Aqueous Film Forming Foams Based on Biodegradable Natural Surfactants and Additives

Project Number WP20-1535

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14. ABSTRACT

The technical objectives of this project are listed below:
- Development of non-fluorinated, biodegradable bioderived film-forming composite formulations based on banana plant for AFFF.
- A natural product that is inherently resistant to fire is the plantain pseudostem (reported to contain phosphates, glycosides, dopamine???).
- Plantain pseudostem sap will be mixed in various ratios with surfactants in the fluorine-free AFFF formulation and will be tested for firefighting efficiency
- Nano fibrillated plantain pseudostem has good flame resistance properties and can be used as additives.
- Plantain pseudostem sap has good flame resistance properties and can be mixed with the cellulosic surfactant to enhance flame resistance
- Spreading coefficient and Benchtop fire suppression testing to downselect the formulations and additives
- 28-ft² fire performance to demonstrate the potential of the formulation to meet the MIL-F-24385F standard., and biodegradability

15. SUBJECT TERMS

PFAS, Surfactant, AFFF, PFAS-free firefighting formulations, PFAS-Free alternative

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Project Team

- **T.S. Sudarshan - Materials Modification Inc.**
- **Kris Rangan- Materials Modification Inc.**

Background

- The project Period: September 2020-2022
- Statement of Need (SON) Number #: SON-WP20-A1

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.

Background

- All parts of banana plant are flame retardant (Leaves, and stem) (Not a tree but herb)
- Banana sap has been used to put out fires in many Asian countries
- Growing groves of banana trees around CA towns could help reduce wild fires.
- Bananas suppose to contain many nutrients/minerals, fiber, potassium that help with its properties

Two approaches:

- ➢ Banana sap from stem and banana peel could be used directly as an additive in PFAS-free foams.
- ➢ Cellulose extracted from banana peel powder has good film forming capabilities, good surface properties and can be made into a biodegradable surfactant

Technical Objectives

- **Development of non-fluorinated, biodegradable bio-derived film-forming composite formulations based on banana plant for AFFF.**

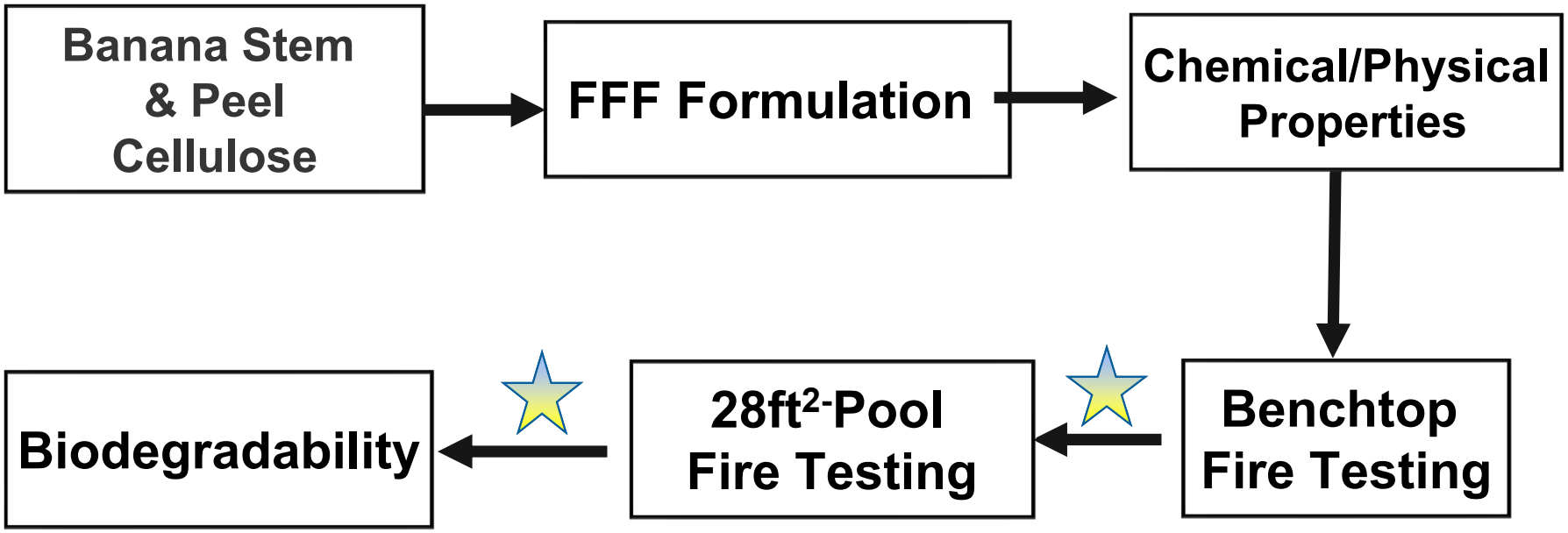
- **A natural product that is inherently resistant to fire is the plantain pseudostem (reported to contain phosphates, glycosides, dopamine???).**

