EMULSION CHARACTERIZATION STUDY FOR IMPROVED BILGEWATER TREATMENT AND MANAGEMENT

WP18-1114

Dr. Jared Church
Naval Surface Warfare Center, Carderock Division

Project Outbrief
29 April 2022

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14. ABSTRACT

The technical objectives of this project are:
Advance the current understanding of chemically stable emulsions formed in Armed Forces vessels through m ultiscale investigation using innovative micro and macro analytical tools for emulsion characterization and modeling analysis
●Task 1: Scoping Study for Review of Armed Forces Vessels Oil in Water Emulsions
●Task 2: Characterization of Prepared and Extracted Bilgewater Emulsions
●Task 3: Data Analysis, Interpretation and Publication

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Expertise in Navy bilgewater characterization and treatment using chemical, electrochemical, and physical methods and micro and macro scale characterization techniques.

Dr. Woo Hyoung Lee

University of Central Florida – Department of Civil, Environmental and Construction Engineering

Expertise in solution characterization including development of novel microsensors, interfacial tension measurements, and colloid imaging.

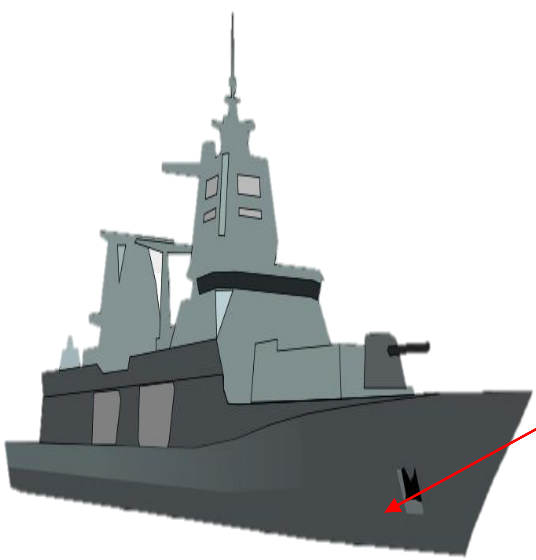
Dr. Jeffrey Lundin

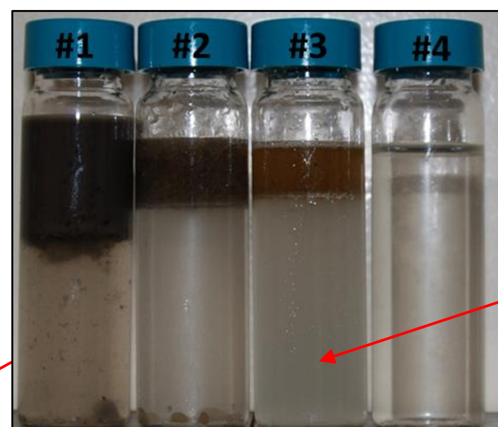
Naval Research Laboratory – Chemistry Division

Expertise in solution characterization and chemical analysis including differential scanning calorimetry (DSC), zeta potential and emulsion size distribution, nuclear magnetic resonance (NMR) spectroscopy, and liquid chromatography-mass spectroscopy (LC-MS).

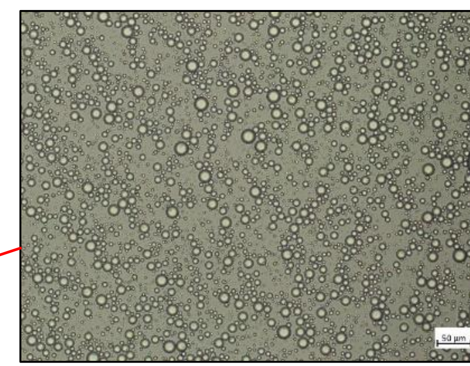
Background

- WPSON-18-C1, Advancing Emulsion Science for Application in Armed Forces Vessels
  - Bilgewater is a regulated shipboard wastewater composed of seawater, various fuels, lubrication oils, cooling water, and other pollutants → Oil discharge limited to 15 parts per million
  - Emulsions generated in bilgewater make the removal of oil more difficult
  - Improved understanding of bilgewater emulsions will inform treatment system selection, operation profiles, and problematic cleaners
- WP18-1114, Emulsion Characterization Study for Improved Bilgewater Treatment and Management initiated in 2018





Bilgewater samples from four Navy ships



Oil-in-Water Emulsion

Technical Objective

Advance the current understanding of chemically stable emulsions formed in Armed Forces vessels through multiscale investigation using innovative micro- and macro- analytical tools for emulsion characterization and modeling analysis

- **Task 1:** Scoping Study for Review of Armed Forces Vessels Oil-in-Water Emulsions
- **Task 2:** Characterization of Prepared and Extracted Bilgewater Emulsions
- **Task 3:** Data Analysis, Interpretation and Publication

Technical Approach

Task 1: Scoping Study for Armed Forces Oil-in-Water Emulsions

- Literature, technical, and regulation review
- Shipboard personnel interviews

Review Article Publication

1. Documentation of common bilgewater contaminants
2. Provides comprehensive and consistent emulsion preparation and analysis techniques
3. Captures industry's "tools-of-the-trade" for emulsion characterization

Task 2: Prepared and extracted solution characterization

A. Neat Detergents:

- Chemical characterization (NMR/LC-MS/GC-MS
- CMC/Interfacial Surface Tension (IFT)
- Zeta potential
- Micelle size (DLS)

