FINAL REPORT

Aqueous Film Forming Foams Based on Biodegradable Natural Surfactants and Additives

SERDP Project WP20-1535

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The objective of this Limited Scope Research work is the development of non-fluorinated, biodegradable bio-derived film-forming composite formulations based on parts of plantain that can be used instead of toxic and bio-persistent polyfluorinated firefighting foams. The aim was to develop firefighting products that meet the performance requirements specified in MIL-F-24385F, which are also environmentally compatible and non-toxic.

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List of Acronyms

Acronym	Expanded Form
AFFF	Aqueous Film Forming Foam
DoD	Department of Defense
EDS	Energy-dispersive X-ray spectroscopy
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FFFC	Fire Fighting Foam Coalition
MMI	Materials Modification, Inc.
NMR	Nuclear Magnetic Resonance Spectroscopy
NRL	U.S. Naval Research Laboratory
OECD	Organization for Economic Co-operation and Development
PFAS	Per/polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PI	Principal Investigator
POC	Point of Contact
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
WP	Weapons Systems and Platforms

Keywords
AFFF, Banana, Biopersistance, C-8, Fire, foam, fuel, PFAS, PFOA, PFOS, Siloxanes.

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Abstract

Introduction and Objectives

The objective of this Limited Scope Research work is the development of non-fluorinated, biodegradable bio-derived film-forming composite formulations based on parts of plantain that can be used instead of toxic and bio-persistent polyfluorinated firefighting foams. The aim was to develop firefighting products that meet the performance requirements specified in MIL-F-24385F, which are also environmentally compatible and non-toxic.

Technical Approach

A natural product that is inherently resistant to fire is plantain. Various parts of plantain, including fibers, stems, leaves, and banana peels, are fire-resistant and completely biodegradable. Plantain sap has been reported to contain, in addition to various glycosides, dopamine, which has been reported to be a flame retardant. In this project, plantain sap and cellulose-derived from banana peels were mixed in various ratios with siloxane and hydrocarbon surfactant in the fluorine-free AFFF formulation and were tested for surface tension, foam formation, stability, and gasoline pool firefighting efficiency.

Results

The banana sap containing a mixture of organic chemicals did not exhibit pool fire quenching properties. The banana peel powders contained potassium as the major inorganic content and, as such, did not contribute to the firefighting. Water-soluble cellulose derived from banana peel powder was tested as a foam stabilizing additive to siloxane and hydrocarbon surfactants in the PFAS-free firefighting foam formulations. The banana peel-derived cellulose demonstrated low viscosity than commercial polysaccharide additives and excellent firefighting capability when mixed with conventional surfactants. The banana-cellulose mixed surfactant formulations could potentially replace AFFF formulations with scaled-up production of banana-cellulose powders and optimization of the PFAS-free formulations towards meeting the Mil-Spec standard.

Benefits

PFAS-free pool firefighting foams have considerable financial, socio-economic, public health, and environmental advantages over bio-persistent and toxic AFFF products. The new formulations based on plantain developed in this effort are compatible with environmental regulations while having the potential to meet the Mil-spec standard. This limited scope initiative has demonstrated that readily biodegradable natural products could be used in the firefighting formulations if modified into a water-miscible form. The natural product-based formulations can result in PFAS-free Class B foams in fighting against liquid fuels with further research work and the optimization of the formulation.

Executive Summary

Aqueous film-forming foams (AFFFs) are extensively used in Class-B firefighting operations against flammable liquid fires because of their effectiveness and ease of application. AFFF foams are extensively used in the U.S. military, as well as in most civilian applications in America, as 3% or 6% concentrates. Despite the effectiveness of the AFFFs, there are increasing concerns about the ecosystem risks with the AFFF products. The objective of this Limited Scope Research work was the development of PFAS-free, biodegradable bio-derived film-forming composite formulations for the replacement of polyfluorinated AFFF formulations. Natural, biodegradable, and environmentally non-damaging components for firefighting formulations based on plantain plant parts were evaluated in combination with other PFAS-free surfactants. The chemical extracted from the banana peels was evaluated for composition, surface tension, and as an additive to surfactants in the firefighting formulations. The chemical extract was not effective against fuel fire due to the lack of any fire quenching ingredients such as phosphorus and higher surface tension >30 mN/m. Therefore, an alternative approach of using cellulose derived from banana peels in the firefighting formulation was investigated. The cellulose derived from banana peel was chemically modified to a water-soluble formulation. The banana-peel-derived modified cellulose successfully quenched the gasoline fuel fire in a benchtop setup when mixed with low surface tension surfactants. Therefore, banana-peel-derived cellulose products could be a potential additive in the firefighting surfactants to improve foam stability and firefighting performance.

Introduction

New biodegradable, fluorine-free formulations for firefighting foams developed in this project will enable complete replacement of polyfluorinated AFFF formulations currently used in order to meet environmental requirements and ensure the safety of DoD personnel at airfields and onboard ships. This work addresses the F.Y. 2020 STATEMENT OF NEED (SON) topic Number: WPSON-20-A1 of the Strategic Environmental Research and Development Program (SERDP) under the Weapons Systems and Platforms (WP) Program Area.

Objectives

The objective of this Limited Scope Research work is the development of non-fluorinated, biodegradable bio-derived film-forming composite formulations based on banana stem sap and cellulose derived from banana peels. The aim was to develop firefighting products that meet the performance requirements specified in MIL-F-24385F. The product developed were also environmentally compatible and non-toxic with higher spreading coefficient, and low bio-persistency.

Background:

Aqueous film-forming foams (AFFFs) are extensively used in Class-B firefighting operations against flammable liquid fires because of their effectiveness and ease of application. AFFF foams are extensively used in the U.S. military, as well as in most civilian applications in America, as a 3% or 6% concentrate. The concentrate is usually mixed with either fresh or seawater and applied with a nozzle to form a foam layer on top of the burning fuel.

The fluorinated surfactants in AFFF agents provide a positive spreading coefficient and enable film formation on top of the burning fuel, thus cutting off the oxygen supply to it. The ability of a foam to coat the surface of the fuel is given by the spreading coefficient), which is calculated as (surface tension of fuel) – (surface tension of foam) – (interface tension between foam and fuel). Thus, the interfacial surface tension of the foam solution must be lower than the surface tension of the fuel that is burning [Table 1] [1].

