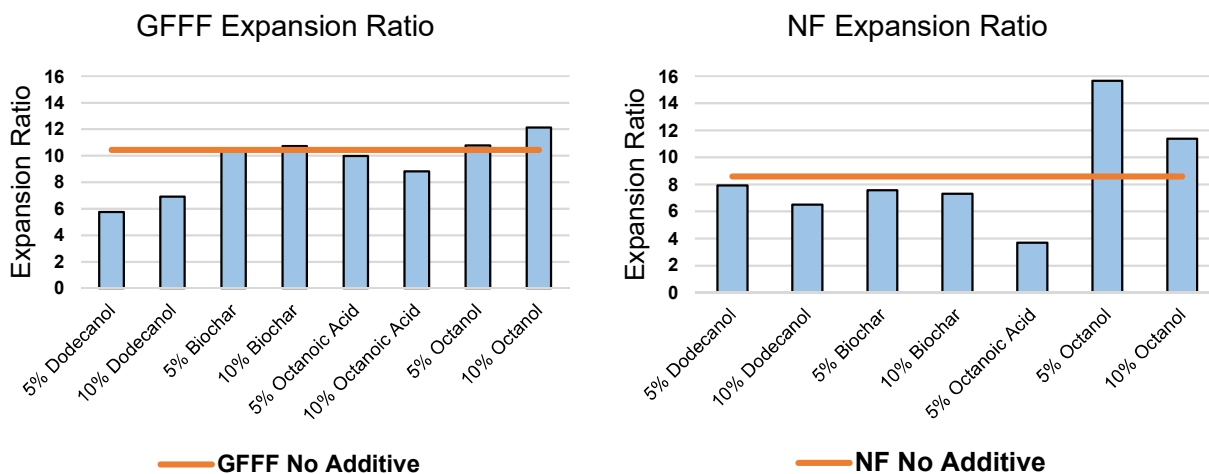


Figure 5: Foam expansion ratio measurements for GFFF at 3% with various additives.

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 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 6.

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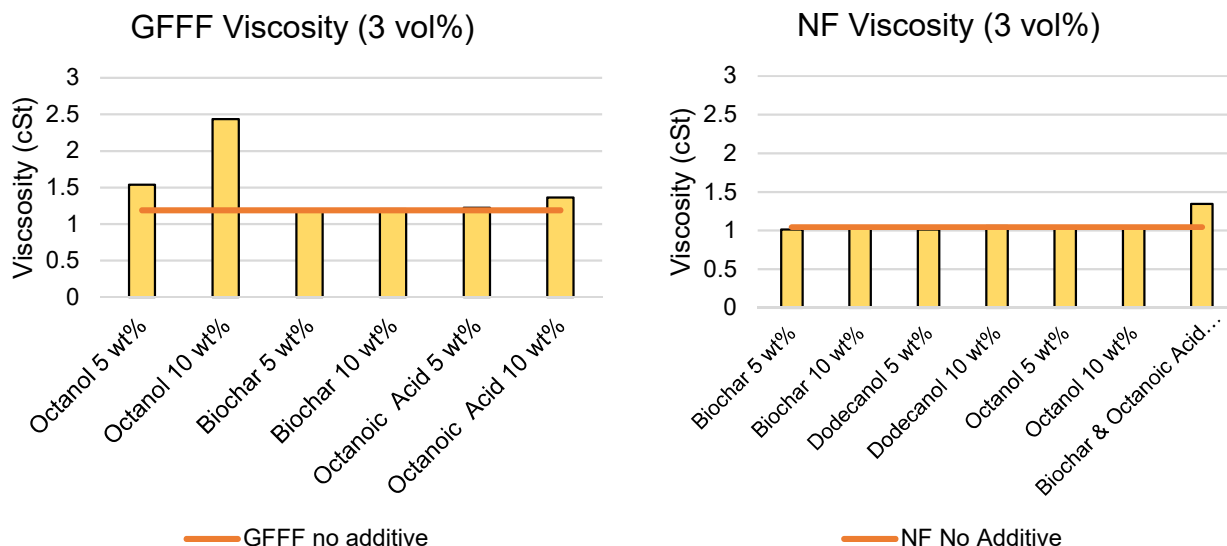


Figure 6: Viscosity measurements for GFFF at 3% with various additives.

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 is intriguing, as it indicates that varied ratios of additives mixed together may 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 2 (GFFF) and 3 (NF):

Table 2: Time to extinguish and burnback time for GFFF in small-scale fire tests.

| | (seconds) | (seconds) |
|--------------------------|---------------------|----------------|
| Mixture: | Time to extinguish: | Burnback time: |
| 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 |

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Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

Table 3: Time to extinguish and burnback time for NF in small-scale fire tests.

| | (seconds) | (seconds) |
|------------------------------|---------------------------|-----------------------|
| Mixture: | Time to extinguish | Burnback time: |
| 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, 6 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 4.

Table 4: Time to extinguish and burnback time determined for larger-scale fire tests.

| Concentrate | Additive | Extinguishment Time (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 which was 25 seconds faster than GFFF alone. This is a significant improvement over the baseline of 95 seconds for GFFF. Additionally, this additive **improved the burnback time by more than 4-fold**, from 42 seconds for the baseline GFFF to 183 seconds, which is much closer to approaching the required burnback time of 360 seconds in the MIL-

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

PRF-24385. Interestingly, the 10% octanol solution in GFFF had a slight improvement for extinguishment time and a 2-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 seconds (43 seconds versus 49 seconds. Additionally, the 10% biochar improved the burnback time by 40 seconds from 260 seconds to 300 seconds. 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 is significant, as it shows that biochar is particularly compatible with NF, and biochar does 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.

Implications for Future Research and Benefits Section

The experimental effort described in this report demonstrates 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 PFAS⁵⁰⁻⁵² 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 to 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.

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

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 we expect 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.

3 Objective

The aim of the work presented in this report was to identify viable PFAS replacement materials for firefighting foams that are functionally similar, but pose significantly less threat to the health of the end user and the environment. While PFAS are a common ingredient in AFFF utilized for fuel fire suppression due to their stability at elevated temperatures and oleophobicity, the NDAA has ordered their use to be illegal by 2024. In accordance with the SON, the goal 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 firefighting foam solutions for the DoD in the near future, JHU/APL focused on COTS compounds and additives that are already commercially available and can be utilized as a drop-in component for existing PFAS-free firefighting foams. We then aimed to assess the performance, storability and compatibility of these additive foam mixtures. Assessment of these parameters is critical to enabling sustained manufacture and use of PFAS-free fire suppression technologies by maintaining performance requirements while meeting environmental regulations.

Leveraging JHU/APL's previous experience in simulant development and test and evaluation work, JHU/APL conducted an extensive literature review in order to identify chemical additives that would mimic the chemical and physical properties of PFAS required for fire suppression. The most promising functional additives were down-selected and assessed in mixture with two different existing PFAS-free firefighting foams for their surface tension, foam expansion ratio, and viscosity. These critical property values, defined in the MIL-PRF-24385 and MIL-PRF-32725 are essential in predicting the fire-fighting capacity, and were utilized for further down-selection for both small (9-inch) and larger-scale (28 ft²) fire testing. Assessment of time to extinguish the fire and burnback time in the foam-additive mixtures helped to determine the additives that most improved fire-fighting capacity of the selected PFAS-free foams.

This work was a first step in identifying drop-in additives that can meet the urgent needs of the DoD to provide high-performing firefighting foams while reducing toxicity and meeting environmental requirements for use. The data collected in this Limited Scope effort and report proved that a number of environmentally friendly alternatives to PFAS, including octanol and biochar, show promising improvement in critical performance parameters, such as time to extinguish a fuel fire, and burnback time. Simultaneously, determination that some chosen additives diminished firefighting performance indicates that there is a significant effort that can be pursued in order to understand the molecular chemical basis of additive chemistry as it relates to altering the chemical and physical properties of the PFAS-free firefighting foams. The results of this effort point to risk reduction for follow-on work, as the initial data confirmed that fire suppression can be enhanced with COTS alternatives, reducing the time and effort required to develop and synthesize novel materials on the short timeline provided by the upcoming NDAA change to PFAS use in AFFF. Ultimately, future work is necessary to further understand the molecular mechanisms responsible for improved foam performance, which can aim to inform novel formulations on both short and longer timescales.

4 Background

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 US DoD on military installations.^{24,25} AFFF have conventionally been composed of a hydrocarbon-based surfactant and a fluorosurfactant, such as per/poly-fluoroalkyl substances (PFAS).^{26,27} The use of PFAS (Figure 1) is critical to the fire suppression, as PFAS enable the foam to blanket the fuel surface, smother the fire, and isolate the fuel source from oxygen.²⁸ The water content of the foam cools the fuel, allowing the foam blanket to suppress the release of flammable vapors.

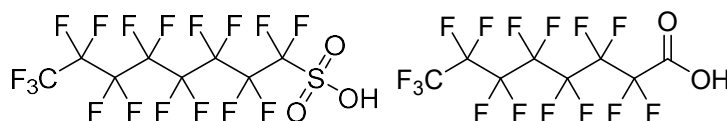


Figure 1: Structures of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), common perfluoroalkyl substances (PFAS) added to AFFF.

PFAS are extremely effective as surfactants in AFFF for firefighting, as the strong C-F bonds are exceptionally strong, leading to high heat capacity, resistance to degradation, and high chemical stability. Additionally, their oleophobicity, lack of affinity for oils, promotes formation of a continuous film over the fuel surface.²⁹ The high temperature stability of the AFFF is critical given its need to perform continuously at high operating temperatures. The addition of PFAS allows the foam to quickly coat the fuel surface, isolating it from the oxidizing source, thereby successfully extinguishing the fire. The foam film is highly affected by the presence of oil vapors, specifically at the oil-foam interface. The increase of oil vapors from the fuel source directly effects the stability of the foam film, wherein the foam structure collapses with the introduction of the fuel vapors.²⁸ For all of these reasons, PFAS containing firefighting foams have long been used for their ease and efficiency in firefighting.

In recent decades, however, PFAS use and exposure has been linked to a variety of detrimental health effects and ecotoxicological concerns.^{30–35} Over time, widespread use of AFFF has led to bioaccumulation in waters and soils, which has impacted wildlife and human populations. Recent studies have found elevated levels of PFAS and toxic PFAS byproducts in water, fish, and human blood serum near AFFF contaminated sites, such as airports and DoD installations.^{36,37} Due to rising concern regarding the environmental and national health implications on the use of PFAS in AFFF, the 2020 NDAA prohibited the use of AFFF containing PFAS effective on October 2024.