B. Prepared Emulsions:

- Surfactant type
- Surfactant Concentration
- CLSM
- Oil concentration
- Microprofiles
- Environmental factors

C. Extracted Bilgewater:

- Chemical characterization (NMR/LC-MS/GC-MS)
- Oil concentration
- Microprofiles
- DSC

Test hypothesis

Identification and characterization of Navy cleaners

Environmental impacts on simulated bilgewater emulsion stability

Role of experimentally determined properties of cleaners on emulsion stability

Extracted bilgewater characterization

Impact of fuel additives on emulsion stability

Machine learning for predicting emulsion stability

Task 3: Fundamental knowledge

1. Correlate data to specific trends
2. Develop mechanisms
3. Test hypotheses

Task 3: Multiparameter analysis

- Fit collected data to an existing or developed analytical model
- Test model

Task 3: Peer-Review Publications

1. Uncommon solution investigated for emulsion stability
2. Novel characterization methods investigated to determine emulsion stability
3. Unique data set applied to existing emulsion stability models

Task 3: Emulsion Stability Database

1. Decision map to identify stabilizing mechanisms
2. Translate stabilizing mechanisms to treatment issues and solutions
3. Inform decision makers of possible repercussions to changes in ship cleaners or treatment time

Results: Characterization of Emulsifiers used on Armed Forces Vessels

- Identified the most common cleaning/surfactant based products found on ships
- Characterized commercial cleaners for emulsion stability properties

Most procured cleaners by the Navy

Cleaner	Primary surfactants	CMC (ppm)	Surface tension (mN/M)	IFT with NSBM#4 (mN/M)	Micelle size (nm)	Zeta Potential (mV)
AFFF 6% (Chem Guard)	• Flourosurfactant (e.g. Capstone 1157)	3,399	15.2 ± 0.2	2.3 ± 0.6	55 ± 2	-24 ± 5
B&B™ 3100 (Vantage)	• Cocamide diethanolamine • 1-buoxyethanol (alcohol ethoxylate)	361	25.0 ± 0.5	7.8 ± 0.1	21 ± 1	-28 ± 6
Super Blast Off (Elsco Inter. Inc.)	• Cocamide diethanolamine	934	27.7 ± 0.5	14.6 ± 0.2	111 ± 7	-63 ± 3
Calla 855 (Zip-Chem Products)	• Alcohol ethoxylate (c10-c14) • Cocamide diethanolamine • Capriloamphorionate	328	27.3 ± 0.3	5.7 ± 1.1	5 ± 2	-39 ± 8
Power Green (LHB Industries)	• Surfactant blend	3,824	26.1 ± 0.7	3.5 ± 0.4	7 ± 5	-13 ± 3
PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	• Alcohol ethoxylate	1,871	30.5 ± 0.1	1.3 ± 0.3	6 ± 1	-13 ± 2
Solid Surge Plus NP (Ecolab # 6117905)	• Alcohol ethoxylate (c12-16)	98	27.4 ± 0.3	7.3 ± 0.1	23 ± 5	-15 ± 4
Type 1 Detergent (MILSPEC: MIL-D-16791)	• Alkyl aryl polyether alcohol	87	30.2 ± 0.4	2.5 ± 0.3	18 ± 1	-28 ± 6

Extracted Bilgewater Characterization

Approach: Bilgewater extracts from three different Navy ships were analyzed for various water quality parameters using standard methods.

Results:

- Samples collected from three U.S. Navy vessels in late Spring 2019
- Quality of bilgewater can range significantly from sample to sample, which can make emulsion management difficult
- The variability of bilgewater quality was similar to what has been reported in literature

Extracted bilgewater samples

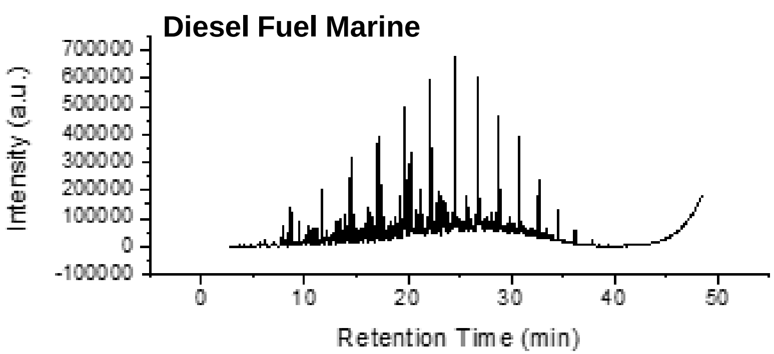
Properties of extracted bilgewater samples