Table 1: Surface tension of some common fuels

Fuel	**SFT (20-24 ^{o}C) mN/m**
Gasoline	20.7
Cyclohexane	24.95
F-34	25.8
Jet fuel	26.7
Diesel	28.3
Biodiesel	31.5

Additives such as water glass, graphite, heavy spar (barite), or silicones may be added to the formulations in order to further enhance the effectiveness of firefighting through the formation of crust and chart [2]. Chelating additives are also added to enable foam formation even when mixed with hard or seawater [3].

Despite the effectiveness of the AFFFs, there are increasing concerns about the ecosystem risks with these materials. A 1994 ecosystem risk assessment for foam extinguishing agents found that direct run-off of AFFFs into water bodies results in the destruction of aquatic life due to excessive biological and chemical oxygen demand [4]. AFFFs are persistent chemicals that accumulate in the blood of humans and other animals. The U.S. Congress recently passed legislation (FAA Reauthorization Act of 2018 (HR 302)), directing the Federal Aviation Administration to change its requirement that airports use firefighting foam containing highly fluorinated chemicals [5]. While newer short-chain fluorosurfactants have been introduced into the market since 2000, their toxicity and their persistence in the environment are not well established and still are under investigation. This necessitates the development of non-fluorinated alternatives to current AFFF foams [6].

In recent years, research has shown that other classes of surfactants, like siloxane [7] and, more recently, ionic liquid-based surfactants [8], can also form films on the militarily relevant fuels. Their complex synthetic processes, however, remain a problem. Researchers from the University of Cologne developed a simpler method to synthesize siloxane surfactant, but the surfactant was less effective in terms of film formation than previous formulations [9]. In an earlier SERDP funded work, MMI developed carbohydrate functionalized siloxanes [Figure 1] with promising results [10].

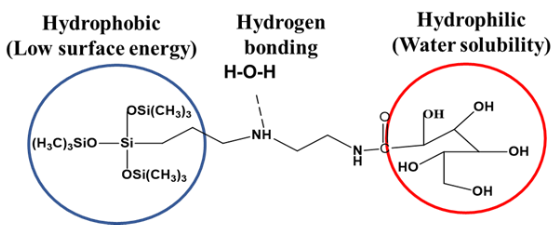

Figure 1. Structure of trifunctional molecule with hydrophobic/hydrophilic ends

In addition, MMI has assisted CertainTech Inc. in a DoD-funded effort to produce and test polyoctahedral silsesquioxanes ("POSS") based surfactants as fire-stopping foam materials [11]. While MMI's own PFAS-free and CertainTech's POSS-based formulations offer the basics and knowledge for developing fluorine-free foams, such composites entailed a primary hydrophobic polymeric backbone of siloxane, which themselves degrade very slowly.

The need, therefore, is the development of alternate film-forming materials that are as effective as the fluorinated and siloxane-based surfactants, without the associated ecological issues.

A firefighting foam, as mentioned earlier, is made of several constituents – a film-forming component and additives that can enhance the fire resistance of the composite formulation and increase stability/foaming behavior.

In this work, **natural, biodegradable, and environmentally non-damaging components** for firefighting formulations based on plantain plants were evaluated in combination with fluorine-free surfactants. PFAS-free film-forming materials for firefighting applications must meet the requirements of MIL-F-24385F, in terms of fire suppression performance, in order to ensure personnel safety and viability of the system. Materials development, therefore, included rigorous specification performance tests to capture the range of challenging fire situations.

Natural fire-retardant additive

There are many flame-retardant additives that are added to a variety of products, and most of them are hydroxides of magnesium and aluminum, borates, and organo-halogen and organophosphorus compounds. In moving towards more environmentally friendly products, it is attractive to use biodegradable, non-toxic, and safe additives.

A natural product that is inherently resistant to fire is the part of the plantain plant. In some parts of rural India, the plantain pseudostem fiber, blended with natural dyes, is used in making fire-resistant and waterproof goods such as handbags, doormats, purses, papers, and cloth. The layers of the pseudostem are also used to put out small fires. The plantain pseudostem is greaseproof, fire-resistant, and completely biodegradable.

There are few studies reported on the cotton coating with sap derived from plantain pseudostem to impart fire resistance to it [12][13][14]. Plantain sap has been reported to contain, in addition to various glycosides, dopamine [15], which has been reported to be a flame retardant [16]. Additionally, the flame retardancy of plantain pseudostem may be attributed to the presence of calcium and sodium phosphates and magnesium, calcium, and potassium chloride, all of which could enhance char formation and retard fire. The char morphology of the treated cotton fabric shows a thick intumescent coating with the presence of long-chain aromatic compounds [17].

In this project, plantain plant sap was mixed in various ratios of surfactants in the PFAS-free firefighting formulations and was tested for firefighting efficiency.

Cellulose as a film-forming polymer

The natural product that has widely been studied for film-forming surfactant use is protein. Protein-based firefighting foam was first developed in the 1930s, and since then, there have been further developments that have led to compounds like Regular Protein (R.P.) foams that are known to provide post-fire security through the production of a homogeneous, stable foam blanket that has excellent heat resistance, and drainage characteristics. However, the surface tension of foam fluids is around 55 mN m^{-1} at total protein concentrations of 10 μg ml^{-1} [18]. This is insufficient for use in firefighting applications. Film Forming Fluoro-protein foam has been developed by combining fluorochemical surfactants with protein foam [19], but this obviously uses fluorinated products that we are seeking to avoid.

The film-forming behavior of cellulosic polymers has been recently recognized [20], [21], but their potential in film-forming firefighting applications has not been investigated in the literature. Cellulose-based polymeric surfactants have attractive properties such as associative characteristics in water as well as good rheological and surface-active properties caused by the adsorption behavior at the interface. Cellulose-based surfactants were synthesized as early as the 1980s by modification of hydrophilic cellulose backbones with hydrophobic long alkyl chains [22], [23]. An interesting earlier study has shown that the surface tension of epoxidized soybean oil grafted hydroxyethyl cellulose was as low as 26 mN m^{-1}[24]. This is again insufficient for use in Class B firefighting because the interfacial surface tension must be below 20 mN/m.