- **Plantain pseudostem sap will be mixed in various ratios with surfactants in the fluorine-free AFFF formulation and will be tested for firefighting efficiency**

Technical Objectives

- **Nano fibrillated plantain pseudostem has good flame resistance properties and can be used as additives.**
- **Plantain pseudostem sap has good flame resistance properties and can be mixed with the cellulosic surfactant to enhance flame resistance**
- **Spreading coefficient and Benchtop fire suppression testing to downselect the formulations and additives**
- **28-ft² fire performance to demonstrate the potential of the formulation to meet the MIL-F-24385F standard., and biodegradability**

Technical Approach



Technical Approach

Activity / Months	1	2	3	4	5	6	7	8	9	10	11	12	13-24
1. Materials Procurement													
2. Synthesis and characterization of banana cellulose													
3. Synthesis and characterization of nanofibrillated plantain pseudostem													
4. Formulation of film-forming foam concentrate and testing													
5. Biopersistance Testing													
6. LifeCycle Assessment													
7. Reporting and planning for future R&D													
8. Contingencies in project performance													

Results

Extraction of Banana Sap

Banana Stem

Blending then squeezing in cheese cloth

Banana Sap

Banana Sap

Rotovap

Dried Banana Sap

Banana Stem was acquired from a grocery store

Banana Sap Data

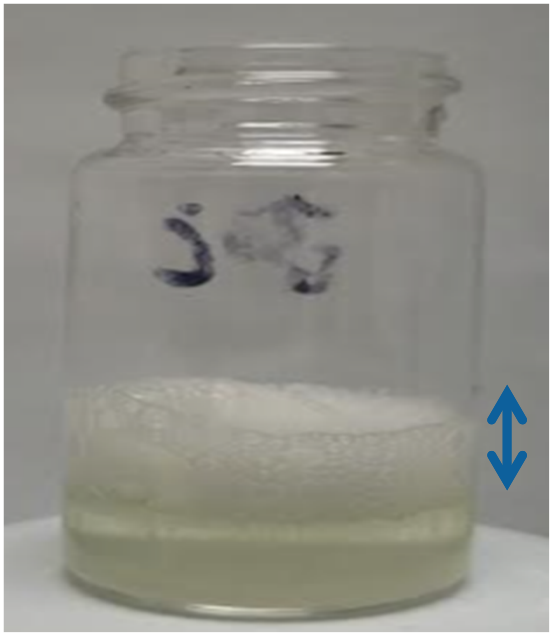
Banana Stem (g)	Banana Sap Extracted (g)	Dried Banana Sap Extracted from 50g Sap (g)
429.00	162.19	1.82

Banana Sap (g)	Surface Tension
10	33.15 (±0.3)

Dried Banana Sap %	Surface Tension of 1% Solution
1	42.81 (±0.5)

Foam Stability Testing Apparatus

1cm of foam



- 3g of gasoline was inserted to a 20ml vial in order to make a 1cm layer
- Then 1cm of foam is displaced on top of the gasoline surface
- Finally, the time when all foam has deteriorated was recorded