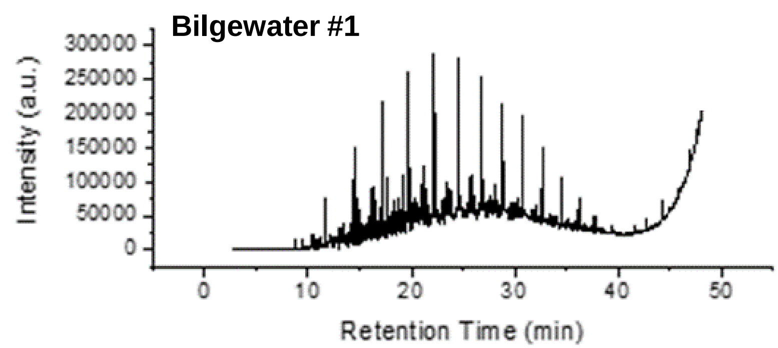
Parameter	Bilgewater #1	Bilgewater #2	Bilgewater #3
pH	7.0 - 7.2	5.1	7.8 - 8.4
Conductivity (mS/cm)	16.3 ± 0.1	1.74 ± 0.05	24.0 ± 0.4
Turbidity (NTU)	1,104 ± 104	10,402 ± 20	52 ± 2.3
COD (mg/L)	1279 ± 87	42,800 ± 1,500	547 ± 11
TS (mg/L)	13,793 ± 146	3,043 ± 502	20,320 ± 500
TSS (mg/L)	4,248 ± 212	1,848 ± 58	256 ± 16
UV_{254} (cm^{-1})	0.22 ± 0.02	0.381 ± 0.00	0.08 ± 0.01
Alkalinity (mg/L $CaCO_3$)	230 ± 4.1	5 ± 0.0	92 ± 2.4
TN (mg/L N)	12 ± 3.6	18 ± 13.7	12 ± 1.3
TP (mg/L PO_4^{3-})	3.8 ± 0.1	12.6 ± 0.5	0.3 ± 0.1
HEM (ppm)	50,000	50,000	3,000

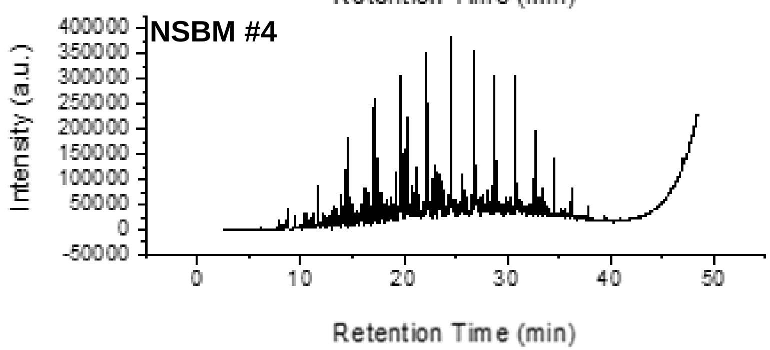
Extracted Bilgewater Characterization

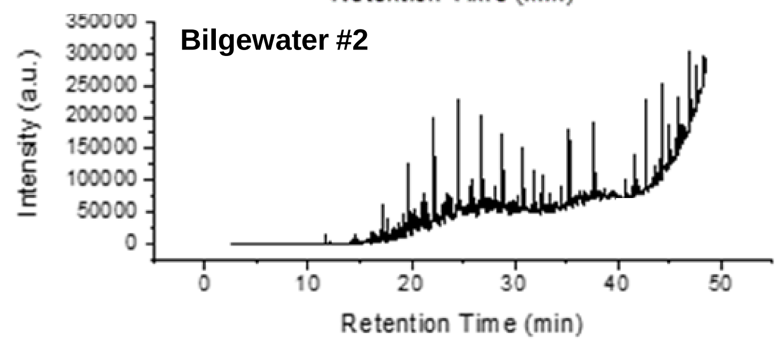
Results (Con't):

- GC-MS and LC-MS work focused on identifying the components in the oil and aqueous phase, respectively
- NSBM #4 seems to be representative of actual bilge oils



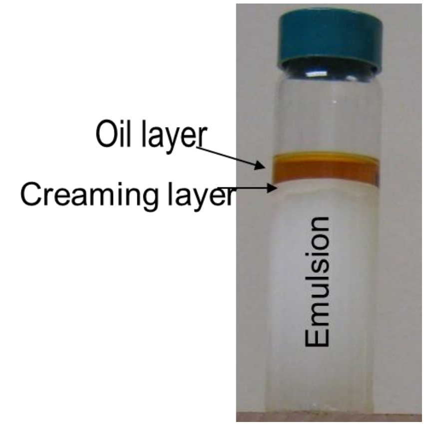






Environmental Impacts on Simulated Bilgewater Emulsion Stability

Approach: Prepared emulsions with 10% NSBM #4, Navy cleaners (7x CMC concentration) and various temperatures, pH, suspended solids, and salt concentrations



Analysis: Visually observed the formation of an oil or cream layer

Results:

- Environmental impacts were different for kinetic vs coalescence emulsion stability.
- Environmental impacts varied from cleaner to cleaner.