Currently, PFAS are an essential component in military grade fire suppressants, as there are currently no non-PFAS foams that meet the latest requirements for military use as specified by MIL-PRF-24385.³⁸ While PFAS have shown great success in combating the coupling destruction effects of heat and oil through the presence of C-F bonding, the fluorine-free foams are inherently unstable under these conditions.³⁹ Current approaches to PFAS replacement focus on mimicking the oleophobicity and high thermal capacity of the compounds, including long chain carbon-based compounds, siloxanes, brominated and chlorinated species, and a variety of other chemical compounds.^{40–43} While many of these emerging ‘green’ and on the market formulations show a great deal of promise, there are no PFAS-free firefighting foams that meet the MIL-PRF-24385 (although some meet recently released guidelines for PFAS-free foams in the MIL-PRF-32725⁴⁴) for chemical and physical properties, and fire-fighting performance. Additionally, 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.

5 Materials and Methods

5.1 Materials: All PFAS-free foams were obtained directly from the company vendors. The following functional additives were purchased: 1-dodecanol (Millipore Sigma, Cas No. 112-53-8), 1-octanol (Millipore Sigma, Cas No. 111-87-5), octanoic acid (Millipore Sigma, >99% purity, Cas No. 124-07-2), octane-1-sulfonic acid (Millipore Sigma, >98% purity, CAS No. 5324-84-5), dodecanoic acid (Millipore Sigma, CAS No. 143-07-7), dodecane-1-sulfonic acid (Millipore Sigma, CAS No. 2386-53-0), Tetradecamethylheptasiloxane (Fisher Scientific, 95% purity, CAS No. 19095-23-9) RDP (BenchChem, 98% purity, CAS No. 57583-54-7), biochar (BiocharDG, CAS No. 7440-44-0), magnesium oxide (Thomas Scientific, CAS No. 1309-48-4), and baking soda (sodium bicarbonate, Nutricost Baking Soda).

5.2 Surface Tension Measurements: Surface tension measurements were conducted using a Kibron Aqua Pi tensiometer (Figure 2). This device uses a hydrophobic probe to measure the downward force exerted on the probe by the liquid. It is highly sensitive and can measure to the nearest 0.1 mN/m. Prior to each test session, it was calibrated with water. Measurements were done on the foam solutions tested (pre-aeration mixture at 3 or 6% volume concentration in water), and 3 mL of solution was used to fill the instrument cup. The probe finalizes measurement at the highest measured surface tension along the pathway, which is usually the lip of the cup.



Figure 2: Kibron Aqua Pi Tensiometer (source: <https://www.kibron.com/product/aquapi>)

5.3 Foam Expansion Ratio Measurements: Expansion ratio testing was conducted by adding 50 mL of the prepared foam solution (pre-aeration mixture at 3 or 6% volume concentration in water, with or without additive) to a 1L glass jar. The foam was whisked with a blender to aerate with the jar held at an approximately 45-degree angle to allow air to enter the foam (Figure 3, A). The solution was blended until no liquid was present and subsequently poured into a smaller glass jar with a total volume of 140 mL. Foam was leveled off at the top of the jar, and the mass of the jar plus foam (Figure 3, B) was compared to the mass of the empty jar for the expansion ratio calculation as follows:

$$\text{Foam expansion ratio} = \frac{V\rho}{m_f - m_i}$$

where V = jar volume, ρ = solution density (assumed to be approximately 1 g/cm³ due to large volume of water), m_f = mass jar + foam, and m_i = mass empty jar.

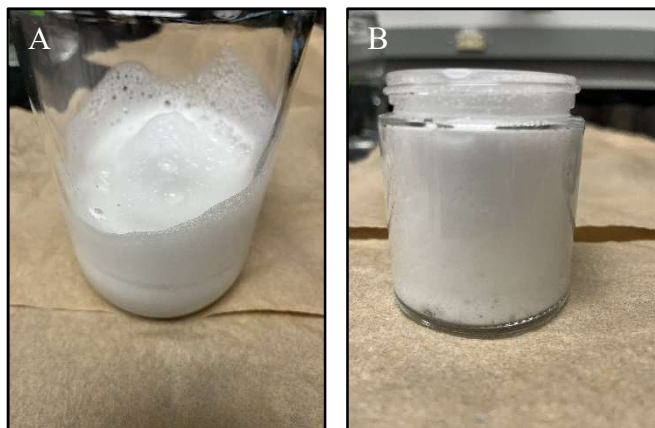


Figure 3: Foam expansion ratio testing: A) Aerated foam after blending, B) foam filled jar for measurement of mass and calculation of foam expansion ratio.

5.4 Viscosity Measurements: Initial viscosity measurements were conducted on a Brookfield Ametek LV rotational viscometer, however, data collected with that instrument was inconsistent and varied significantly with temperature. In order to achieve more consistent results and more closely follow the MIL-PRF-24385, a capillary viscometer was utilized (Figure 4). Viscosity measurements were conducted exclusively on the prepared foam solution (pre-aeration mixture at 3 or 6% volume concentration in water, with or without additive).



Figure 4: Capillary viscometer used for viscosity measurements.

Capillary viscometers operate by measuring the time required for a sample to flow through a capillary. The time in seconds is proportional to viscosity of the sample. The viscosity can be directly calculated by multiplying the time in seconds by the constant that is instrument dependent. The capillary viscometers have a much lower bound of measurable viscosity range (0.6 cSt) which allows for accurate measurement of the aqueous mixture when compared with the previously used rotational viscometer.

5.5 Small-scale fire testing (9-inch pan): The selected additive foam mixtures with GFFF and NF were evaluated for their fire-fighting performance in small-scale testing. This testing was accomplished utilizing an outdoor set up with a 9-inch cake pan (non-stick/PFAS-free). 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. For each test, the pan was filled to about halfway full with water and 125 mL of heptane was poured on top. The fuel was ignited, and after 10 seconds of burning, the foam mixture was gently poured on top of the fire. A stopwatch was used to time from the moment that the foam began to hit the fuel/fire surface until all flames were completely extinguished. This time was recorded as the time to extinguish. Within a minute of putting out the fire, a burnback test was conducted by placing a 3-inch diameter tuna can filled with 25 mL heptane that was lit on fire into the extinguished foam/fuel. The time it took to reignite at least 25% of the 9-inch pan was recorded as the burnback time. Each test was recorded on a video camera in order to confirm recorded times.

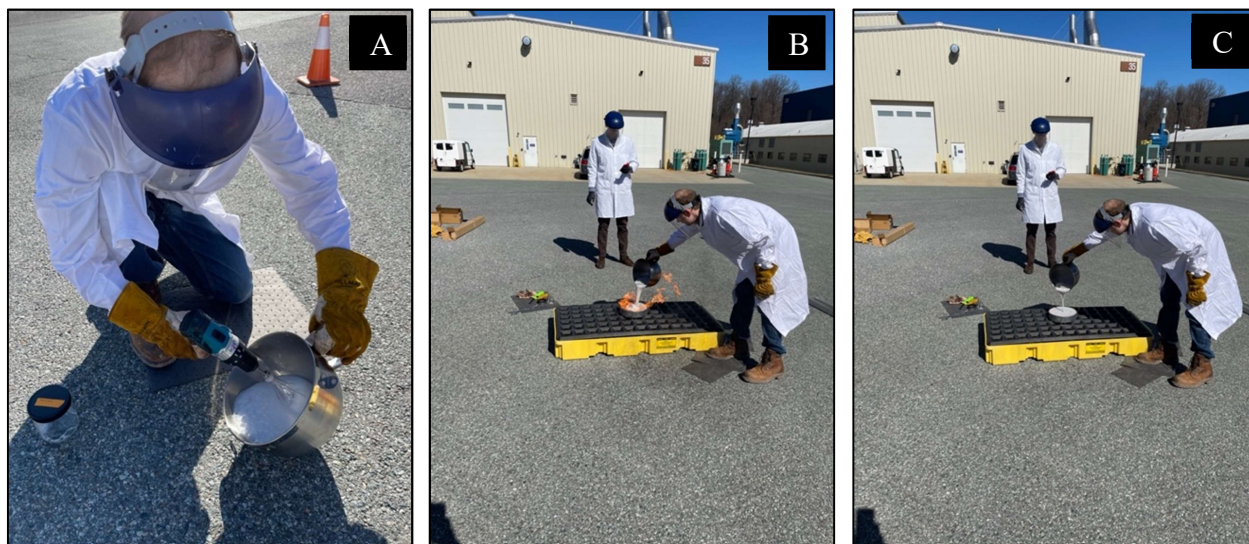


Figure 5: Small-scale fire tests: A) Preparation of foam mixture; B) Pouring foam mixture over fire and collection of time to extinguish; C) Fire completely extinguished by foam mixture.

5.6 Larger-scale fire testing (28 ft²) with Jensen Hughes: Six foam-additive mixtures were chosen for larger-scale testing along with the two control tests for GFFF and NF. The larger-scale fire testing was completed under the supervision of Jerry Back at Jensen Hughes in collaboration with the NRL–CBD facility. Testing began by filling the 28 ft² pool approximately halfway with water. Next, 10 gallons of fuel (gasoline) was poured over the water, and the fire was lit within 30 seconds. Extinguishing began 10 seconds after ignition. Foam was sprayed using a 2 gallon per minute nozzle, with a total foam solution of 10 gallons available for testing. Foam was sprayed until extinguishing time, the time at which no visible fire was present, was reached, and this time was documented. Foam continued to be sprayed until the 90 second mark, at which time the burnback testing began. If the fire had not been extinguished by 90 seconds,

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

the foam spray was continued until 120 seconds, but burnback was not performed. If extinguishing was not reached at 120 seconds, an AFFF solution on standby was used to extinguish the flame.

Burnback testing utilized a metal pan filled with 1 inch of fuel. Ignited outside of the pool, the pan was then placed in the center and balanced until fully floating on the foam surface. Once the flame had ignited the pool surface, the pan was removed and extinguished separately. Burn back time was determined by the point at which ~25% of the pool had reignited. While burnback was being performed, expansion ratio and drain time were evaluated. These were measured by first spraying foam onto a sloped metal surface and collecting the foam within two graduated cylinders. These were then weighed for expansion ratio and allowed to rest until drain time was reached.



Figure 6: Preparation of the foam solution.



Figure 7: Ignited fuel in 28 sq ft pan and application of foam-additive mixture.



Figure 8: Extinguished fire.



Figure 9: Burnback testing.

5.7 Storability and compatibility testing of chemical additives with PFAS-free foam concentrates.

Stability testing was performed using a vacuum oven set at 65°C for a period of 10 days, as described in the MIL-PRF-24385. Samples were prepared in 100 mL glass jars by adding the appropriate amount of concentrate for a 3% solution by volume and the associated additive at either 5% or 10% by mass. Glass jars were sealed and placed in the pre-heated oven, which had all valves closed to prevent exchange of air. After 10 days, samples were removed from the oven and allowed to cool to room temp before introducing water to create the foam solution. Solutions rested overnight to allow mixing prior to testing for surface tension, expansion ratio, and viscosity, as previously described. Stability testing was only conducted with foam-additive mixtures that were down-selected for larger-scale fire testing.