The modification of cellulose is thus necessary in order to decrease the interfacial surface tension to 20 mN/m and lower. Combining it with non-polar silicone derivatives can induce a new combination of properties, which could reduce the surface tension values to below 20mNm^{-1}.

In this project, cellulose derived from banana peels was modified to be miscible in water. The banana cellulose mixed surfactant formulations were prepared and evaluated for pool firefighting application.

Materials and Methods

Materials

Banana and banana stems were purchased from local grocery stores. Siloxane surfactants were synthesized in-house. Gasoline fuel was purchased from Merrifield Citgo or Costco, Fairfax, VA gas stations.

Surface Tension Measurements

The surface tension of the foam formulations was measured using the pendant drop method. Rame-hart Model 250 goniometer/tensiometer was used to collect the surface tension data. About 2 mL of the test liquid was delivered through a Teflon needle into an external atmosphere (air), and the liquid drop image was recorded and analyzed using DROPimage Advanced software. The surface tension of the test formulation was obtained from the data collected from a drop in air.

Benchtop Fire Testing

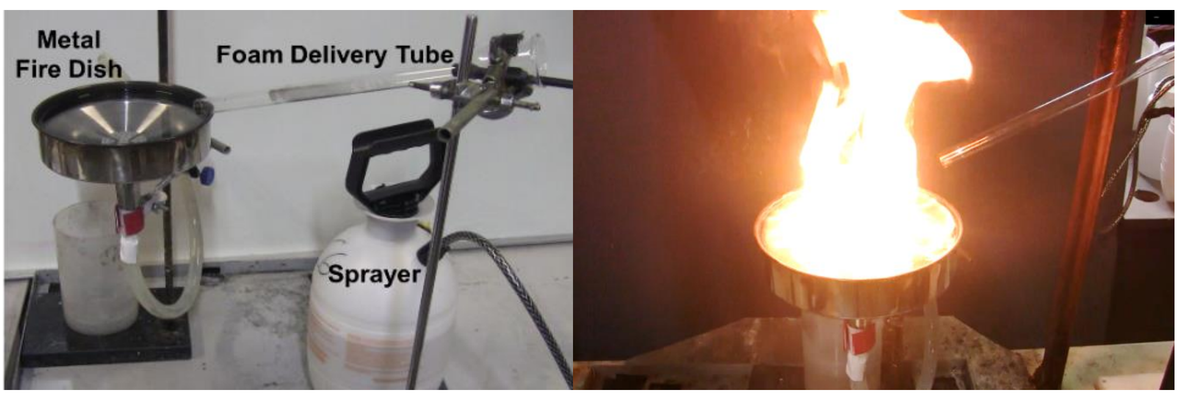

Figure 2. Photographs of the bench-top setup designed in-house.

Bench-top firefighting testing was conducted to down-select the best performing Banana-based fluorine-free formulations. This test was conducted using in-house facilities. MMI has modified the benchtop test unit extensively from the first-generation set-up previously built with the direction provided by U.S. Naval Research Laboratory (NRL) scientists [25]. The benchtop fire testing apparatus consists of a 248-cm^2 (18-cm diameter) area stainless steel funnel (instead of glass dish) with a tube connected at the bottom to collect the drained liquid. The foam was generated using a pump-sprayer instead of a sparger. The pressure in the sprayer was maintained by pumping air 25 times. This pressure resulted in the foam flow rate of 1000 mL/min. This process eliminated the use of sparger to generate foam bubbles. Another advantage of the sprayer method was that it avoided the problem of particles clogging from banana/cellulose powders. Foam flow rate, expansion ratio, and time to extinguish the fire were monitored during the fire testing. A small-scale fire test setup is provided in Figure 2. The foam generated was applied to a 1 cm-thick layer of gasoline stainless steel dish (the large-mouth funnel). The flame was lit and was allowed to burn for 1 minute before applying the foam. The video was recorded, and the extinguishing time was measured in seconds.

Technical Approach

In this limited scope SERDP project, a Class B firefighting formulation that consisted of banana sap and banana cellulose with low-surface tension surfactants was developed.

The tasks were driven by the following hypotheses:

(a) Silicone grafted cellulose derived from bananas can produce films with surface tension below 20 mNm^{-1}.
(b) Cellulose derived from plantain parts such as stem and peels can be used as additives.
(c) Plantain sap has good flame resistance properties and can be mixed with the cellulosic surfactant to enhance flame resistance

Accordingly, the hypotheses-driven tasks were organized as under:

(a) Synthesis of silicone-grafted cellulose and assessment of its film-forming capabilities.
(b) Extraction of plantain sap through hydraulic milling and solvent extraction processes and assessment of its fire-retardant properties.
(c) Synthesis of dispersible cellulose derived from plantain parts through the introduction of polar functional groups and assessment of its fire-retardant properties.
(d) Formulation of the eco-compatible foam through various combinations of banana sap or banana cellulose and low-surface tension surfactants and assessment of their firefighting properties.

Results and Discussion

Synthesis of Silicone Grafted Cellulose

Cellulose acetate was dissolved in a solution consisting of acetone and dimethylformamide. 15-18% methyl hydro siloxane-(dimethylsiloxane) copolymer was added. Subsequently, a drop of platinum catalyst was also added. The solution was allowed to stir at room temperature for 1 hour and was poured into a petri dish and allowed to dry for a period of 24 hours. Photographs of the films formed are provided in Figure 3.

Figure 3. The film with a lower amount of siloxane (left). The film with a higher amount of siloxane (right)

Unfortunately, the polymer film formed

was insoluble in water. This approach was not pursued further because the siloxane-functionalized cellulose was not amenable to preparing water-based foam formulations.

Extraction of Sap from Banana Stem

The banana stem was blended, and then the sap was filtered using a cheesecloth and squeezing the blended stem. The pH of the sap was 7. The sap was then roto-evaporated to extract the water and obtain dried banana sap. The process steps are provided in Figure 4.