Environmental conditions tested

Environmental Factor	Tested Values
Temperature	5, 25, 35°C
pH	Unadjusted, 4, 10
Suspended Solids	0 and 1,000 ppm
Salt Concentration	0 and 35,000 ppm

Additives	Sample	Type 1 4°C	Type 1 25°C	Type 1 35°C	SDS 4°C	SDS 25°C	SDS 35°C	B&B 4°C	B&B 25°C	B&B 35°C	Powergreen 4°C	Powergreen 25°C	Powergreen 35°C
No additions	Unadj.												
	pH 4										Oil + creaming	Oil	Oil
	pH 10			Oil									
SS (1,000 ppm)	Unadj.			Oil					Oil	Oil			
	pH 4			Oil						Oil	Oil + creaming	Oil	Oil
	pH 10			Oil					Oil	Oil			
NaCl (35,000ppm)	Unadj.	Oil	Oil	Oil	Oil + creaming	Oil	Oil		Oil	Oil	Oil	Oil	Oil
	pH 4		Oil	Oil	Oil + creaming	Oil	Oil		Oil + creaming	Oil	Oil + creaming	Oil	Oil
	pH 10		Oil + creaming	Oil	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil	Oil	Oil	Oil
NaCl + SS	Unadj.		Oil	Oil + creaming	Oil + creaming	Oil	Oil		Oil + creaming	Oil	Oil	Oil	Oil
	pH 4		Oil + creaming		Oil + creaming	Oil	Oil		Oil	Oil	Oil + creaming	Oil	Oil
	pH 10				Oil + creaming	Oil	Oil	Oil	Oil	Oil	Oil + creaming	Oil + creaming	Oil + creaming

Additives	Sample	Calla 4°C	Calla 25°C	Calla 35°C	Solid Surge 4°C	Solid Surge 25°C	Solid Surge 35°C	PRC 4°C	PRC 25°C	PRC 35°C
No additions	Unadj.				Oil + creaming		Oil		Oil	Oil
	pH 4					Oil	Oil			Oil + creaming
	pH 10	Oil + creaming	Oil	Oil + creaming			Oil	Oil + creaming	Oil	Oil
SS (1,000 ppm)	Unadj.	Oil + creaming	Oil	Oil			Oil		Oil	Oil
	pH 4		Oil	Oil	Oil + creaming	Oil	Oil + creaming		Oil + creaming	Oil
	pH 10	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil
NaCl (35,000ppm)	Unadj.	Oil + creaming	Oil	Oil	Oil	Oil	Oil + creaming	Oil + creaming	Oil	Oil
	pH 4	Oil + creaming	Oil	Oil			Oil + creaming		Oil	Oil
	pH 10	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil	Oil	Oil	Oil
NaCl + SS	Unadj.	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil + creaming	Oil + creaming	Oil	Oil
	pH 4		Oil	Oil	Oil + creaming	Oil + creaming	Oil + creaming			Oil
	pH 10	Oil + creaming	Oil	Oil		Oil + creaming	Oil		Oil	Oil

Additives	Sample	Triton-X 4°C	Triton-X 25°C	Triton-X 35°C	6% AFFF 4°C	6% AFFF 25°C	6% AFFF 35°C	Blast Off 4°C	Blast Off 25°C	Blast Off 35°C
No additions	Unadj.	Oil + creaming	Oil	Oil	Oil + creaming	Oil + creaming	Oil + creaming	Oil	Oil + creaming	Oil
	pH 4		Oil + creaming	Oil + creaming	Oil + creaming	Oil + creaming	Oil + creaming	Oil + creaming	Oil	Oil
	pH 10	Oil + creaming	Oil + creaming	Oil	Oil	Oil	Oil + creaming	Oil	Oil	Oil + creaming
SS (1,000 ppm)	Unadj.	Oil + creaming	Oil + creaming	Oil	Oil + creaming	Oil + creaming	Oil	Oil + creaming	Oil	Oil + creaming
	pH 4		Oil	Oil	Oil + creaming	Oil + creaming	Oil + creaming	Oil + creaming	Oil + creaming	Oil
	pH 10	Oil + creaming	Oil + creaming	Oil	Oil + creaming	Oil + creaming	Oil + creaming	Oil	Oil	Oil + creaming
NaCl (35,000ppm)	Unadj.	Oil	Oil	Oil	Oil	Oil	Oil	Oil + creaming	Oil	Oil
	pH 4	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil	Oil	Oil	Oil
	pH 10	Oil	Oil	Oil	Oil	Oil	Oil	Oil + creaming	Oil	Oil
NaCl + SS	Unadj.	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil	Oil + creaming	Oil	Oil
	pH 4		Oil	Oil	Oil + creaming	Oil + creaming	Oil	Oil + creaming	Oil + creaming	Oil
	pH 10		Oil + creaming		Oil + creaming	Oil + creaming	Oil + creaming	Oil + creaming	Oil	Oil

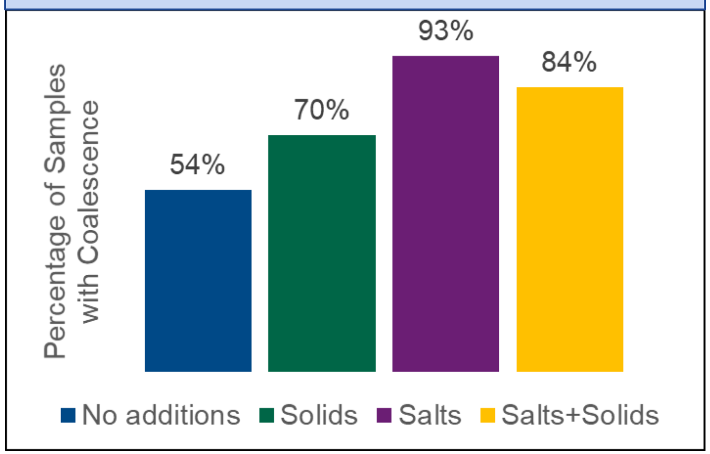
Oil
Oil + creaming
No oil layer formation