6 Results and Discussion

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: PFAS-free concentrate identification and enhancement through the introduction of oleophobic compounds

Task 2: Identify and characterize selected additive and foam mixtures

Task 3: Small-scale testing of foam extinguishing performance

Task 4: Fire-fighting performance large scale testing at Jensen Hughes

Task 5: Evaluate storability and compatibility of chemical additives with COTS PFAS-free fire suppressant foam concentrate

6.1 Results from Task 1: PFAS-free concentrate identification and enhancement through the introduction of oleophobic compounds. 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 foam candidates were selected for chemical property testing and assessment with chosen COTS additives. These were: *Firestopper Terminator 136 FFC*, and *Greenfire GFFF*. Initial characterization testing was conducted with the two PFAS-free foams, and following inconsistent results with the *Firestopper* product and recommendations from JHU/APL collaborator Jerry Back at Jensen Hughes, work was ceased with *Firestopper*. Per the recommendation of Jensen Hughes, *National Foam (NF) Avio F3 Green KHC* was selected for testing as an alternative to the *Firestopper* product, and due to time limitations, testing was only conducted with NF at 3% concentrate and with the additives that indicated the most promising results with GFFF. Both the GFFF and NF products are recognized for having decent performance by industry standards and had been previously subjected to testing through external and government partners.

Identification of additives for the PFAS-free foams involved a thorough understanding of the roles of major components of the AFFF PFAS containing PFAS-free concentrates in fire suppression, and in particular, how inclusion of oleophobic compounds, such as PFAS, influences firefighting ability. During the proposal stage of this work, JHU/APL utilized safety data sheets (SDS) to gain information as to the primary components of various PFAS-free foam concentrates. As noted in the proposal, the SDS identified the following major components: propylene glycol, monobutyl ether, sodium decyl sulfate, sodium octyl sulfate, sodium laureth sulfate, butanedioic acid, 2-sulfo, C-isodecyl ester, disodium salt, 1-dodecanol, and 1-tetradecanol. With this information in hand, list of categories for potential additives was developed and presented in the proposal (Table 1).

Table 1: Categories of additive with potential compounds of interest based on preliminary literature review.

| Category | Chemical | Ecological Toxicity* |
|--|---------------------------|---|
| Non-fluorinated analogues of common PFAS additives | 1-dodecanol ¹² | H410 – very toxic to aquatic life with long lasting effects |
| | 1-octanol ¹³ | H412 – harmful to aquatic life with long lasting effects |
| | Octanoic Acid | H402 – harmful to aquatic life |
| | Octane-1-sulfonic acid | None |
| | Dodecanoic Acid | H401 – toxic to aquatic life |
| | Dodecane-1-sulfonic acid | Not classified |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

| | | |
|---|--|---|
| Halogenated Compounds - polybrominated | 2,2',4,4',5,5'-hexabromobiphenyl | None |
| | Bromoform | H411 – toxic to aquatic life with long lasting effect |
| Halogenated Compounds – polychlorinated | Trichloroethylene | H412 – harmful to aquatic life with long lasting effects |
| | Chlordane | H401 – toxic to fish and other water organisms H413 – May cause long-term adverse effects in the aquatic environment |
| Non-Halogenated Compounds (Greener Alternatives) - Siloxanes/Polysiloxanes/ Silicones ¹⁰ | Methyltrimethoxysilane | None |
| | Decamethylcyclopentasiloxane | None |
| | Polydimethylsiloxane (GP-907) | Not classified |
| Non-Halogenated Compounds (Greener Alternatives) - Oleophobic Compounds | Hydrogenated polyisoprene | None |
| Non-Halogenated Compounds (Greener Alternatives) | diethylene glycol butyl ether | None |
| | Biochar | None |
| | Salt (Sodium Chloride) | Not a hazardous substance |
| | Sodium Bicarbonate | Not a hazardous substance |
| Non-Halogenated Compounds (Greener Alternatives) - Betaine Compounds | Betaine | Not classified by GHS |
| | Cetyl Betaine | Not classified by GHS |
| Non-Halogenated Compounds (Greener Alternatives) - Silica aerogels | DOWSIL™ VM-2270 Aerogel Fine Particles | Not classified as hazardous |
| Traditional retardants | Ammonium Polyphosphate | None |

**Ecological toxicity based on Globally Harmonized System of Classification and Labeling of Chemicals (GHS) Hazard Statements.*

As the literature review on certain potential additives began, some categories were immediately ruled out due to potential issues with ecotoxicology and human toxicity. For example, while halogenated compounds can offer properties similar to those of PFAS, such as high heat capacity and stability, and have been previously used as fire retardants,⁴⁵ they have also been shown to cause similar environmental and health issues associated with PFAS, such as bioaccumulation.^{46–49} Ultimately, a number of additives were identified for potential testing (Table 2) 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 2: List of potential additives for PFAS-free foam concentrates. Green indicates high priority, yellow indicates medium priority, and red indicates low priority based on literature review and assessment of their likely ability to improve fire-fighting capabilities.

| Non-Fluorinated Analogues* | Uses/Reasoning |
|----------------------------|---------------------------|
| 1-dodecanol | foaming agent, emulsifier |
| 1-octanol | viscosity controller |
| octanoic acid | hydrophobic, film forming |
| octane-1-sulfonic acid | foaming agent |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

| | |
|---|---|
| dodecanoic acid | freezing point depressor, surface active agent |
| dodecane-1-sulfonic acid | ion-associating reagent |
| | |
| Green Alternatives | Uses/Reasoning |
| 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 >1000 deg C temps |
| phosphates ¹⁶⁻¹⁸ | (RDP) super effective flame retardant additive |
| betaine compounds | no info found |
| oleophobic coatings ^{19,20} | most oleophobic coatings contain PFAS, PFPE ect (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).

6.2 Task 2: Identify and characterize selected additive and foam mixtures. The base values for surface tension, foam expansion ratio, and viscosity in the PFAS-free foams without additives were determined and shown in Table 3, below:

Table 3: Base values for surface tension, foam expansion ratio, and viscosity for the two PFAS-free foams with no additives.

| PFAS-free Foam | Surface Tension (mN/m) | | Foam Expansion Ratio (no units) | | Viscosity (cSt) | |
|----------------|------------------------|------|---------------------------------|------|-----------------|------|
| | 3% | 6% | 3% | 6% | 3% | 6% |
| Greenfire GFFF | 34.9 | 35.0 | 10.44 | 9.29 | 1.52 | 1.19 |
| National Foams | 35.53 | ND | 8.59 | ND | 1.05 | ND |

The goal of surface tension measurements was to observe a potential decrease in surface tension with additives present, as this will 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). The observations for surface tension indicated that several additives improved surface tension of the GFFF solution by lowering the surface tension value calculated

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

(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 wt% loading of additive was not significant enough to impact surface tension values.

In the case of foam expansion ratio results, several additives increased the foam expansion ratio with increasing wt% additive in solution. Some additives had no impact on expansion ratio, and no additive caused a significantly lower expansion ratio, however some increased the expansion ratio significantly. All expansion ratio results were found to fall between 5.5-15.5 (no units). The MIL-PRF 24385 recommends that foam expansion ratio fall above 5, and feedback from co-performers at Jensen Hughes have recommended 7-10 as the ideal range.

The goal for viscosity, based on the MIL-PRF-24385 was to achieve a value of >3 centistokes (cSt) at temperatures around 25°C, and in general to increase the viscosity relative to the base values.

Surface Tension: The surface tension results for the best performing mixtures (those that reduced surface tension compared with the stock solution) are shown in Figure 10 and Figure 11. Full data can be found in Appendix A.

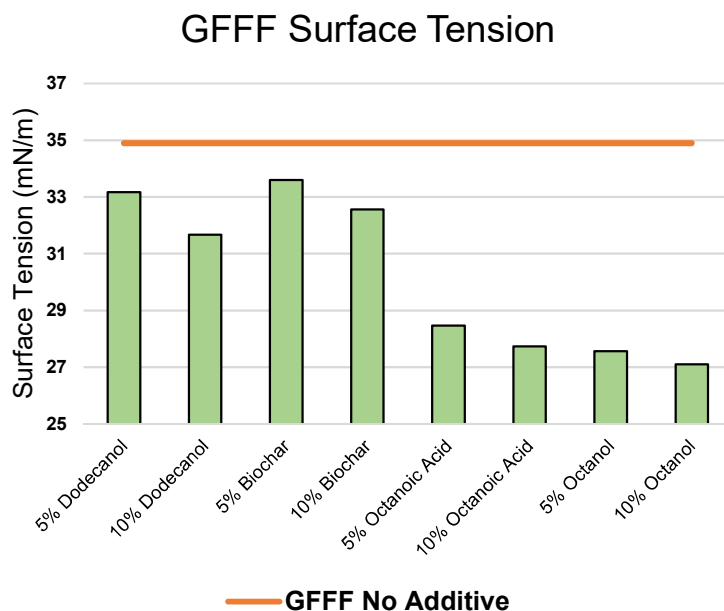


Figure 10: Surface tension measurements for GFFF at 3% with various additives.

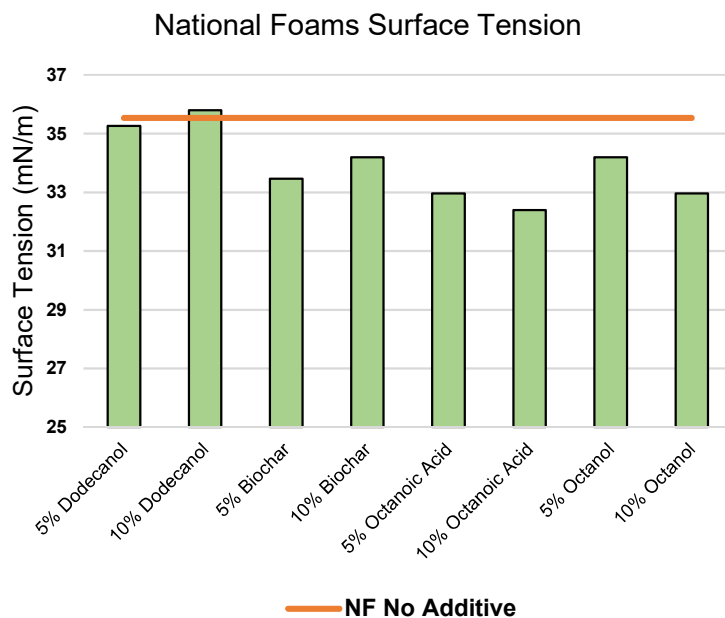


Figure 11: Surface tension measurements for NF at 3% with various additives.