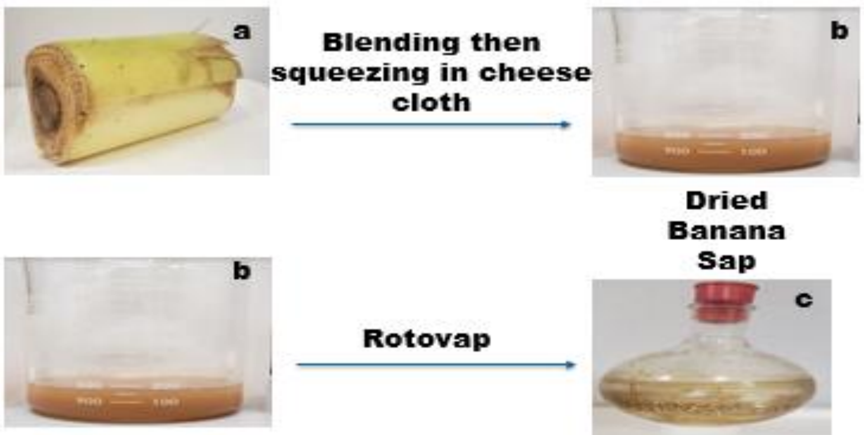

Figure 4. Process of sap extraction from the banana stem (a) to banana sap (b) and then finally dried banana sap (c).

Table 2. Banana Sap extraction data

Experiment #	Banana Stem (g)	Banana Sap Extracted (g)	Dried Banana Sap Extracted from 50g Sap (g)
1	387.25	214.44	2.63
2	429.00	162.19	1.82

The dried banana sap was only 0.6% of the starting banana stem. The concentration of banana sap was low and may result in scale-up issues. The surface tension of 1% solution of dried banana sap was measured. The data is detailed in Tables 3 and 4. The surface tension values were high and, therefore, could not be used as such to replace fluorinated surfactants in the foam formulations. Therefore, efforts were focused on using banana sap with traditional low surface tension surfactants.

Table 3. Surface Tension of as-prepared Banana Sap

Experiment #	Banana Sap (g)	Surface Tension (mN/m)
1	10	33.15 (±0.3)

Table 4. Surface Tension of 1% of Dried Banana Sap Aqueous Solution

Experiment #1	Dried Banana Sap %	Surface Tension (mN/m)
1	1	42.81 (±0.5)

Foam Stability of 1% Dried Banana Sap Solution

A 1% solution of banana sap was prepared with a variety of surfactants such as Dowsil 501W, trisiloxane, Ninol (a cochin oil based amide, Cocamide diethanol amide), sodium lauryl ether sulfate (SLES), and a commercial soap detergent. To test the foam stability of formulations, the foam solutions were generated in a vial by shaking the vial, and 1cm of foam was extracted and placed on top of gasoline, which was in another vial. 3g of gasoline in a 20ml vial is equivalent to 1cm. The time that it takes for all of the foam to dissipate was recorded in seconds. The foam stability data are provided in Tables 5 to 9.

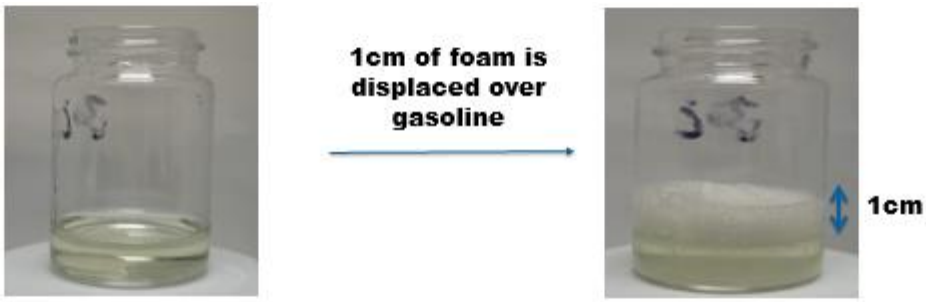

Figure 5. Foam stability testing setup

Table 5. Foam Stability of 1% Dried Banana Sap Solution and Trisiloxane

Dried Banana Sap %	Trisiloxane %	Foam Stability Time (s)
1.0	1.0	79
1.0	2.0	120
1.0	3.0	162

Table 6. Foam Stability of 1% Dried Banana Sap and Dowsil 501W

Dried Banana Sap %	Dowsil 501W %	Foam Stability Time (s)
1.0	1.0	33
1.0	2.0	25
1.0	3.0	20

Table 7. Foam Stability of 1% Dried Banana Sap Solution and SLES

Dried Banana Sap %	SLES %	Foam Stability Time (s)
1.0	1.0	42
1.0	2.0	30
1.0	3.0	35

Table 8. Foam Stability of 1% Dried Banana Sap and Commercial Detergent

Dried Banana Sap %	Commercial Detergent %	Foam Stability Time (s)
1.0	1.0	91
1.0	2.0	117
1.0	3.0	131

Table 9. Foam Stability of 1% Dried Banana Sap and Ninol

Dried Banana Sap %	Ninol %	Xanthum Gum %	Foam Stability Time (s)
1.0	1.0		54
1.0	2.0		41
1.0	3.0		440 (7:20)
2.0	3.0		741 (12:21)
1.0	3.0	0.2	0

Out of all the foam stability testing conducted, the best performing solutions were 1% dried banana sap paired with either 3% of trisiloxane, Ninol, and commercial detergent. A solution consisting of 2% dried banana sap and 3% Ninol lasted the longest over gasoline.

Unfortunately, none of these formulations were able to quench the gasoline pool fire in a benchtop scale fire testing. Banana sap was not sufficient in concentration to make any impact on the firefighting ability of the surfactants. Therefore, it was decided to extract banana sap from banana peels. Another reason for the change of approach was the scarcity of banana stem products from local grocery markets.

Preparation of Banana Peel Powder

Banana peels were collected and put into a dehydrator overnight. The following day, the dried banana peels were then blended to obtain a powder. Photographs of the steps are provided in Figure 6, and %yield data is provided in Table 10.