Environmental Impacts on Simulated Bilgewater Emulsion Stability

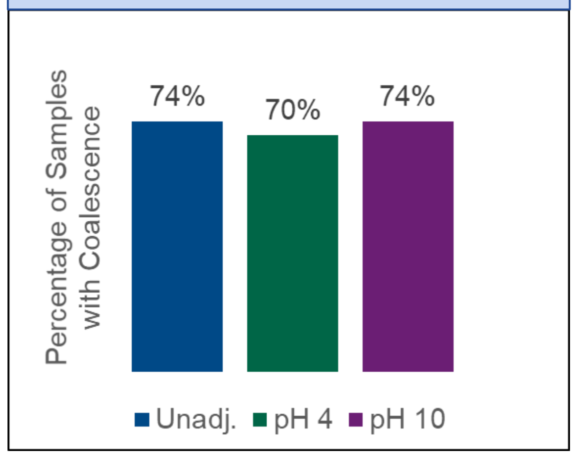
Results (con't):

- Salt concentration is a critical factor in controlling the coalescence stability of emulsions
- Initial pH has a minimal impact on stability because of the buffering capacity of the cleaners
- Emulsions at 4°C are more stable, however, exhibit higher tendency to form a creaming layer

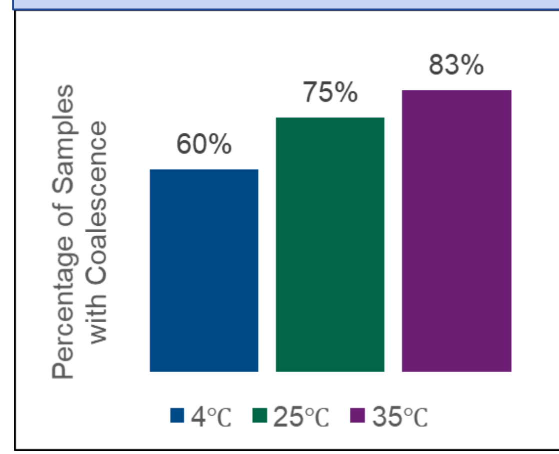
Solids and Salts



pH



Temperature

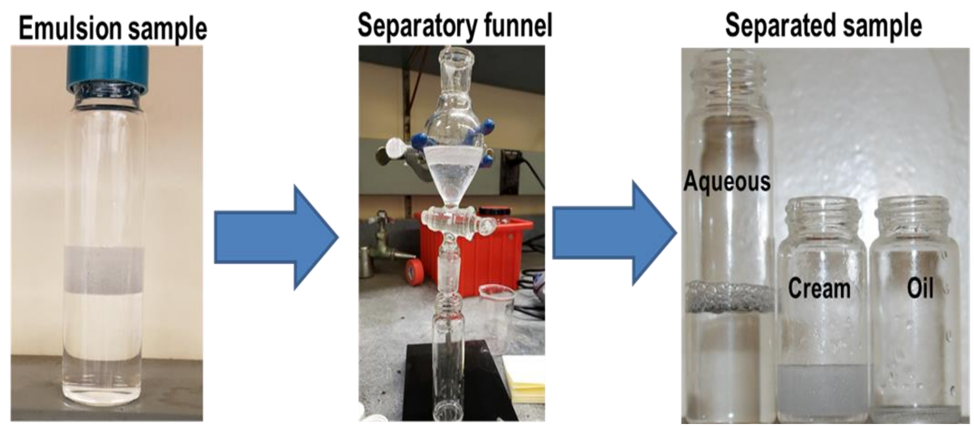


Role of Experimentally Determined Properties of Cleaners on Emulsion Stability

Approach: Prepared emulsion systems with varying IFT and CMC for emulsion stability (room temp, 2 min homogenization @ 20,000 rpm or 10 shakes) for both reference surfactants and Navy cleaners

Analysis:

1. IFT for each surfactant type and surfactant concentration with mineral oil
2. Bulk emulsion stability→ Visual observations and macrophase separation
3. Droplet size analysis→ Microscopy and laser diffraction