Foam Stability Data with Banana Sap

Banana Sap (g)	Trisiloxane %	Foam Stability Time (s)
20	0.5	15
20	1.0	60
20	1.5	165
20	3.0	400

Banana Sap (g)	Dowsil 501W %	Foam Stability Time (s)
20	0.5	26
20	1.0	17
20	1.5	37
20	2.0	0
20	2.5	15
20	3.0	10

Banana Sap Paired with a 3% solution of trisiloxane performed the best

Foam Stability Data with Dried Banana Sap

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

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

Dried banana sap and trisiloxane did not fair as well as non dried banana sap

Foam Stability Data with Dried Banana Sap

Dried Banana Sap %	Sodium Lauryl Ether Sulfate %	Foam Stability Time (s)
1.0	1.0	42
1.0	2.0	30
1.0	3.0	35

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

Neither 501W or Sodium Lauryl Ether Sulfate performed well with dried banana sap

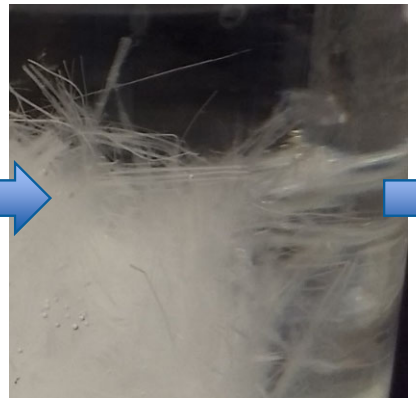
Foam Stability Data with Dried Banana Sap

Dried Banana Sap %	Ninol%	Xanthan 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

Dried banana sap paired with a 3% COCOAMIDE MIPA (Ninol) foamed the best

Extraction of Cellulose from Banana Stem

Banana Stem



Plantain Fibers

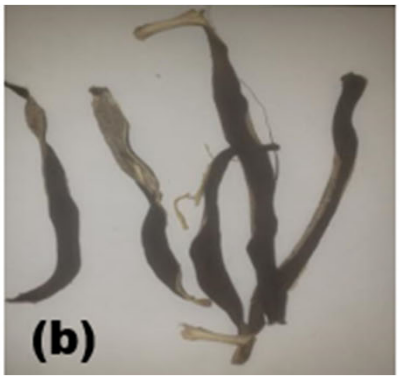
Optical Image of Fibers

Plantain cellulose fibers were difficult to grind and disperse in a solution. Therefore, further work was conducted using banana peel.

Banana Peel Powder

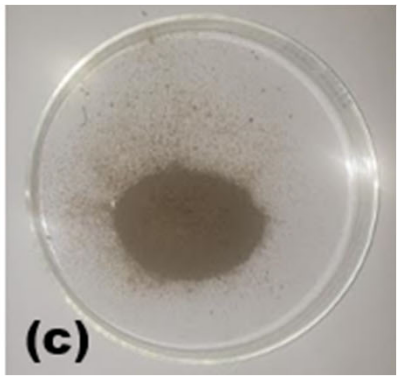
Banana peel

Dehydrate

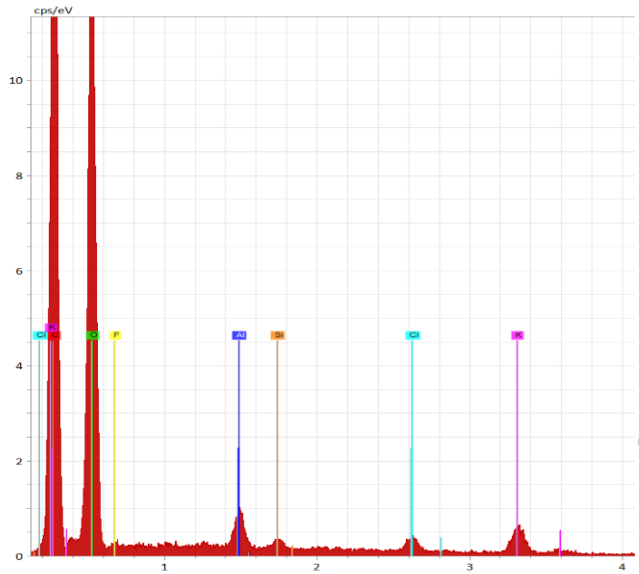


Dried Banana peel

Grind



Banana peel powder
12% Yield



EDS data of the banana peel powder

The major elements are carbon, nitrogen, oxygen, potassium and chlorine. No other inorganic elements found in the banana peel. This result was different than the statement that banana peel is enriched with the minerals like potassium, phosphorus, magnesium and calcium.