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.

Foam Expansion Ratio: The foam expansion ratio results for the best performing mixtures (those maintained a foam expansion ratio between ideal values of 7-10 a.b.u.) are shown in Figure 12 and Figure 13. Full data can be found in Appendix B.

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

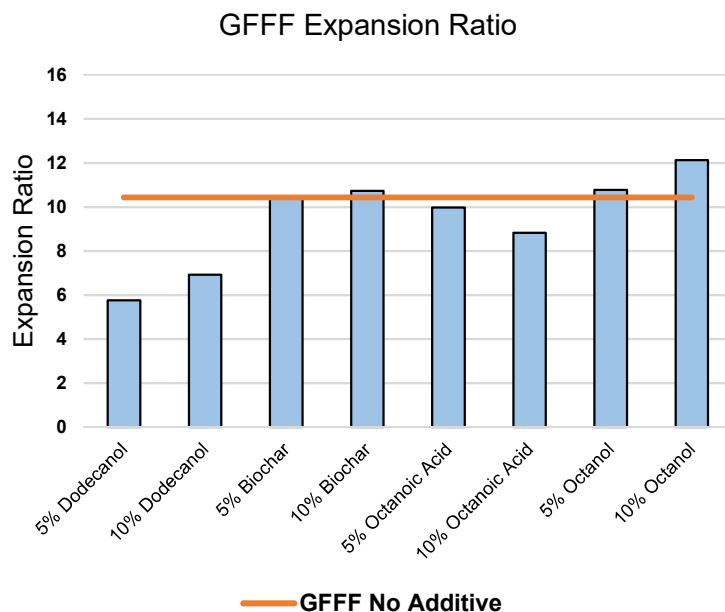


Figure 12: Foam expansion ratio measurements for GFFF at 3% with various additives.

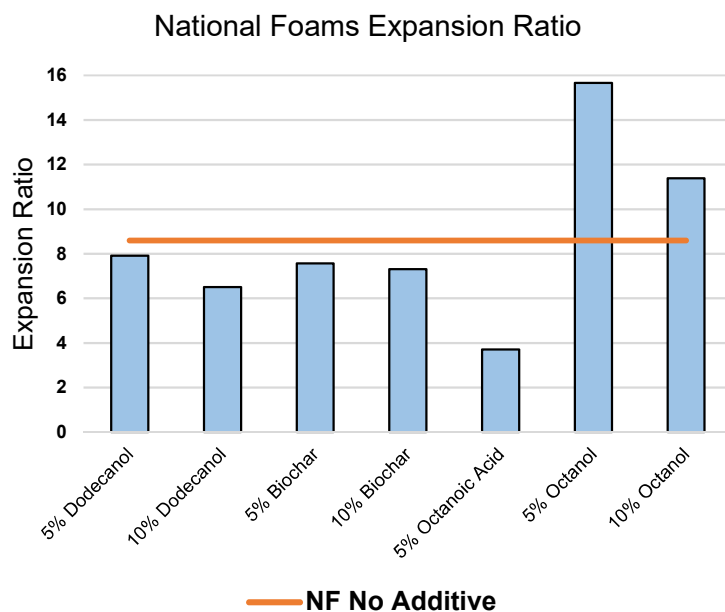


Figure 13: Foam expansion ratio measurements for NF at 3% with various additives.

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 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

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

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.

Viscosity: The viscosity results for the best performing mixtures (those that increased the viscosity and ideally increased to above a value of 3 cSt) are shown in Figure 14 and Figure 15. Full data can be found in Appendix C.

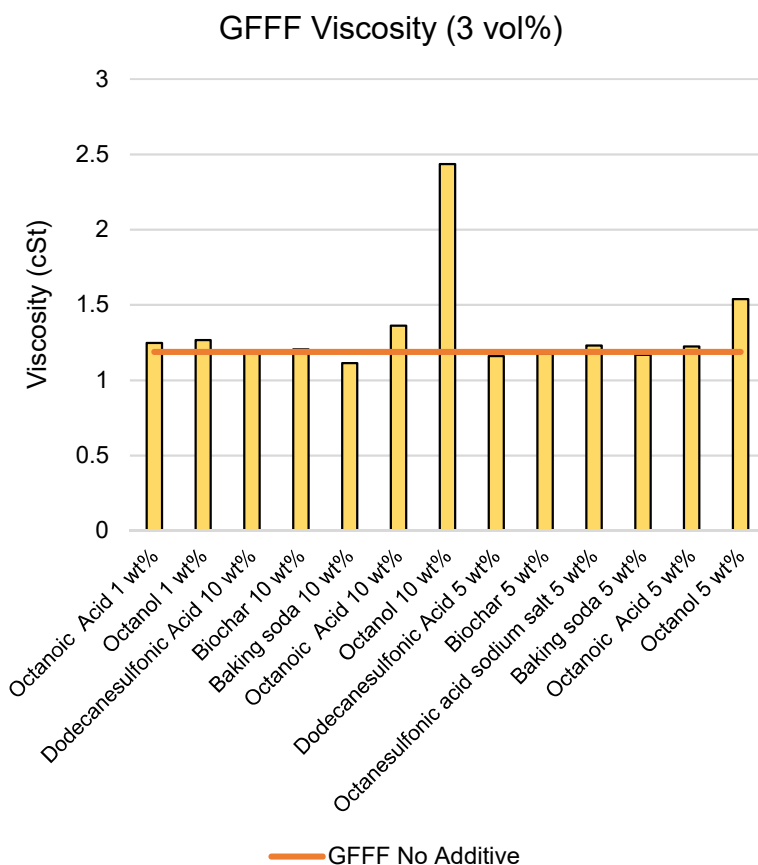


Figure 14: Viscosity measurements for GFFF at 3% with various additives.

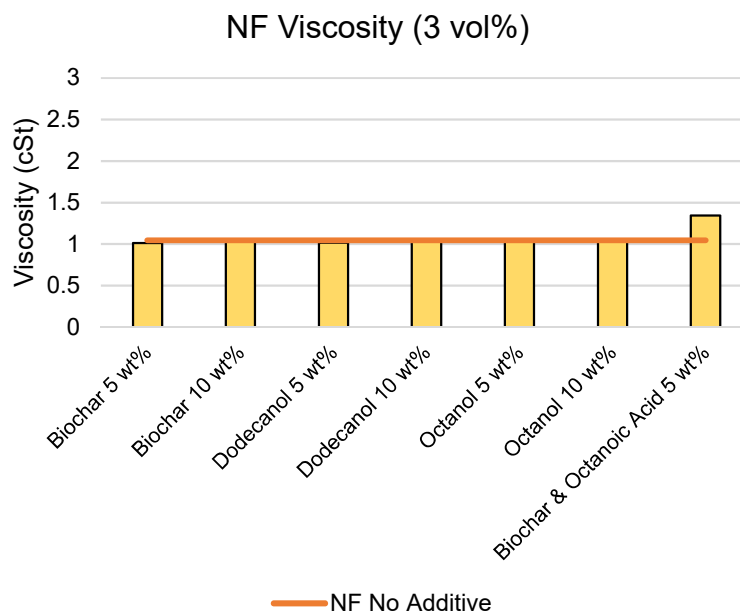


Figure 15: Viscosity measurements for NF at 3% with various additives.

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 is intriguing, as it indicates that varied ratios of additives mixed together may have different influences on chemical and physical properties compared with single additive mixtures.

6.3 Task 3: Small-scale testing of foam extinguishing performance. The results of the small-scale fire-testing are listed in Tables 4 and 5:

Table 4: Time to extinguish and burnback time for GFFF in small-scale fire tests.

| GFFF | (seconds) | (seconds) |
|------------------------------|----------------------------|-----------------------|
| Mixture: | Time to extinguish: | Burnback time: |
| GFFF | 13.0 | 107.5 |
| GFFF (replicate) | 10.85 | 67.2 |
| 5% octanol | 5.85 | 73.7 |
| 5% octanol (replicate) | 6.9 | 97.0 |
| 10% octanol | 7.93 | 116.5 |
| 10% octanol (replicate) | 17.54 | 130.6 |
| 5% octanoic acid | 12.09 | 110.3 |
| 5% octanoic acid (replicate) | 11.69 | 90.9 |
| 10% octanoic acid | 11.55 | 58.8 |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

| | | |
|--------------------------------|-------|-------|
| 10% octanoic acid (replicate) | 9.94 | 49.0 |
| 5% dodecanol | 12.25 | 94.4 |
| 10% dodecanol | 11.4 | 116.0 |
| 5% biochar | 12.45 | 58.42 |
| 10% biochar | 8.13 | 80.8 |
| 5% biochar, 5% octanol | 10.46 | 89.1 |
| 10% biochar, 10% octanol | 9.92 | 94.2 |
| 5% biochar, 5% octanoic acid | 12.41 | 113.3 |
| 10% biochar, 10% octanoic acid | 9.74 | 120.5 |

Table 5: Time to extinguish and burnback time for NF in small-scale fire tests.

| NF | (seconds) | (seconds) |
|--------------------------------|--------------------|----------------|
| Mixture: | Time to extinguish | Burnback time: |
| NF 3% | 2.72 | 199.1 |
| NF 3% | 3.22 | 129.4 |
| 5% biochar | 7.35 | 199.9 |
| 5% biochar | 4.03 | 129.4 |
| 10% biochar | 5.82 | 124.6 |
| 10% biochar | 4.83 | 199.1 |
| 5% octanol | 6.5 | 136.9 |
| 5% octanol | 7.53 | 133.5 |
| 10% octanol | 6.32 | 107.2 |
| 10% octanol | 4.52 | 151.7 |
| 5% octanoic acid | 9.51 | 221.3 |
| 5% octanoic acid | 9.39 | 170.2 |
| 10% octanoic acid | did not extinguish | n/a |
| 10% octanoic acid | did not extinguish | n/a |
| 5% dodecanol | 12.15 | 183.1 |
| 10% dodecanol | 6.38 | 158.7 |
| 5% biochar, 5% octanol | 4.97 | 137.6 |
| 10% biochar, 10% octanol | 4.69 | 161.9 |
| 5% biochar, 5% octanoic acid | 5.63 | 206.8 |
| 10% biochar, 10% octanoic acid | did not extinguish | n/a |

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 maintained the extinguishing time observed with the GFFF without additive. 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

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

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.

6.4 Task 4: Fire-fighting performance larger scale testing at Jensen Hughes. Based on the results from Task 3, 6 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 6.