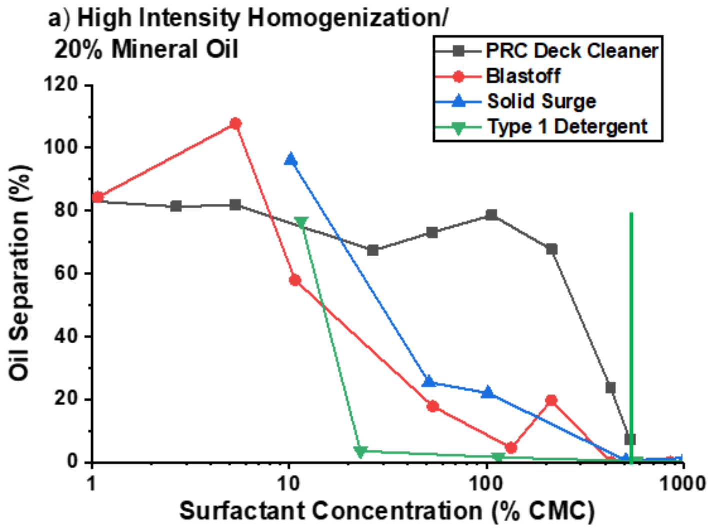
Schematic of macrophase oil separation

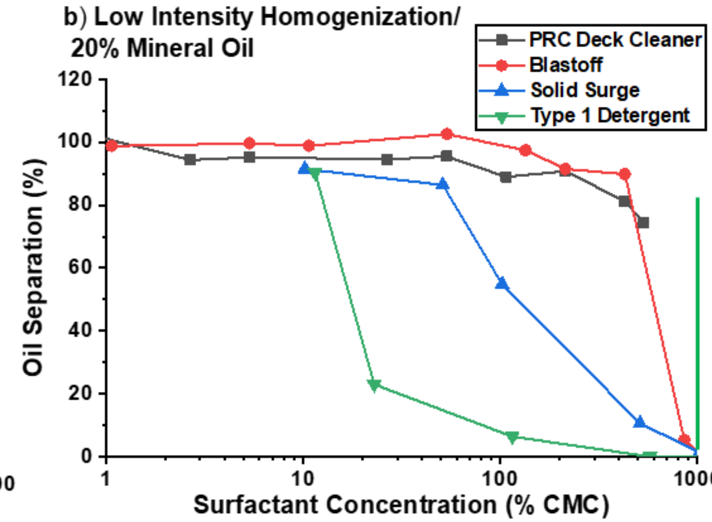
Results:

- Emulsions shifted from predominantly separated oil to stabilized emulsions at concentrations correlating closely with CMC for all surfactant types, oil concentrations, and homogenization intensities.
- This relationship was also validated for commercial cleaners commonly found aboard ships.
- CMC is a more practical way to evaluate a cleaner's likelihood of developing stable (>3 days with no observable oil separation) emulsions in bilgewater.

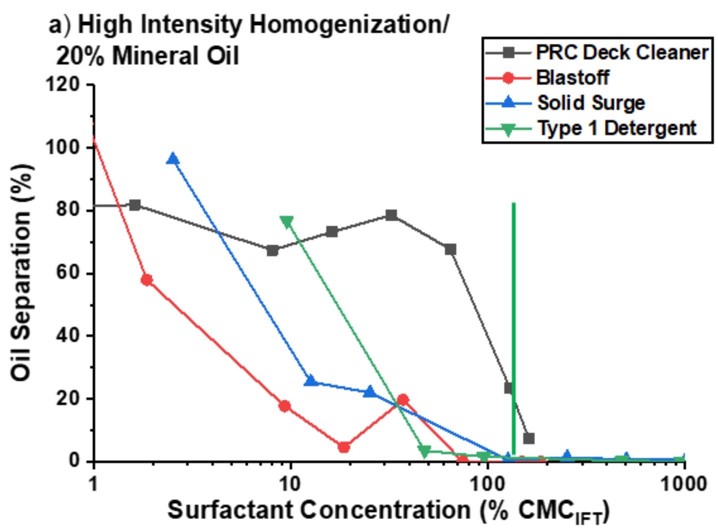
Role of Experimentally Determined Properties of Cleaners on Emulsion Stability

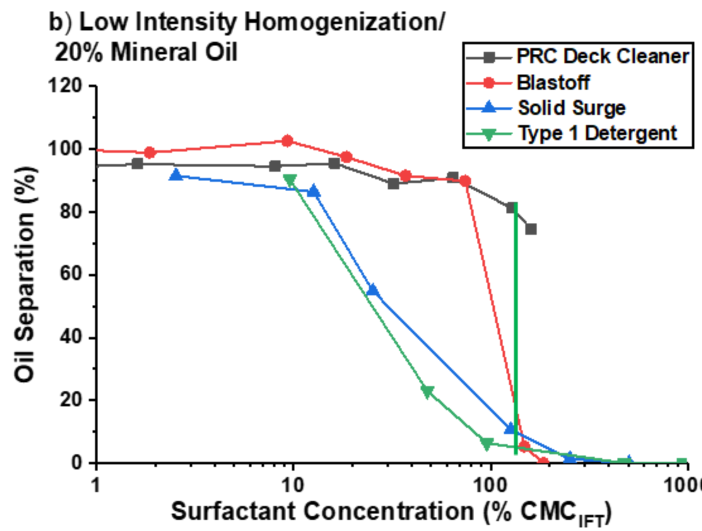
CMC based on ST





CMC based on IFT





Macrophase oil separation as a function of surfactant concentration in model oil-in-water emulsions after 72 h for emulsions prepared with high (a) and low (b) intensity homogenization.

Impact of Fuel Components on Bilgewater Emulsions

Motivation: To explore the transport of additives from the oil/fuel phase to aqueous phase of a bilgewater system and to determine the impacts that these additives have on water quality and emulsion stability.

Approach:

- Model bilgewater fuels and oils were exposed to DI water for 24 hrs.
- The DI water was then extracted and used for water quality analysis and emulsion stability testing.