Banana Peel Powder as Additive

- **Banana peel powder + Polysorbate 80 + Dowsil 501W polytrisiloxane surfactant + Water**
- **The foam formulation was tested on gasoline pool fire. 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 banana powder.**
- **Isolated the cellulose in the banana peel and modify it to be a water-soluble formulation.**

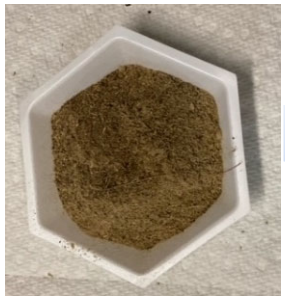
Banana Cellulose

- **Banana peel powder + Polysorbate 80 + Dowsil 501W polytrisiloxane surfactant + Water**
- **The foam formulation was tested on gasoline pool fire. 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 banana powder.**
- **Isolation of the cellulose in the banana peel and modify it to be a water-soluble formulation.**

Banana Cellulose (CL)

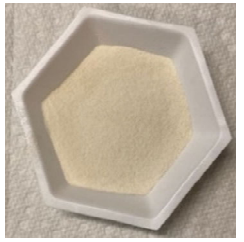
Dried Banana

Ground powder



Ethanol Extraction

NaOH Treatment



After bleaching

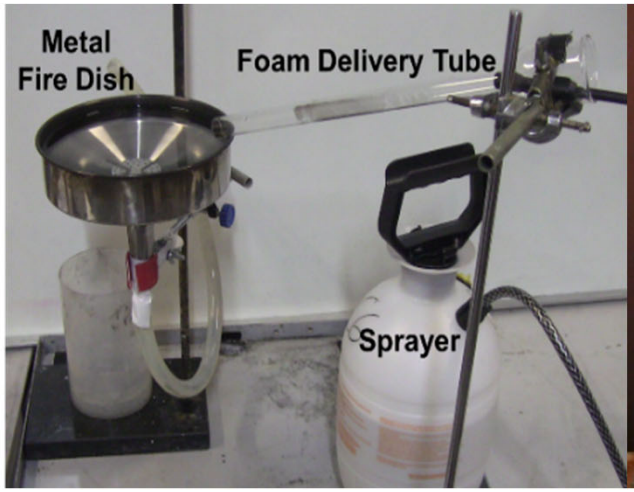
Chemical Treatment

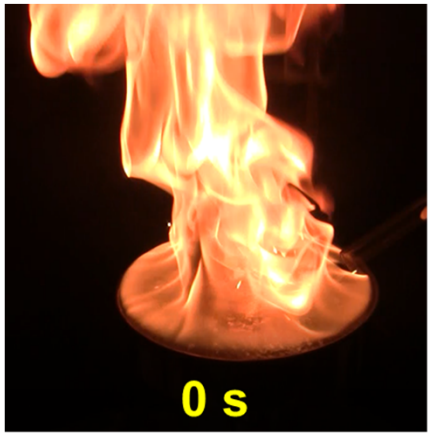
Water Soluble Cellulose (Banana CL)