Table 6: Time to extinguish and burnback time determined for larger-scale fire tests.

| Concentrate | Additive | Extinguishment Time (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 improved extinguishment time by 25 seconds and required 70 seconds. While not at the level of the MIL-PRF-24385, this is a significant improvement over the baseline of 95 seconds for GFFF. Additionally, this mixture improved the burnback time by more than 4-fold, from 42 seconds for the baseline GFFF to 183 seconds, which is much closer to approaching the required burnback time of 360 seconds in the MIL-PRF-24385. Interestingly, the 10% octanol solution in GFFF had a slight improvement for extinguishment time and a 2-fold improvement in burnback time but did not achieve the same level of improvement observed with the 5% octanol solution in GFFF. This indicates that there is a chemical molecular basis for the additive interaction with the baseline PFAS-free foam concentrate, and that more work can be done to both understand the molecular basis for these changes and determine optimal mixture ratios to achieve the best overall performance. 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 connection between these properties and fire-fighting performance.

For NF, biochar was chosen as a promising additive to improve extinguishment time and burnback time. The 5% biochar NF mixture did not improve the extinguishment time, however, the 10% biochar NF mixture did improve extinguishment time by 6 seconds, achieving extinguishment time closer to the MIL-PRF-24385. Additionally, the 10% biochar NF mixture improved the burnback time by 40 seconds from 260 seconds to 300 seconds. This indicates that biochar is a very promising additive for some PFAS-free foams and has the additional benefit of being a more human health and 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 the connection between these properties and fire-

fighting performance. The 5% octanoic acid NF mixture did not extinguish the fire, and it was observed in both the small- and larger-scale testing that octanoic acid in some cases destroyed the mixture's ability to foam. This further points to the chemical molecular basis that is likely influencing the overall firefighting performance with different additives and indicates that more work must be conducted to understand the molecular basis for firefighting performance with different additives.

6.5 Task 5: Evaluate storability and compatibility of chemical additives with COTS PFAS-free fire suppressant foam concentrate. The down-selected foam-additive solutions that were tested at larger-scale were assessed for their stability under accelerated aging conditions in order to determine their long-term storability and compatibility. The 8 foam-additive concentrate mixtures were prepared in 100 mL volumes and placed into an oven at 65°C for 10 days and were then analyzed for surface tension, foam expansion ratio, and viscosity. Due to time constraints, further small and/or larger-scale fire testing was not able to be completed following accelerated aging of the solutions, however, this would be an important test to pursue in future testing in order to better understand the relationship between these critical physical and chemical properties and fire suppression.

The results for surface tension are shown in Figures 16 and 17 below:

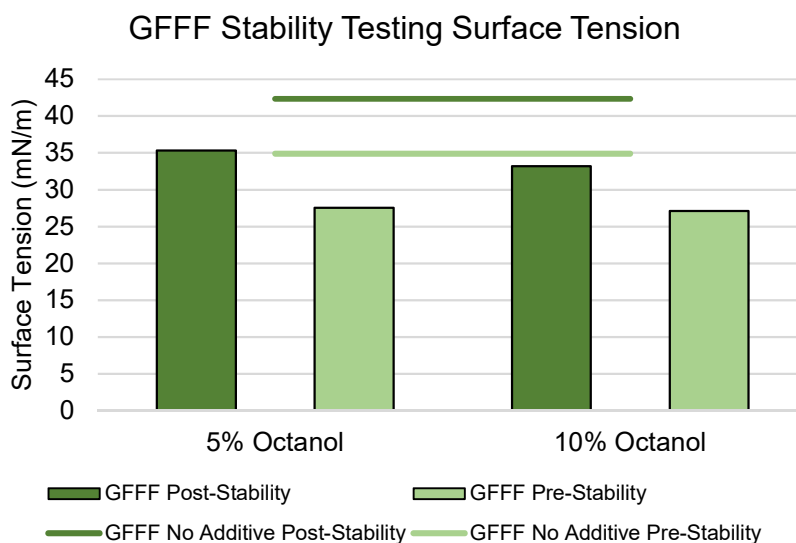


Figure 16: Comparison of surface tension in GFFF pre-stability testing and post-stability testing.

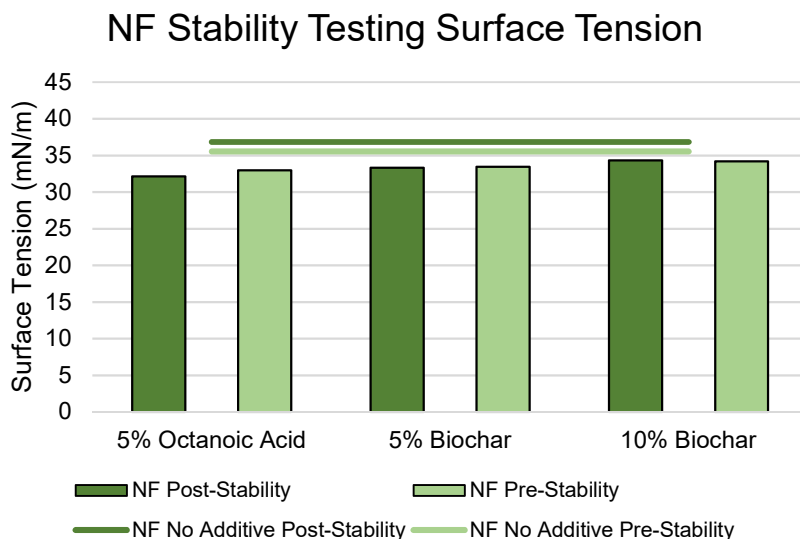


Figure 17: Comparison of surface tension in NF pre-stability testing and post-stability testing.

In both cases of GFFF and NF, the baseline surface tension of the PFAS-free foam without additive increased after undergoing accelerated aging, indicating that there may be long term changes in the spreading coefficient properties of the foams. In the case of GFFF, this pattern was also observed with 5 and 10 wt% octanol additives, indicating that there may be some loss in improved surface tension and spreading coefficient if the solution were to be stored over a long period of time. NF showed slightly different results, where there was very little change in surface tension value after aging. This was the case for both 5% biochar and 10% biochar, both of which improved fire suppression in the larger-scale fire testing. This testing indicates that the biochar is compatible and storable with NF in terms of surface tension and spreading coefficient.

The results for foam expansion ratio are shown in figures 18 and 19 below:

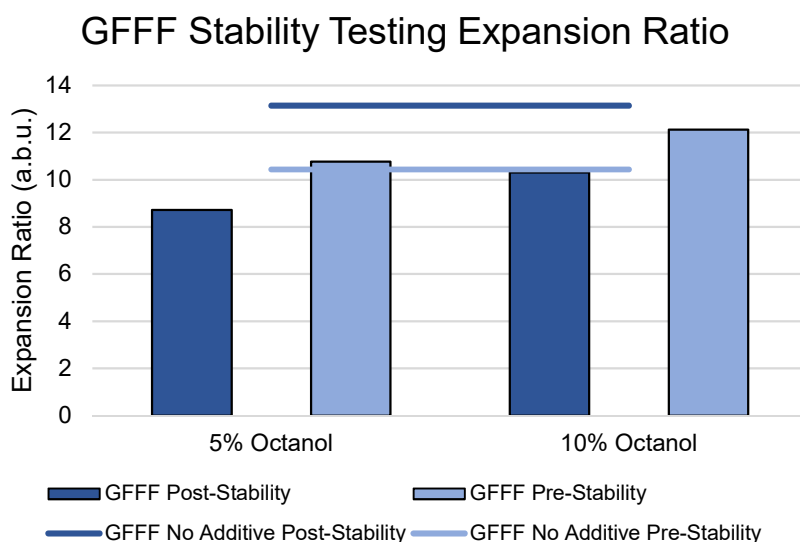


Figure 18: Comparison of foam expansion ratio in GFFF pre-stability testing and post-stability testing.

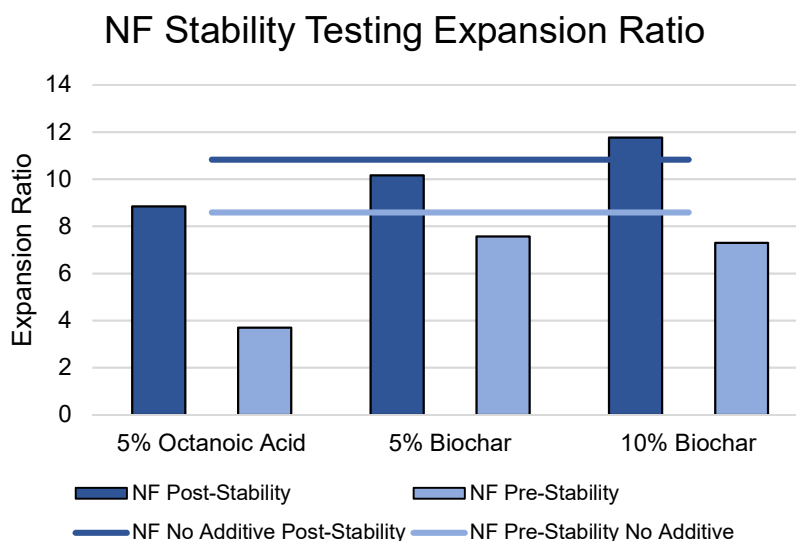


Figure 19: Comparison of foam expansion ratio in NF pre-stability testing and post-stability testing.

In the case of foam expansion ratio, in both GFFF and NF, the aging process seemed to increase the foam expansion ratio, in both cases above the ideal range of about 7-10. In the case of GFFF, both 5 and 10 wt% octanol caused a reduction in foam expansion ratio relative to the foam additive mixture that had not undergone an aging process. This indicates that long term storage may be influenced by the compatibility of GFFF with octanol and cause a reduction in the foaming ability of the foam-additive mixture. In the case of NF, however, foam expansion ratio was increased following the aging process for all three foam-additive mixtures. This unusual result may indicate that long term storability may not influence the compatibility of NF with selected additives and/or that the heating process influences the chemical interactions in such a way that foam expansion is improved. Combined with the surface tension data for biochar in NF, these data may point to biochar, in particular, as an extremely compatible additive with NF both for improving fire suppression and long-term storability.

The results for viscosity are shown in Figures 20 and 21 below:

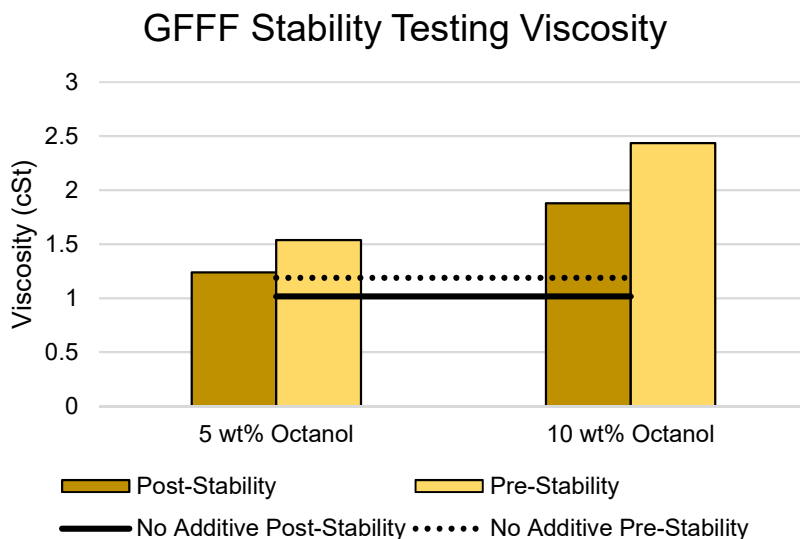


Figure 20: Comparison of viscosity in GFFF pre-stability testing and post-stability testing.