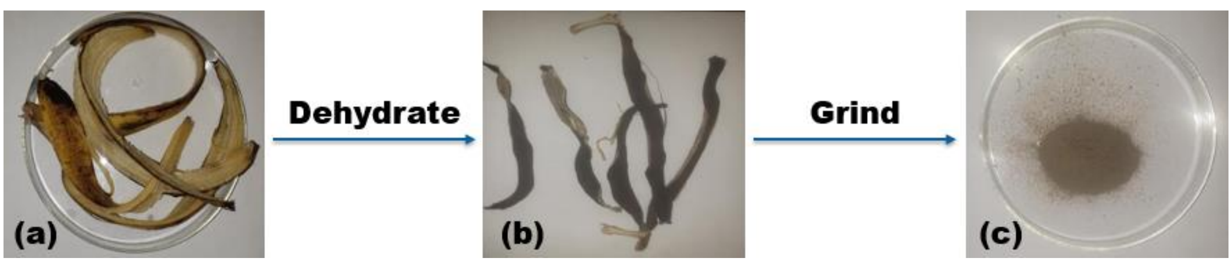

Figure 6. Illustration of banana peels (a), dehydrated banana peels (b), and dehydrated banana peel powder.

Table 10. Banana Peel Powder Data

Experiment #	Banana Peel (g)	Yield (g)	% Yield
1	53.19	7.20	13.5
2	62.59	8.59	13.7
3	93.68	12.65	13.5
4	80.97	11.70	
5	98.19	13.19	
6	66.06	8.25	
7	103.33	13.92	
8	986.47	118.59	12.00

Elemental analysis Banana Peel Powder

The elemental analysis of the as-dried banana peel powder was conducted using energy-dispersive X-ray spectroscopy (EDS). The EDS data is provided in Figure 7. The major elements present in the dried banana powder are carbon, nitrogen, oxygen, potassium, and chlorine. No other inorganic elements were found in the banana peel. This result is different than the statement that banana peel is enriched with the minerals like potassium, phosphorus, magnesium, and calcium [26]. ***Specifically, our EDS data did not show any phosphorus, which is essential for the flame quenching.***

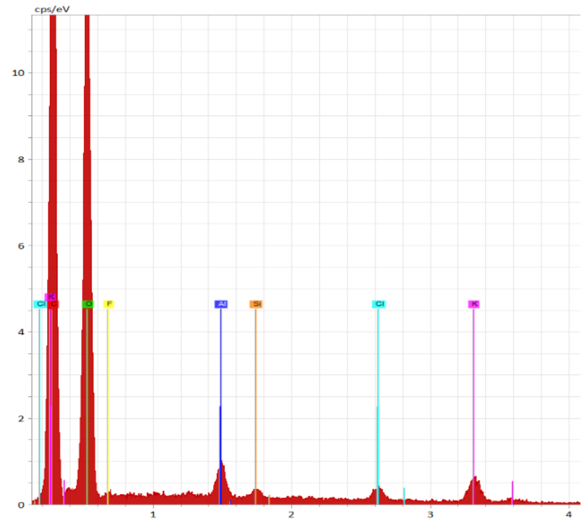

Figure 7. EDS data of the banana peel powder.

Alcohol Extraction of Banana Peel Powder

100 g of banana peel powder was extracted with isopropyl alcohol using a Soxhlet extractor provided in Figure 8. The banana peel powder was placed on a cellulose thimble, and organic materials from the peel powder were continuously extracted using hot isopropyl alcohol for 24 hours. The collection flask was rotary evaporated to remove the excess solvent. The remaining material was a dark, sap-like substance that smelled distinctly of burnt sugar. Sample yield was 1.26 g overall, and when mixed in a 1% solution with distilled water, it did not foam and did not provide any readable surface tension results.

Figure 8. Alcohol extraction of organic chemicals from banana peel powder.

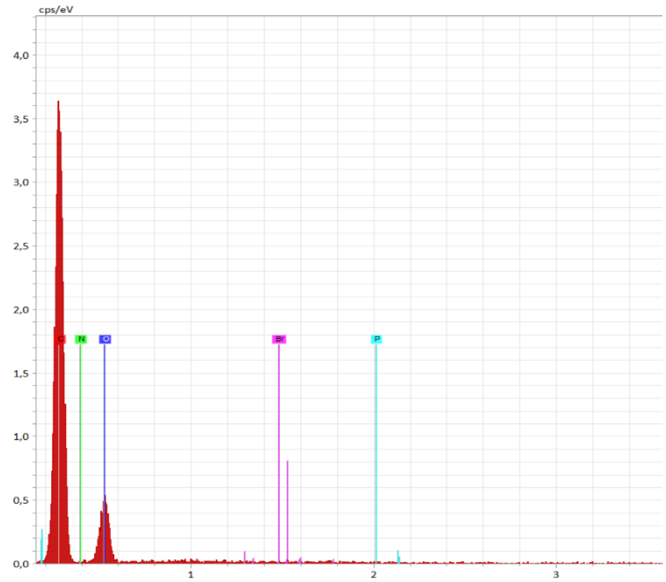

Figure 9. EDS data of the sap extracted from banana peel powder.

The elemental analysis of the alcohol extracted sap conducted using EDS showed no inorganic chemicals due to the extraction alcohol medium. The EDS data also indicates that potassium from the banana peel powder was not extracted during Soxhlet extraction. The EDS data is provided in Figure 9. The extracted sap was soluble in water, and the surface tension was >35 mN/m. We did not conduct further chemical analysis of the sap. However, according to a literature report by Waghmare and Kurhade, the alcoholic extract of the banana peel powder contained eight different organic compounds. The chemicals include Vitamin E (31.3%), 1, 2 Benzene dicarboxylic acid mono (2-ethyl hexyl ester (13.47%), β- tocopherol (11.37%) and estragole (11.18%). These organic chemicals have medicinal values, and their use in fire foam application was unsuccessful. Therefore, we decided to focus on the ***use of banana peel powder and cellulose derived from banana peels***.

Foam Stability Testing of Banana Peel Powder

Banana peel powder was prepared by dehydrating the banana peels then blending them until a fine powder had been formed. This powder was then mixed with various surfactants, including Polysorbate 80 (Tween 80) and Dowsil 501W polytrisiloxane to evaluate the effect of banana-peel powders on the firefighting capability of conventional surfactants.