~ 5% Yield

1kg peel yields about 50 g of water soluble cellulose

Fire Testing





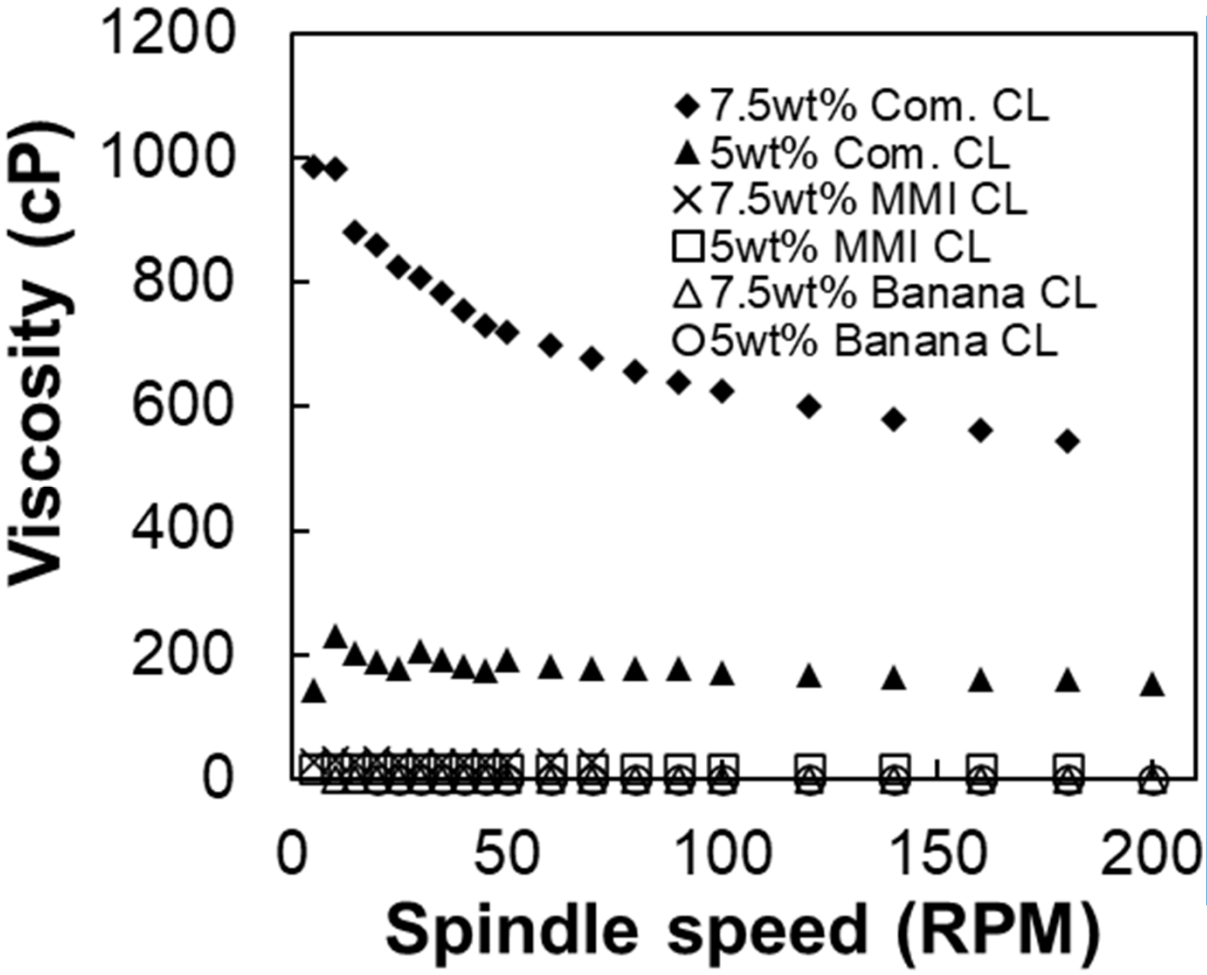
- Sparger was replaced with pump sprayer
- Glass container was replaced with a SS container for pool fire.
- This new benchtop fire testing setup mimics the MilSpec nozzle closely, with little aeration in foam production.