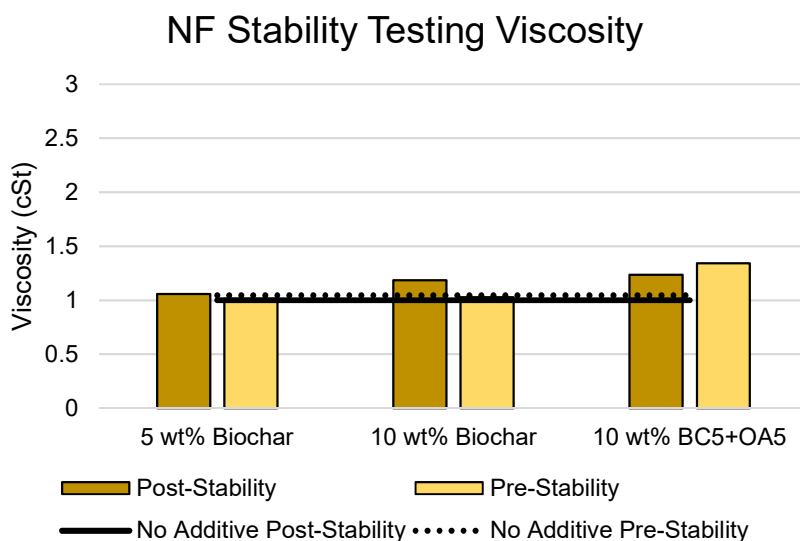


Figure 21: Comparison of viscosity in NF pre-stability testing and post-stability testing.

In the case of GFFF, viscosity was decreased following the aging process in the no additive standard and in both the case of 5 and 10 wt% octanol, indicating that long-term storage may reduce viscosity and impact overall fire suppression ability. However, in both the case of 5 and 10 wt% octanol, the viscosity was still increased relative to both pre- and post-stability additives, indicating that even after the aging process, the octanol does improve viscosity overall. For NF, viscosity was only slightly decreased in the no additive standard following the aging process, indicating NF to be a relatively stable material to begin with. Additionally, viscosity in NF remained relatively unchanged or increased following the aging process for all additives, further indicating that NF even in the presence of biochar additives, in particular, is stable and compatible over long periods of time. Combined with surface tension and foam expansion ratio data for

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

NF, biochar can further be confirmed as an exceptional additive as it both improves fire suppression, as shown in the small- and larger-scale fire testing, and chemical and physical properties are not easily affected by aging processes. Biochar as an additive may be stable in a PFAS-free foam concentrate over long periods of time.

7 Conclusions and Implications for Future Research

The experimental effort outlined in this report has clear implications that a number of COTS functional additives do improve fire suppression in PFAS-free firefighting foams. In particular, octanol and biochar were determined to improve two different PFAS-free foams, GFFF and NF, respectively, overall firefighting performance in time to extinguish a gasoline fire and in burnback time. These COTS additive, both of which provide a more eco-friendly, degradable, and reduced toxicity alternative to PFAS^{50–52}, may be a time-sensitive solution to respond to the urgent need by the DoD to procure new alternative 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 results of the work conducted through this Limited Scope effort first showed that a variety of functional additives, based on extensive literature review, can alter the physical and chemical properties of PFAS-free foams. These properties, including surface tension, foam expansion ratio, and viscosity, are critical parameters that inform the overall firefighting ability of the foam. Dodecanol, octanol, octanoic acid, and biochar were selected for further testing, as these functional additives both decreased surface tension (thus increasing the spreading coefficient) and increased the viscosity. While not all of these additives ultimately had a significant impact on fire performance in subsequent testing, the results of the chemical and physical property testing showed that with the right additive ratios mixed with particular PFAS-free foams, these properties can be tunable to produce an ideal fire suppressing mixture.

Subsequent small- and larger-scale fire testing confirmed the results from assessment of the chemical properties, showing that both time to extinguish the fuel fire and burnback time was influenced by varied concentration ratios of additives in the PFAS-free foams. In small-scale testing, it was found that octanol at 5 wt% additive in GFFF could improve time to extinguish by nearly two-fold, while 10 wt% of octanol did not improve time to extinguish but did improve the burnback time by greater than 30 seconds. These types of results clearly indicate that varied ratios of additives in the foam mixture can have vastly different influence on critical fire performance parameters, and that additional experimental research is crucial to determining ideal reaction mixtures. Similarly, tests with NF at small-scale found that biochar at 5 or 10 wt% could improve the burnback time, while an additive like octanoic acid seemed to destroy NF's ability to foam at all, despite changes observed in the chemical and physical property testing. These results indicate that molecular scale chemical properties are playing a significant role in influencing critical firefighting parameters and that additional work must be done to characterize the chemical interactions between the foam and additives in solutions. Larger-scale fire testing helped to confirm results of the small-scale testing, but provided a larger time scale to more easily visualize and characterize the effects on time to extinguish and burnback time. Overall, it was determined that 5 wt% octanol improved performance of GFFF by decreasing time to extinguish by 25 seconds and increasing burnback time by 141 seconds, both coming closer to MIL-PRF-24385 requirements. Additionally, biochar improved performance of NF by decreasing time to extinguish by 6 seconds and increasing burnback time by 40 seconds. Both of these results were deemed significant by fire suppression experts at Jensen Hughes and NRL who helped to run these tests, and the results are an exciting step in determining improved capabilities for existing PFAS-free foam formulations.

The PFAS-free foam-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. These results followed trends observed in general for GFFF, where all chemical and physical properties were negatively affected in the no additive stock solution following accelerated aging. In the

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

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 no additive NF stock solution pre- and post-stability aging testing. This is significant, as it shows that biochar is particularly compatible with NF, and biochar does 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.

Next Steps:

The next steps for this work will leverage JHU/APL expertise in molecular scale material and chemical properties modeling in order to assess and predict big picture 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 fire suppression results that meet military needs. The benefits of both the work to date and potential follow-on work is to provide a basis for both these COTS additives and novel related analogues to be incorporated into future emerging PFAS-free firefighting foam formulations. Additional follow-on work will be conducted by following the tasks outlined below:

Task 1: Molecular scale characterization of foam-additive mixtures to determine chemical characteristics of foam-additive interactions

JHU/APL will utilize a combination of analytical techniques, including nuclear magnetic resonance (NMR) spectroscopy, Fourier-Transform Infrared (FTIR) Spectroscopy, and high-resolution mass spectrometry (HRMS), to characterize the chemical interactions between the PFAS-free firefighting foams and functional additives determined in the Limited Scope work to improve fire suppression in these foams. This will allow for determination and development of a trend in the chemical and physical properties to compatibility and fire suppression capability. A model of the relationship between chemical interactions and mixing ratios of additives with surface tension (spreading coefficient), foam expansion ratio, and viscosity will directly inform Task 2, as molecular scale properties can be utilized to determine alterations to molecular scale properties and determine analogues and further additives for testing to achieve ideal firefighting performance. This could be extended further - combining experimental and computational approaches to identify proper mixing ratios of additives in a wider variety of PFAS-free foams and identifying additional analogues of high performing additives determined in the Limited Scope Portion of the work. For example, studies have shown that the starting material for the pyrolysis process can significantly alter the molecular characteristics of the biochar material, resulting in a wide range of functional groups and chemical make-up.⁵³⁻⁵⁵ Classes of these different 'biochar' materials may further improve fire suppression and should be reviewed as potential candidates for further testing. A more complete analytical determination of chemical interactions utilizing JHU/APL expertise in molecular scale property metadynamics simulations could develop a model to explain the behavior of additives in varied PFAS-free foams

Task 2: Identify additional analogues of successful functional additives for testing

JHU/APL will utilize determined relationships between chemical interactions of additives with PFAS-free foam solutions to determine additional additives and analogues of successful additives for further experimental testing. For example, biochar, which is a general term for biomass that has undergone pyrolysis, can be produced from a wide variety of organic starting materials. Studies have shown that the

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

starting material for the pyrolysis process can significantly alter the molecular characteristics of the biochar material, resulting in a wide range of functional groups and chemical make-up.⁵³⁻⁵⁵ Classes of these different ‘biochar’ materials may further improve fire suppression and should be reviewed as potential candidates for further testing. JHU/APL will identify additional analogues and related chemical compounds to those previously found to improve fire suppression, including octanol and biochar, and down-select these related materials for chemical and physical property testing and fire suppression tests through Tasks 3 and 4.

Task 3: Chemical and physical property testing of identified foam-additive solutions in varied mixture ratios and molecular scale characterization for down-selection

Foam-additive mixtures identified in Task 2 will be analyzed for surface tension (spreading coefficient), foam expansion ratio, and viscosity as has been described throughout this report. As has been observed through the Limited Scope effort, noted in the literature, and will be further modeled through Task 1 of follow-on work, changes to these physical and chemical properties in the foam-additive mixtures can inform overall fire suppression performance and are an extremely useful tool for down-selection of additives. Additives identified in the Limited Scope effort along with novel analogues identified in Task 2 will be tested systematically in varied mixing ratios (as different additives have been shown to differently influence the three properties tested) in order to determine ideal mixtures for firefighting. Additionally, the Limited Scope effort only focused on two PFAS-free firefighting foams for testing due to time limitations, and in follow-on work JHU/APL will work with expertise at Jensen Hughes to identify at least two additional PFAS-free foams currently on the market for testing with successful additives. Ultimately, a Design of Experiment will be utilized to assign PFAS-free foams with additives at varied mixing ratios for testing in order to conduct comprehensive testing of combinations and to determine the variables that most influence chemical and physical properties and thus fire suppression capability. The foam-additive mixtures that most positively influence the surface tension, foam expansion ratio, and viscosity and bring them closer to the standards set out in the MIL-PRF-24385 will be down-selected for fire testing in Task 4. Finally, the down-selected foam-additive mixtures will be characterized at the molecular scale as described in Task 1 in order to compare the chemical characteristics of novel foam-additive mixtures with previously collected data and further develop out a model for molecular scale mixture characteristics influence on firefighting performance.