Since banana peel powder does not foam on its own, it was necessary to add foaming agents and/or surfactants to the formulation to see the effects on foam stability. In order to test foam stability, approximately 3 mL of foam was placed on 3g of gasoline in a small vial. The stability time was measured to be the time in seconds that it took from the initial placement of the foam on the gas surface to the first appearance of gasoline through the foam (when there is no longer a full layer of foam on the surface of the gasoline).

Foam Stability Testing of Banana Peel Powder with Dowsil 501W and Glucopon 225

500 mL of tap water was mixed with 2g of Dowsil 501W and 4g of Glucopon 225. 10 mL of this mixture was placed in a vial along with various concentrations of banana peel powder. The vial was then ultrasonicated and allowed to cool down before it was agitated and the foam was formed. Table 11 displays the foam stability times for various formulations.

Table 11. Foam Stability of Banana Peel Powder, Dowsil 501W, and Glucopon 225 Formulations

Banana Peel Powder	Foam Stability Time (s)
0%	96
1%	15
1.5%	28
2%	70
2.5%	6
3%	27
3.5%	6
4%	Insufficient amount of foam
5%	Didn't foam

When 0.4% Dowsil alone was tested, there was insufficient foam produced in order to conduct foam stability testing. When 0.4% Dowsil and 0.8% banana peel powder (both ultra-sonicated and not ultra-sonicated) were tested, there was an insufficient amount of foam produced in order to conduct foam stability testing. Dowsil and/or banana powder on their own did not foam sufficiently enough, so the addition of Glucopon 225 surfactant was necessary to conduct the foam stability testing. Based on the data, it seemed that the addition of banana peel powder was detrimental to the foam stability time of the Glucopon and Dowsil formulations. Therefore, other surfactants were tested for their stability times with banana peel powder.

Foam Stability Testing of Banana Peel Powder with Ninol (Cocamide DEA)

50g of water was mixed with both 0.5g and 1g of banana peel powder to form 1% and 2% banana peel solutions, respectively. These were then ultra-sonicated for 5-10 minutes and allowed to cool to room temperature. Approximately 10 mL of these solutions were placed in a vial according to the amount of Ninol (0.1, 0.2, and 0.3g). The vial was then agitated, and the foam produced was placed on top of gasoline. The foam stability times for these various solutions are seen in Table 12.

Table 12. Foam Stability of Banana Peel Powder and Ninol Formulations

Banana Peel Powder	Ninol	Foam Stability Time (s)
0%	1%	64
0%	2%	64
0%	3%	71
1%	1%	55
1%	2%	57
1%	3%	435, 455* Without sonication: 227
2%	1%	30

2%	2%	49
2%	3%	138, 485*

*Repeated trials were done in some cases to ensure that the results could be replicated.

Banana peel powder, in addition to the Ninol surfactant formulation, seems to increase the foam stability, particularly in 3% Ninol solutions.

A firefighting test was attempted for 2% banana powder and 3% Ninol. Unfortunately, the banana powder clogged the sprayer and prevented the flow of foam. Therefore, the fire testing did not provide any practical data. Further stability testing and surface tension measurements need to be conducted on filtered banana peel powder in water.

Foam Stability of Banana Peel Powder and a Commercial Detergent

The foam stability times for the commercial dish soap and the banana peel powder were tested. 10 mL of the solution was placed in a vial according to the amount of the commercial dish soap and agitated to create a foam. The resulting foam stability time can be seen in Table 13.

Table 13. Foam Stability of Banana Peel Powder and the Commercial Dish Soap Formulations

Banana Peel Powder	Commercial Dish Soap	Foam Stability Time (s)
0%	1%	57
0%	2%	96
0%	3%	56
1%	1%	197
1%	2%	334
2%	1%	66
2%	2%	115

The addition of banana powder improved the foam stability of the foam formulation. It is interesting to note that the effect of banana powder varies with the type of surfactants.

Filtered Banana Peel Powder and Ninol

Various filtration methods were tested in order to determine the solution that was free of particulates and had the best stability time. Filtered banana peel powder was prepared, placing the desired amount of banana peel powder in a liter of water and stirring on a stir plate overnight. This was subsequently ultrasonicated 3-4 times in 10-minute increments in a glass beaker. It was then filtered using a cheesecloth to remove the large particulates.

Based on the solution with the best foam stability time, 2% filtered banana powder solution and 3% Ninol were tested. This can be seen in Table 14.

Table 14. Foam Stability Time of Various Levels of Filtration for Banana Peel Powder Solutions

Banana Peel Powder	Percent Ninol	Foam Stability Time (s)
0%	3%	170
2% (unfiltered)	3%	350
2% (filtered using sieve)	3%	387

2% (filtered using cheesecloth)	3%	270

Filtered Banana Peel Powder and Cocamidopropyl Betaine

A 2% banana peel powder solution was tested for foam stability with various concentrations of Cocamidopropyl betaine surfactant. The foam stability and surface tension measurements of these solutions can be seen in Table 15.

Table 15. Foam Stability of Banana Peel Powder and Cocamidopropyl Betaine Formulations

Banana Peel Powder	Cocamidopropyl Betaine	Foam Stability Time (s)	Surface Tension (mN/m)
0%	0%	---	71
2%	0%	---	43
2%	1%	27	27.67
2%	1.5%	40	30.61
2%	2%	38	28.48
2%	2.5%	30	30.99
2%	3%	24	31.61

*--- indicates that there was no foam generated. The first row is testing tap water.

The foam stability of Cocamidopropyl Betaine is very poor and not suitable for fire testing.

Fire Testing of Banana Peel Powder

Selective foams with banana peel powder was fire tested on gasoline fuel with a sparger setup. The foam flow rate was 1 L/min. The foam expansion coefficient measured was 12.8. The foam was unable to fill the dish surface and was unable to quench the flame. There was a film at the surface of the gasoline that was likely excess banana powder. The foam itself dispersed from the gas layer into the water layer. This indicates that the powder broke the gasoline layer. This formulation may have had excess banana powder. One method to overcome this would be to attempt to isolate the cellulose in the banana peel and convert it into a **water-soluble formulation**. One approach is to extract cellulose from banana stems and peels and use them in foam formulations to increase foam stability.