Fire Testing Data

Composition	Banana CL (g)	Trisiloxane Surfactant (g)	Water (g)	% Banana CL	% Trisiloxane Surfactant	Quench Time (s)
1	40.00	30.00	2000	2	1.5	**37**
2	60.00	30.00	2000	3	1.5	**82**
3	20	25	1000	2	2.5	**23**
4	10	10	1000	1	1	**-**
5	15	15	1000	1.5	1.5	**162**
6	17.5	15	1000	1.75	1.5	**101**

Fire Testing Data (Demo)

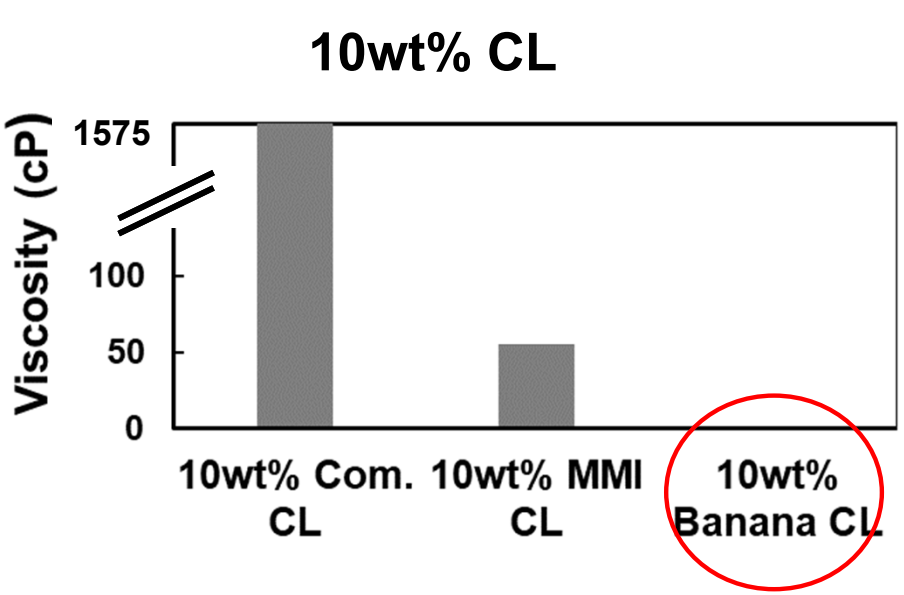
Viscosity Data

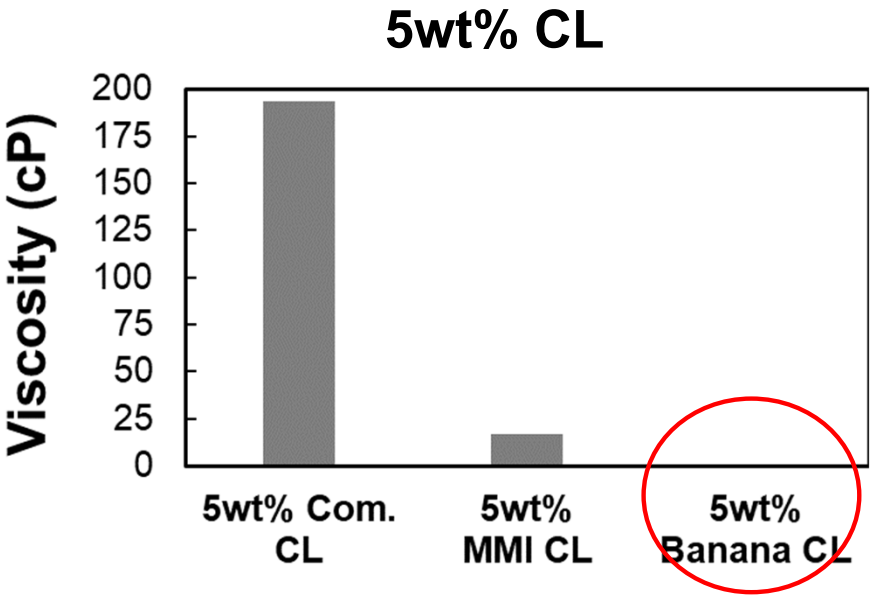


- Viscosity of banana peel derived cellulose product (Banana CL) was a fraction of commercial cellulose product with similar concentration.
- Utilized the approach from this project to produce a cellulose product (MMI-CL)
- Low viscosity banana cellulose products stabilized trisiloxane surfactant foams on top of gasoline.