Experimental set up for extracting water miscible components from bilgewater oils

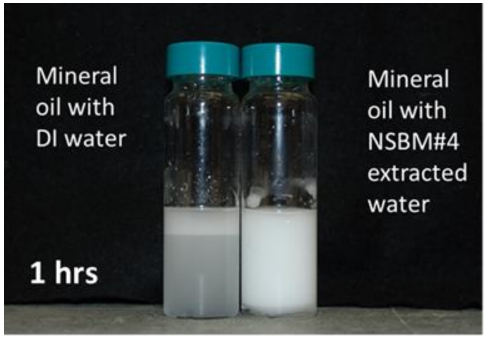
Analysis:

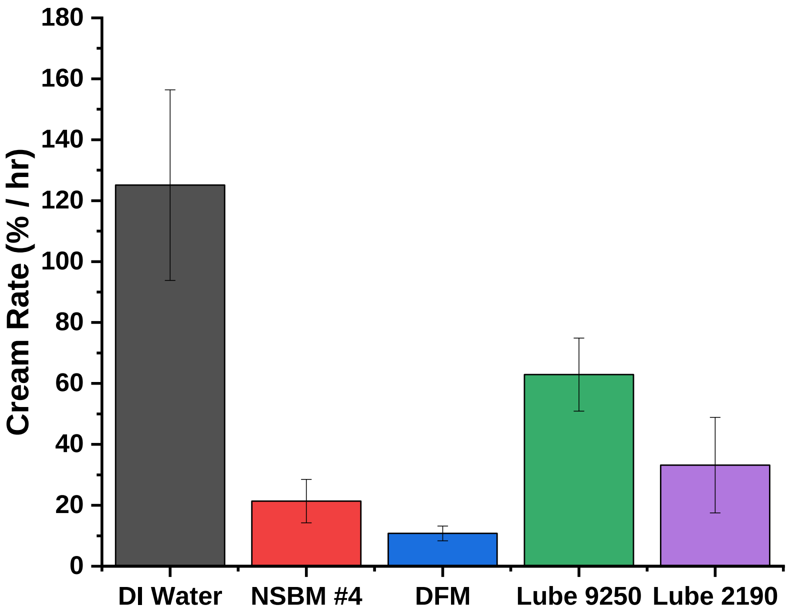
- Determine emulsion stability based on
  i. Visual observations
  ii. Creaming rate
- Conductivity, pH, surface tension UV192, LS/MS, and GC/MS to identify transport of compounds from the oil to water phase

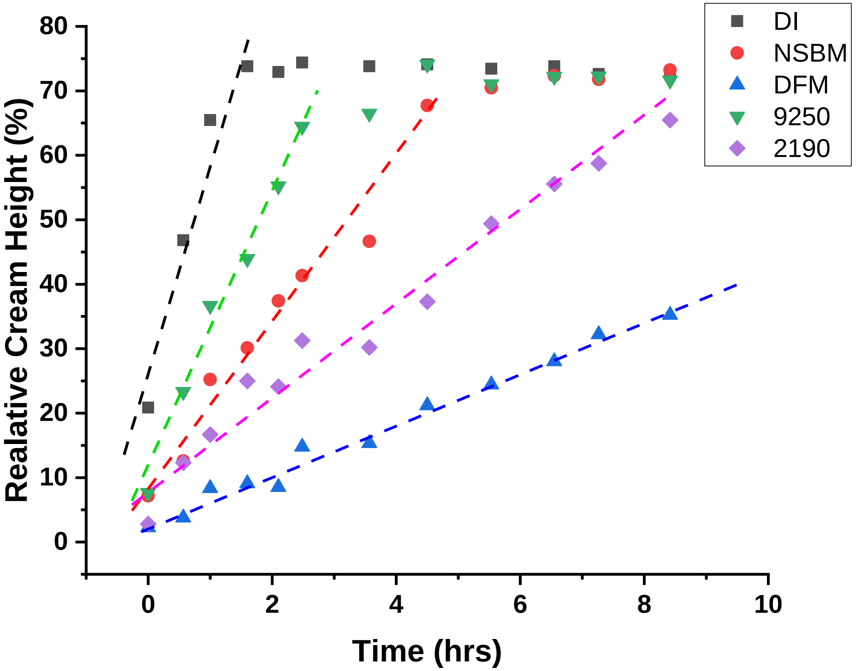
Impact of Fuel Components on Bilgewater Emulsions

Results

- Emulsions prepared with NSBM #4 components are more stable than emulsions prepared with the DI water control
- Compounds found in DFM are most likely to stabilize emulsions, followed by Lube Oil 2190, and then by Lube Oil 9250
- Further research is needed to identify the compounds that contribute to emulsion stability (WP19-1407)







Development of Emulsion Stability Model

Approach: Evaluated various regression and classification machine learning models trained on data from over 1,000 different synthetic emulsions prepared with:

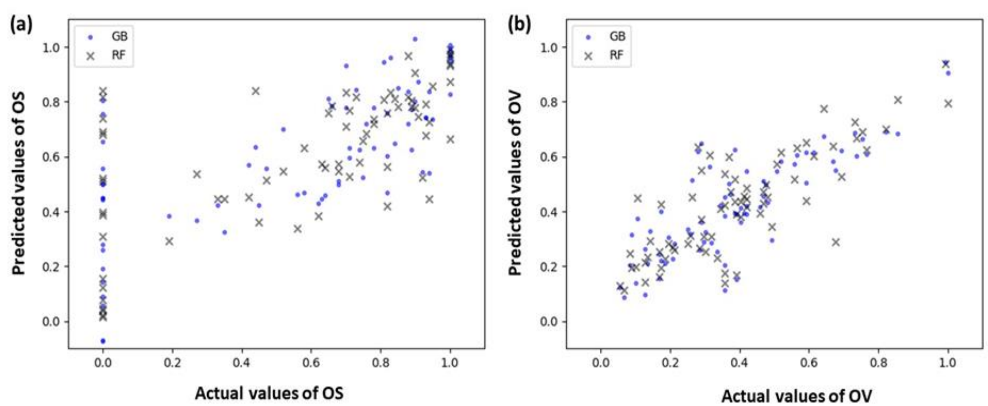
- Various types of cleaners/ surfactants
- Various surfactants concentrations
- Various oil types and concentration
- Different homogenization intensities
- Different environmental conditions

Analysis:

- Image processing used to developed an "oil value" based on the normalized RGB color for creaming vs oil samples.
- Oil value and environmental data was entered into various regression and classification models and were evaluated to develop an emulsion stability prediction model.