Extraction of Cellulose Fibers from Banana Stem Pulp

Initial attempts were made on using banana stem to extract cellulose. A 1L solution consisting of 10g of sodium hydroxide dissolved in 1L of water was prepared. 50g of banana stem pulp was added to this solution. The mixture was then heated to 100℃ for 6 hours. Then the pulp was washed with water until pH 7 was achieved. The pulp was then suspended in a solution consisting of 35g of sodium hypochlorite (bleach) dissolved in 1L of water. The mixture was allowed to sit and stir for 24 hours at room temperature. The pulp was again washed with water to obtain a pH of 7. Then the pulp was suspended in another solution made by dissolving 175g of sodium hydroxide in 1L of water. The mixture was allowed to sit for 1 hour at 60℃. The weight of the remaining product was then determined and stored in a cool environment.

Table 16. Banana Stem Pulp Cellulose Extraction Data

Experiment #	Banana Stem Pulp (g)	Yield (g)
1	50	1.49
2	50	4.93
3	100	1.61
4	100	0.49

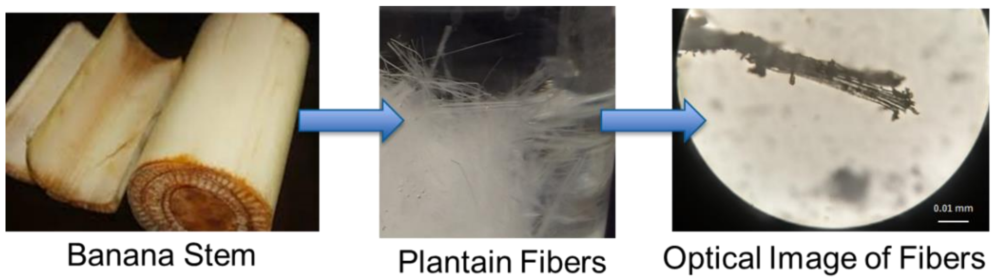

Figure 10. Photographs of cellulose fibers derived from banana stem

The cellulose derived from the banana stem was in the form of long fibrils as shown in Figure 10. The cellulose fibrils were not amenable for grinding into fine powders. ***The fibrils were not dispersible in water and could not be used as such in the foam formulations. Therefore, it was decided not to pursue the use of banana stem in the foam formulations. The scarcity of banana stem for the research work (probably due to lack of imports from abroad influenced by Covid) also made it difficult to work with the banana stem.*** Therefore, it was decided to extract cellulose powders from banana peels which were readily available.

Cellulose Powder Extraction from Banana Peel Powder

To extract the cellulose from the banana peel powder, a procedure from "extraction and properties of cellulose from banana peel" was followed [27]. First, to extract the fat from the banana peel powder, 20 g of banana peel powder was soaked in 200 mL of 90% ethanol solution. This solution was then mixed for 2 hours in a 50 °C hot bath. The sample was then filtered and rinsed 3 times with distilled water through centrifuging and removing the supernatant fluid. This was then left overnight to dry at 60 °C.

To extract the protein from the banana peel powder, the resulting powder was then soaked in approximately 300 mL of 11.6 pH NaOH solution. This solution was then mixed at 50 °C overnight. The sample was then filtered and rinsed 3 times with distilled water through centrifuging and removing the supernatant fluid. This was then left overnight to dry at 60 °C. This resulting powder was ground into a relatively fine powder and sieved.

To remove the lignin, the sample was then bleached using a 15% hydrogen peroxide solution soaked for 3 hours. Bleach could also be used in this step. This process was repeated twice, once with 20g and another time with 40g of banana peel powder. The resulting mass after each stage can be seen in Table 17.

Table 17. Extraction of Cellulose from Banana Peel Powder

Mass of banana peel powder (g)	Mass after fat extraction (g)	Mass after protein extraction (g)
20	11.6	6.17
40	33.55	21.91

The reaction time and reactant concentrations were to be optimized to increase the cellulose yield.

Synthesis of Water-Soluble Cellulose from Synthetic Cellulose

Since cellulose is typically water-insoluble, chemical modifications were made to the as-extracted cellulose to allow better miscibility in water. This was first tested with synthetic cellulose to determine the appropriate process for introducing water miscible functional groups to cellulose. 25g of cellulose was mixed with 480 mL of 50:50 isopropanol and ethanol mixture. After specific chemical treatments the resulting liquid was then filtered through vacuum filtration and rinsed with 70% ethanol to produce a yellow powder. The yield was 70.77g. However, the solid was found to be insoluble in water or alcohol.

This procedure above was also conducted with 50:50 isopropanol: water, 100% water, and 100% ethanol mixtures. The solubility and pH of the resulting solutions can be seen in Table 18.

Table 18. Solubility and pH of Water Dispersible Cellulose Synthesized in Various Solvent Mixtures

Solvent Mixture	Solubility in water	Solubility in ethanol	pH in water	pH in ethanol
50:50 isopropanol: ethanol	Insoluble	Insoluble	---	---
50:50 isopropanol: water	Partially soluble	Insoluble	12	8-9
100% water	Partially soluble	Partially soluble	10-11	8
100% isopropanol	---	---	---	---

*--- indicates that there was insufficient and/or unreliable data collected for those values.

Preparation of Water Dispersible Cellulosefrom banana cellulose

The use of a 50/50 Water/IPA mixture for the synthesis of Banana Cellulose derivative resulted in water-insoluble products and, therefore, not suitable for the preparation of foam solutions. Therefore, the method was modified by using a 10/90 Water/IPA mixture as the solvent for the chemical treatments, which resulted in water dispersible cellulose derivatie (Banana-CL)

<u>Banana cellulose derivative obtained was more soluble in water than commercially available cellulose derivatives</u>. The viscosity of the 30% banana cellulose solution was <5 cP compared to >800 cP of similar commercial cellulose derivative as provided in Figure 11.