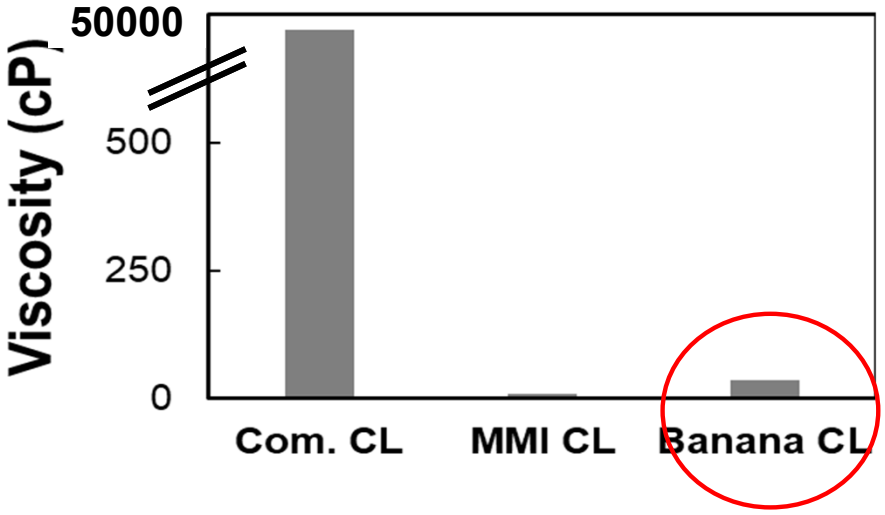
Banana CL is an excellent bio-derived additive for fire fighting foams.

Viscosity Data





Data for the 6% Concentrate



CL= Cellulose Product

Key Points

- Banana cellulose demonstrated solubility in water with low viscosity (<5 cP)
- Efficient foam generation and stability with trisiloxane surfactants.
- No flame quenching inorganic elements (P, S) were identified in the banana peel.
- Banana-derived cellulose could be used as additives in PFAS-free formulations

Next Steps

- Yield of Banana Peel → Cellulose Derivative = 5% (1 kg of peel provides 50 g of Cellulose powder). Large scale production of Banana CL needs to be investigated.
- Further characterization of Banana CL such as Molecular weight, chemical structure etc. can provide further insight into the functioning of Banana CL as an additive to PFAS-free foams.
- Investigation of Banana CL as a replacement of viscous polysaccharide (Xanthan gum) in commercial PFAS-free products
- Different types of banana may have different cellulose content and yield.

Technology Transfer

None at this time based on Limited Scope Research effort.

Future Research

- Investigation of mechanism to understand how such low viscosity is produced and how that helps in flame suppression in trisiloxane surfactant formulation.
- Need to do a limited scope effort in understanding how bioderived cellulose from other banana varieties or other plants can be potential surfactants for trisiloxane or other potential PFAS replacements
- Biodegradability needs to be characterized and understood better – we need them to be stable for extended periods of time in the fire trucks

BACKUP SLIDES

WP20-1535: Aqueous Film Forming Foams Based on Biodegradable Natural Surfactants and Additives

Performers: Materials Modification Inc.

Technology Focus

- *Development of biodegradable bio-derived PFAS-free fire fighting formulations based on banana plant*

Research Objectives

- Investigation of Banana sap from stem and banana peel as used additives in PFAS-free firefighting foams.
- Cellulose extracted from banana peel powder as additive to PFAS-free firefighting foams.

• Project Progress and Results

- Banana cellulose demonstrated solubility in water with low viscosity,
- Efficient foam generation and stability with trisiloxane surfactants.
- Banana-derived cellulose could be used as additives in PFAS-free formulations replacing viscous polysaccarides

Technology Transition

- Large scale production of Banana CL
- Investigation of Banana CL as a foam stabilizer in commercial PFAS-free products