Task 4: Fire suppression testing of selected foam-additive mixtures

As described throughout this report, small- and larger-scale fire testing will be conducted in order to assess the time to extinguish and burnback time of foam-additive mixtures down-selected in Task 4. The small-scale fire tests will be utilized as an initial screening to determine if there are any foam-additive mixtures that either stand out as exceptional in improving performance compared to the baseline PFAS-free foam solutions or completely fail in producing a foam that can extinguish the fire. Data from small-scale testing can be utilized for positive feedback into Task 1, where chemical interactions will be studied with a variety of analytical methodologies. This information will be compared to previously collected data and help to further develop an understanding of the relationship between chemical interactions at the molecular scale and firefighting performance.

Larger-scale fire testing (28 ft²) will be conducted in collaboration with Jensen Hughes on further down-selected foam-additive mixtures from small-scale fire testing. The larger-scale fire testing will be conducted as described throughout this report. Dependent on the agreed upon final scope of this effort, even larger-

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

scale fire tests (50 ft²) will be conducted with Jensen Hughes and NRL-CBD on the best performing 1-2 foams at the 28 ft² pan size.

An optional extension of fire testing, which would in parallel expand the scope of tasks 1-3, is considering additional firefighting use cases such as: the presence of seawater, the combustion of fuel mixes, and performance under different ambient conditions such as temperature.

Task 5: Storability and compatibility testing and assessment of manufacture and distribution and scale to meet NDAA goals

As was described in this report, the final assessment of the best performing foam-additive mixtures will be to test their storability and compatibility by conducting accelerated aging experiments. Following the aging process, the foam-additive mixtures will be assessed following the protocol laid out in Tasks 1-4 of the follow-on work plan. The foam-additive mixtures will be assessed at the molecular scale, tested for physical and chemical properties, and undergo fire testing in order to determine how long-term storage and chemical compatibility influences the firefighting ability of the foams. This experimentation will also help to inform an analysis of the ability to manufacture and distribute the foam-additive mixture at scale, including a material cost analysis. A beneficial extension of this work could be to partner directly with PFAS-free foam manufacturers to develop improved formulations, and to determine their capability to scale-up and distribute foam mixture alternatives.

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Strategic Environmental Research and Development Program (SERDP)
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Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

Appendix A – Surface Tension Data

| Concentrate | % Conc | Additive | % Additive | ST |
|-------------|--------|---------------------------------|------------|------|
| GFFF | 3 | octanesulfonic acid sodium salt | 1 | 57.1 |
| GFFF | 3 | octanesulfonic acid sodium salt | 5 | 52.2 |
| GFFF | 3 | octanesulfonic acid sodium salt | 10 | 44.0 |
| GFFF | 6 | octanesulfonic acid sodium salt | 1 | 37.3 |
| GFFF | 6 | octanesulfonic acid sodium salt | 5 | 33.3 |
| GFFF | 6 | octanesulfonic acid sodium salt | 10 | 35.4 |
| GFFF | 3 | dodecanoic acid | 1 | 36.1 |
| GFFF | 3 | dodecanoic acid | 5 | 29.6 |
| GFFF | 3 | dodecanoic acid | 10 | 30.1 |
| GFFF | 6 | dodecanoic acid | 1 | 34.6 |
| GFFF | 6 | dodecanoic acid | 5 | 29.8 |
| GFFF | 6 | dodecanoic acid | 10 | 30.6 |
| GFFF | 3 | dodecanol | 1 | 30.9 |
| GFFF | 3 | dodecanol | 5 | 33.2 |
| GFFF | 3 | dodecanol | 10 | 31.7 |
| GFFF | 6 | dodecanol | 1 | 35.6 |
| GFFF | 6 | dodecanol | 5 | 33.8 |
| GFFF | 6 | dodecanol | 10 | 33.3 |
| GFFF | 3 | Baking Soda | 1 | 35.9 |
| GFFF | 3 | Baking Soda | 5 | 36.6 |
| GFFF | 3 | Baking Soda | 10 | 36.4 |
| GFFF | 6 | Baking Soda | 1 | 36.3 |
| GFFF | 6 | Baking Soda | 5 | 33.9 |
| GFFF | 6 | Baking Soda | 10 | 34.7 |
| GFFF | 3 | Biochar | 1 | 35.3 |
| GFFF | 3 | Biochar | 5 | 33.6 |
| GFFF | 3 | Biochar | 10 | 32.6 |
| GFFF | 6 | Biochar | 1 | 35.0 |
| GFFF | 6 | Biochar | 5 | 31.5 |
| GFFF | 6 | Biochar | 10 | 33.3 |
| GFFF | 3 | Octanoic Acid | 1 | 35.1 |
| GFFF | 3 | Octanoic Acid | 5 | 28.5 |
| GFFF | 3 | Octanoic Acid | 10 | 27.7 |
| GFFF | 6 | Octanoic Acid | 1 | 35.4 |
| GFFF | 6 | Octanoic Acid | 5 | 28.5 |
| GFFF | 6 | Octanoic Acid | 10 | 27.4 |
| GFFF | 3 | Octanol | 1 | 31.2 |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

| | | | | |
|------|---|------------------------|-----|------|
| GFFF | 3 | Octanol | 5 | 27.6 |
| GFFF | 3 | Octanol | 10 | 27.1 |
| GFFF | 6 | Octanol | 1 | 30.9 |
| GFFF | 6 | Octanol | 5 | 27.3 |
| GFFF | 6 | Octanol | 10 | 26.9 |
| GFFF | 3 | dodecane sulfonic acid | 1 | 35.9 |
| GFFF | 3 | dodecane sulfonic acid | 5 | 35.1 |
| GFFF | 3 | dodecane sulfonic acid | 10 | 37.2 |
| GFFF | 6 | dodecane sulfonic acid | 1 | 35.8 |
| GFFF | 6 | dodecane sulfonic acid | 5 | 36.6 |
| GFFF | 6 | dodecane sulfonic acid | 10 | 36.5 |
| GFFF | 3 | N/A | N/A | 34.9 |
| GFFF | 6 | N/A | N/A | 35.0 |
| GFFF | 3 | RDP | 1 | 34.7 |
| GFFF | 3 | RDP | 5 | 34.6 |
| GFFF | 3 | RDP | 10 | 34.1 |
| GFFF | 6 | RDP | 1 | 34.8 |
| GFFF | 6 | RDP | 5 | 34.4 |
| GFFF | 6 | RDP | 10 | 33.1 |
| GFFF | 3 | Magnesium Oxide | 1 | 33.0 |
| GFFF | 3 | Magnesium Oxide | 5 | 33.4 |
| GFFF | 3 | Magnesium Oxide | 10 | 32.3 |
| GFFF | 6 | Magnesium Oxide | 1 | 33.0 |
| GFFF | 6 | Magnesium Oxide | 5 | 32.9 |
| GFFF | 6 | Magnesium Oxide | 10 | 33.8 |
| GFFF | 3 | Octanol | 20 | 26.0 |
| GFFF | 3 | Octanol | 30 | 25.9 |
| GFFF | 3 | Octanoic Acid | 20 | 27.1 |

| Concentrate | Concentrate % | Additive | Additive % of concentrate | Foam Surface Tension |
|----------------|---------------|---------------|---------------------------|----------------------|
| National Foams | 3 | N/A | N/A | 35.53333 |
| National Foams | 3 | Octanol | 5 | 34.2 |
| National Foams | 3 | Octanol | 10 | 32.96667 |
| National Foams | 3 | Octanoic Acid | 5 | 32.96667 |
| National Foams | 3 | Octanoic Acid | 10 | 32.4 |
| National Foams | 3 | Biochar | 5 | 33.46667 |
| National Foams | 3 | Biochar | 10 | 34.2 |
| National Foams | 3 | Dodecanol | 5 | 35.26667 |
| National Foams | 3 | Dodecanol | 10 | 35.8 |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

Appendix B – Foam Expansion Ratio Data

| Concentrate | Concentrate % | Additive | Additive % of concentrate | Foam Expansion Ratio |
|-------------|---------------|---------------------------------|---------------------------|----------------------|
| GFFF | 3 | N/A | N/A | 5.66 |
| GFFF | 6 | N/A | N/A | 6.04 |
| GFFF | 3 | octanesulfonic acid sodium salt | 1 | 6.65 |
| GFFF | 3 | octanesulfonic acid sodium salt | 5 | 6.43 |
| GFFF | 3 | octanesulfonic acid sodium salt | 10 | 6.49 |
| GFFF | 6 | octanesulfonic acid sodium salt | 1 | 9.01 |
| GFFF | 6 | octanesulfonic acid sodium salt | 5 | 8.57 |
| GFFF | 6 | octanesulfonic acid sodium salt | 10 | 7.76 |
| GFFF | 3 | dodecanoic acid | 1 | 8.41 |
| GFFF | 3 | dodecanoic acid | 5 | 9.78 |
| GFFF | 3 | dodecanoic acid | 10 | 7.74 |
| GFFF | 6 | dodecanoic acid | 1 | 7.33 |
| GFFF | 6 | dodecanoic acid | 5 | 8.50 |
| GFFF | 6 | dodecanoic acid | 10 | 9.23 |
| GFFF | 3 | dodecanol | 1 | 7.51 |
| GFFF | 3 | dodecanol | 5 | 5.77 |
| GFFF | 3 | dodecanol | 10 | 6.93 |
| GFFF | 6 | dodecanol | 1 | 6.90 |
| GFFF | 6 | dodecanol | 5 | 6.92 |
| GFFF | 6 | dodecanol | 10 | 8.06 |
| GFFF | 3 | Baking Soda | 1 | 7.29 |
| GFFF | 3 | Baking Soda | 5 | 6.10 |
| GFFF | 3 | Baking Soda | 10 | 7.87 |
| GFFF | 6 | Baking Soda | 1 | 6.17 |
| GFFF | 6 | Baking Soda | 5 | 5.74 |
| GFFF | 6 | Baking Soda | 10 | 7.32 |
| GFFF | 3 | Biochar | 1 | 8.54 |
| GFFF | 3 | Biochar | 5 | 10.42 |
| GFFF | 3 | Biochar | 10 | 10.73 |
| GFFF | 6 | Biochar | 1 | 8.52 |
| GFFF | 6 | Biochar | 5 | 10.46 |
| GFFF | 6 | Biochar | 10 | 10.70 |
| GFFF | 3 | Octanoic Acid | 1 | 8.23 |
| GFFF | 3 | Octanoic Acid | 5 | 9.98 |
| GFFF | 3 | Octanoic Acid | 10 | 8.83 |
| GFFF | 6 | Octanoic Acid | 1 | 5.69 |
| GFFF | 6 | Octanoic Acid | 5 | 7.24 |