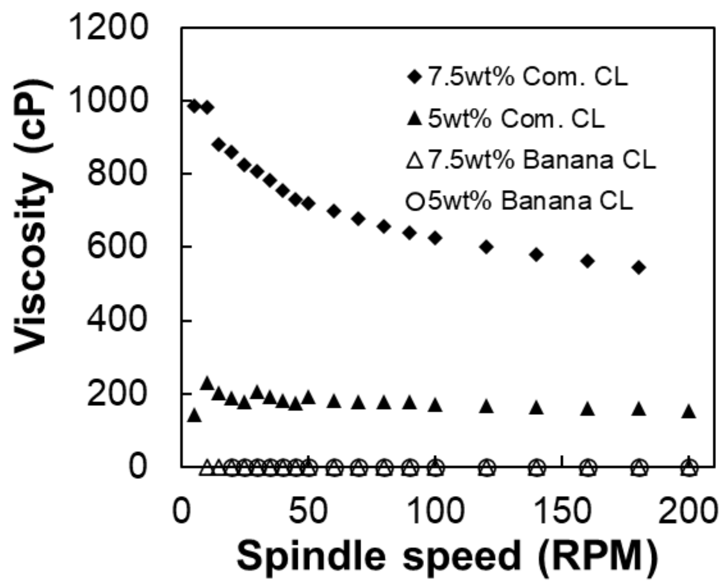

Figure 11. Viscosity data of Banana Cellulose (Banana CL) and Commercial Cellulose (Com. CL) derivatives

Therefore, banana-CL solutions with higher concentration can be produced without **high viscosity issues that are persistent with polysaccharide-based foam formulations.**

Solution 1: 2% Banana-CL, 1.5% siloxane surfactant

Components:

1) 40.00 g Banana-CL
2) 2.0 L distilled H_2O
3) 30.00 g siloxane surfactant

Solution 1:

The measured expansion ratio for solution 1 was 2.02, and based on the foam stability test conducted in a 10 ml vial, formed a film above the gasoline layer, preventing any vapors from escaping the vial. The foam took over 14 minutes to break the seal.

When applied to the benchtop fire test setup, the foam took about 12 seconds to fill the fire dish surface and was able to quench the fire in only 35 seconds. The foam was thick and light enough to float along the gasoline surface in one cohesive unit, from sprayer nozzle to dish surface. The time-lapse images of the fire test are provided in Figure 12.

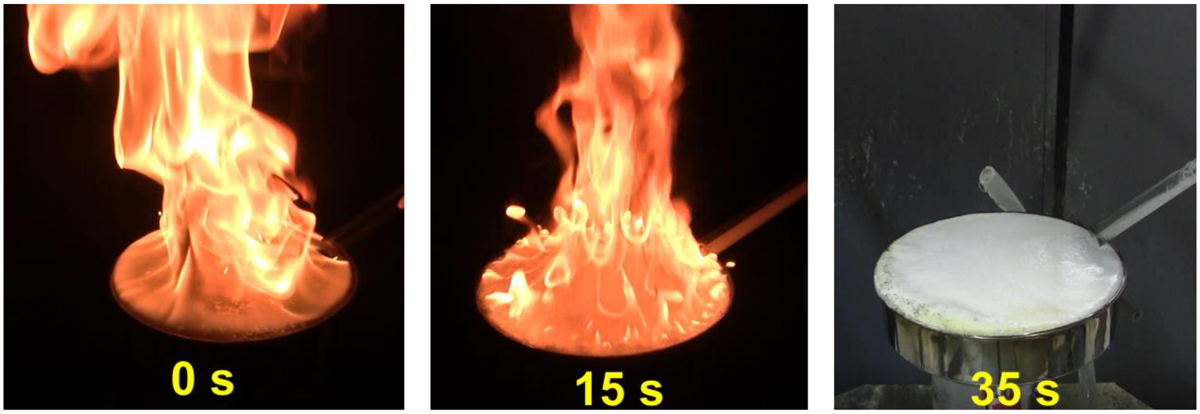

Figure 12. Time lapse images of benchtop fire testing of Banana cellulose stabilized foams

Solution 2: 3% Banana-CL, 1.5% siloxane surfactant

Components:

1) 60.00 g Banana-CL
2) 2.0 L distilled H_2O
3) 30.00 g siloxane surfactant

The foam expansion for solution 2 was 2.3. The foam stability was over 25 minutes. When applied to the fire test setup (3 cm of gasoline on top of 6 cm water, burning for 60 seconds before application of foam), the solution took around 9 seconds to fill the fire dish surface and was able to quench the fire in over 60 seconds (Figure 13), which was considerably longer than the lower concentration solution that preceded it. There are a number of factors that could have led to this result, but it could be inferred that the higher viscosity of the formulation may have an effect on the sealing quality of the foam. Therefore, it is critical to balance the surfactant to foam stabilizer (Banana CL) to achieve greater firefighting performance.

Figure 13. Time lapse image of benchtop fire testing of banana cellulose foam formulations

Preparation of silated banana-Cellulose

The banana-Cellulose can be used as an additive in foam formulations. However, it will be helpful if it can be directly converted into a surfactant. Therefore, banana-Cellulose produced was reacted with aminopropyl tri siloxane in methanol. The aqueous solution of silated banana-Cellulose was foaming. However, the surface tension was 32.86 (±0.01) mN/m. Further experiments will be conducted to reduce the surface tension of silated banana-Cellulose.

Conclusions and Implications for Future Research and Benefits

- No flame quenching inorganic chemicals were identified in the banana peel; however, cellulose derived from the banana peel can be modified as a surfactant by suitable functionalization.
- Optimization of cellulose extraction and functionalization resulted in low-viscosity cellulose derivative than commercially available products.
- Banana cellulose demonstrates high solubility in water and efficient foam generation with PFAS-free surfactants.
- Banana cellulose increased the foam stability of siloxane and hydrocarbon surfactants on gasoline and improved the firefighting performance of PFAS-free foam formulations.
- Since this was a limited scope effort much was learned on the capability of the use of banana sap and of modifying the cellulose derived from the banana. Future detailed efforts can use the cellulose derived through this method treated with other chemicals to enhance the quenching and flame extinguishing capabilities.

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