Strategic Environmental Research and Development Program (SERDP)
Core Solicitation FY22
JHU/APL Proposal Entitled, Functional Additives to Enhance PFAS-Free Fire Suppressants
Proposal #WP22-C2-3284

| | | | | |
|------|---|------------------------|-----|-------|
| GFFF | 6 | Octanoic Acid | 10 | 7.88 |
| GFFF | 3 | Octanol | 1 | 10.01 |
| GFFF | 3 | Octanol | 5 | 10.77 |
| GFFF | 3 | Octanol | 10 | 12.13 |
| GFFF | 6 | Octanol | 1 | 9.74 |
| GFFF | 6 | Octanol | 5 | 9.06 |
| GFFF | 6 | Octanol | 10 | 10.77 |
| GFFF | 3 | dodecane sulfonic acid | 1 | 9.95 |
| GFFF | 3 | dodecane sulfonic acid | 5 | 10.77 |
| GFFF | 3 | dodecane sulfonic acid | 10 | 12.67 |
| GFFF | 6 | dodecane sulfonic acid | 1 | 9.76 |
| GFFF | 6 | dodecane sulfonic acid | 5 | 10.81 |
| GFFF | 6 | dodecane sulfonic acid | 10 | 12.59 |
| GFFF | 3 | N/A | N/A | 10.44 |
| GFFF | 6 | N/A | N/A | 9.29 |
| GFFF | 3 | RDP | 1 | 10.10 |
| GFFF | 3 | RDP | 5 | 11.61 |
| GFFF | 3 | RDP | 10 | 12.39 |
| GFFF | 6 | RDP | 1 | 15.35 |
| GFFF | 6 | RDP | 5 | 12.55 |
| GFFF | 6 | RDP | 10 | 14.20 |
| GFFF | 3 | Magnesium Oxide | 1 | 10.25 |
| GFFF | 3 | Magnesium Oxide | 5 | 12.18 |
| GFFF | 3 | Magnesium Oxide | 10 | 11.46 |
| GFFF | 6 | Magnesium Oxide | 1 | 12.31 |
| GFFF | 6 | Magnesium Oxide | 5 | 13.76 |
| GFFF | 6 | Magnesium Oxide | 10 | 12.78 |

| Concentrate | Concentrate % | Additive | Additive % of concentrate | Foam Expansion Ratio |
|----------------|---------------|---------------|---------------------------|----------------------|
| National Foams | 3 | N/A | N/A | 8.592296 |
| National Foams | 3 | Octanol | 5 | 15.66638 |
| National Foams | 3 | Octanol | 10 | 11.38551 |
| National Foams | 3 | Octanoic Acid | 5 | 3.700701 |
| National Foams | 3 | Octanoic Acid | 10 | No foam |
| National Foams | 3 | Biochar | 5 | 7.571251 |
| National Foams | 3 | Biochar | 10 | 7.303332 |
| National Foams | 3 | Dodecanol | 5 | 7.918104 |
| National Foams | 3 | Dodecanol | 10 | 6.501347 |

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Appendix C – Viscosity Data

| Foam | % | Additive | % | R1 | R2 | R3 | R1 | R2 | R3 | Average | STD |
|------|---|------------------------------------|----|--------|------------|------------|--------------|--------------|--------------|-------------|---------|
| GF | 6 | Stock | 0 | 511 | 526 | 558 | 1.459 927 | 1.502 782 | 1.594 206 | 1.518971667 | 0.06859 |
| GF | 3 | Stock | 0 | 420 | 415 | 413 | 1.199 94 | 1.185 655 | 1.179 941 | 1.188512 | 0.01030 |
| GF | 3 | Dodecanesulfonic Acid | 10 | 418 | 417 | 409 | 1.194 226 | 1.191 369 | 1.168 513 | 1.184702667 | 0.01409 |
| GF | 3 | Dodecanesulfonic Acid | 5 | 406 | 407 | 405 | 1.159 942 | 1.162 799 | 1.157 085 | 1.159942 | 0.00286 |
| GF | 3 | Biochar | 5 | 412 | 408 | 414 | 1.177 084 | 1.165 656 | 1.182 798 | 1.175179333 | 0.00873 |
| GF | 3 | Biochar | 10 | 412 | 417 | 436 | 1.177 084 | 1.191 369 | 1.245 652 | 1.204701667 | 0.03618 |
| GF | 3 | Octanesulfonic acid sodium salt | 5 | 118 | 118 | 122 | 1.217 76 | 1.217 76 | 1.259 04 | 1.23152 | 0.02383 |
| GF | 3 | Octanesulfonic acid sodium salt | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00000 |
| GF | 3 | Baking soda | 5 | 397 | 414 | 416 | 1.134 229 | 1.182 798 | 1.188 512 | 1.168513 | 0.02983 |
| GF | 3 | Baking soda | 10 | 385.00 | 391. 00 | 393. 00 | 1.10 | 1.12 | 1.12 | 1.11 | 0.01 |
| GF | 3 | Octanoic Acid | 10 | 131.21 | 132. 69 | 132. 54 | 1.35 | 1.37 | 1.37 | 1.36 | 0.01 |
| GF | 3 | Octanoic Acid | 5 | 117.00 | 120. 00 | 119. 00 | 1.21 | 1.24 | 1.23 | 1.22 | 0.02 |
| GF | 3 | Octanoic Acid | 1 | 440.00 | 440. 00 | 430. 00 | 1.26 | 1.26 | 1.23 | 1.25 | 0.02 |
| GF | 3 | Dodecanoic acid | 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 3 | Dodecanoic acid | 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 3 | Dodecanol | 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 3 | Dodecanol | 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 3 | Octanol | 1 | 443.00 | 444. 00 | 444. 00 | 1.27 | 1.27 | 1.27 | 1.27 | 0.00 |
| GF | 3 | Octanol | 5 | 533.00 | 541. 00 | 542. 00 | 1.52 | 1.55 | 1.55 | 1.54 | 0.01 |
| GF | 3 | Octanol | 10 | 242.20 | 243. 51 | 244. 93 | 2.42 | 2.44 | 2.45 | 2.44 | 0.01 |
| GF | 6 | Dodecanesulfonic Acid | 10 | 557.00 | 530. 00 | 539. 00 | 1.59 | 1.51 | 1.54 | 1.55 | 0.04 |
| GF | 6 | Dodecanesulfonic Acid | 5 | 535.00 | 550. 00 | 534. 00 | 1.53 | 1.57 | 1.53 | 1.54 | 0.03 |
| GF | 6 | Biochar | 5 | 467.00 | 491. 00 | 475. 00 | 1.33 | 1.40 | 1.36 | 1.36 | 0.03 |

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| | | | | | | | | | | | |
|----|---|---------------------------------|----|---------|---------|---------|------|------|------|------|------|
| GF | 6 | Biochar | 10 | 443.00 | 464.00 | 455.00 | 1.27 | 1.33 | 1.30 | 1.30 | 0.03 |
| GF | 6 | Octanesulfonic acid sodium salt | 5 | 157.00 | 155.00 | 156.00 | 1.62 | 1.60 | 1.61 | 1.61 | 0.01 |
| GF | 6 | Octanesulfonic acid sodium salt | 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 6 | Baking soda | 5 | 508.00 | 525.00 | 516.00 | 1.45 | 1.50 | 1.47 | 1.48 | 0.02 |
| GF | 6 | Baking soda | 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 6 | Octanoic Acid | 10 | 503.05 | 514.29 | 515.02 | 5.19 | 5.31 | 5.32 | 5.27 | 0.07 |
| GF | 6 | Octanoic Acid | 5 | 178.00 | 176.00 | 177.00 | 1.84 | 1.82 | 1.83 | 1.83 | 0.01 |
| GF | 6 | Octanoic Acid | 1 | 150.00 | 150.00 | 149.00 | 1.55 | 1.55 | 1.54 | 1.54 | 0.01 |
| GF | 6 | Dodecanoic acid | 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 6 | Dodecanoic acid | 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 6 | Dodecanol | 5 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 6 | Dodecanol | 10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| GF | 6 | Octanol | 1 | 574.00 | 589.00 | 588.00 | 1.64 | 1.68 | 1.68 | 1.67 | 0.02 |
| GF | 6 | Octanol | 5 | 602.00 | 598.00 | 606.00 | 1.72 | 1.71 | 1.73 | 1.72 | 0.01 |
| GF | 6 | Octanol | 10 | 1091.00 | 1114.00 | 1102.00 | 3.12 | 3.18 | 3.15 | 3.15 | 0.03 |
| NF | 3 | Stock | 0 | 101.00 | 100.00 | 103.00 | 1.04 | 1.03 | 1.06 | 1.05 | 0.02 |
| NF | 3 | Biochar | 5 | 354.97 | 355.50 | 354.67 | 1.01 | 1.02 | 1.01 | 1.01 | 0.00 |
| NF | 3 | Biochar | 10 | 101.00 | 96.00 | 102.00 | 1.04 | 0.99 | 1.05 | 1.03 | 0.03 |
| NF | 3 | Dodecanol | 5 | 356.96 | 355.26 | 354.63 | 1.02 | 1.01 | 1.01 | 1.02 | 0.00 |
| NF | 3 | Dodecanol | 10 | 359.00 | 374.00 | 379.00 | 1.03 | 1.07 | 1.08 | 1.06 | 0.03 |
| NF | 3 | Octanol | 5 | 364.09 | 363.05 | 363.14 | 1.04 | 1.04 | 1.04 | 1.04 | 0.00 |
| NF | 3 | Octanol | 10 | 358.00 | 358.00 | 369.00 | 1.02 | 1.02 | 1.05 | 1.03 | 0.02 |
| NF | 3 | Biochar & Octanoic Acid | 5 | 458.00 | 469.00 | 484.00 | 1.31 | 1.34 | 1.38 | 1.34 | 0.04 |

APPENDIX D - JHU/APL Transmittal Letter

April 28, 2023

RESEARCH AND EXPLORATORY DEVELOPMENT
REDD-2023-318

Strategic Environmental Research and Development Program (SERDP)
4800 Mark Center Drive
Suite 16F16
Alexandria, VA 22350-3605

Attention: Dr. John La Scala, Program Manager, Weapons Systems and Platform
Subject: JHU/APL Limited Scope Final Report
Reference: (a) Contract No. W912HQ22P0049, WP22-3284, Functional Additives to Enhance PFAS-Free Fire Suppressants

Dear Dr. La Scala,

The Johns Hopkins University Applied Physics Laboratory (JHU/APL) is pleased to provide the Limited Scope Final Report, which has been submitted through SEMS. The information provided supports the task assignment VQE15 under Contract W912HQ22P0049.

If you have any questions or comments, please contact me at (240) 228-9433 or via e-mail Marisa.Hughes@jhuapl.edu.

Sincerely,



Marisa J. Hughes, PhD.
Assistant Program Manager
Biological & Chemical Sciences Program