Results:

- Among nine algorithms used for tests, the gradient boosting regressor (GB) achieved the most accurate result (0.093) among other models.
- Sensitivity analysis resulted in salinity as having the largest impact on predicting emulsion stability.
- OV analysis improved prediction precision as compared to manually obtained oil separation (OS) values



Actual and predicted values for (a) OS and (b) OV (GB: Gradient boosting regressor, RF: Random forest regressor)

Key Findings

- Developed baseline understanding of emulsion science and contributing factors for bilgewater systems.
  - Creaming stability vs coalescence stability
  - Representative model emulsions
  - Types of cleaners found in Navy bilges
  - Relevance of self emulsification
  - Techniques for measuring emulsion stability
  - Relevant time scales
- Navy Standard Bilge Mix (NSBM #4) was confirmed to be representative of actual bilgewater samples based on GC/MS analysis of oil phase and cleaner compositions → more suitable than MEPC test fluids for testing Navy equipment.
- Critical Micelle Concentration (CMC) was demonstrated as a practical and experimental method to predict emulsion stability for complex systems. It could be used to flag cleaners that may have a greater risk for contributing to bilgewater emulsions.
- The impact of environmental factors on bilgewater emulsion stability varied between cleaners → should be considered when recommending cleaners for use in bilges.
- Fuel components and additives can have a significant impact to bilgewater emulsions stability → should be investigated further to determine impacts on OPA processes.

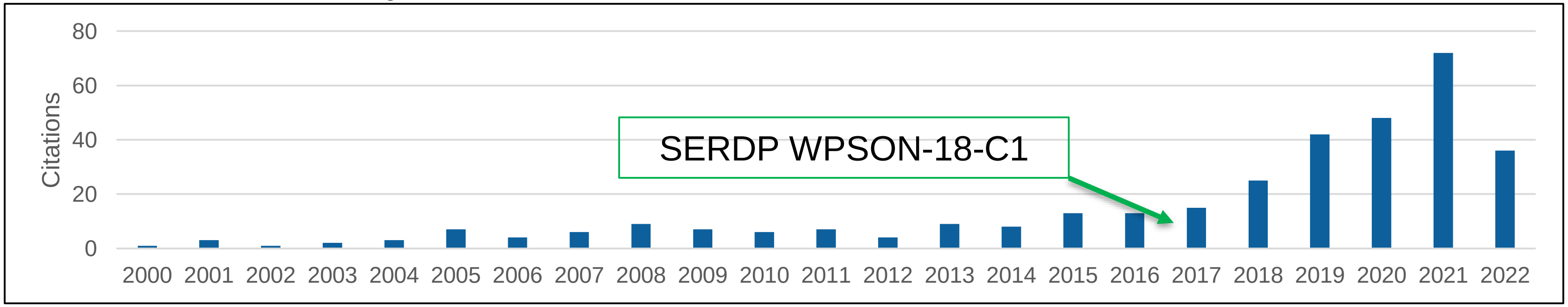
Technology Transfer

- Quarterly meetings were conducted to disseminate knowledge on bilgewater emulsion characterization and stability between SON performers (briefs uploaded to SEMs).
  - Naval Surface Warfare Center, Panama City Division
  - Pacific Northwest National Laboratory
  - University of Minnesota
  - Purdue University
  - Lehigh University
- Conference presentations and publications to transfer knowledge to the emulsion research community.
  - 4 peer reviewed publications, 1 submitted publication, and 2 publications in preparation.
  - 10 conference presentations
- SERDP webinar to share knowledge on emulsion research with DoD community.
  - Waste Reduction and Treatment in Armed Forces Vessels, Webinar #113 (6/04/2020)
- Regular briefs with NAVSEA 05P5 to transfer knowledge to stakeholders.

Transition

- Knowledge gained from WP18-1114 is being used to develop recommendations for bilge cleaners that prevent the generation of stable bilgewater emulsion or negatively impact bilge treatment processes under a NAVSEA funded research effort.
- The role of bilgewater composition and environmental factors on emulsion stability developed under WP18-1114 has validated the selection of the most challenging and representative test conditions for oil pollution abatement equipment and will inform the selection of future testing conditions.
- Knowledge gained from WP18-1114 is being leveraged in SERDP investigation into surfactant transport at liquid-liquid interfaces (WP19-1407) → implications on fluorine-free AFFF development and bilgewater treatment
- Oily wastewater emulsion research community that can accessed for future needs
  - Role of emulsions for in situ incineration for oil spill response (Bureau of Safety and Environmental Enforcement (BSEE) proposal)
  - Redhill oil spill response
- Transition of knowledge to the general research community
  - 4x increase of bilgewater publications from 2016-2021 as compared to the previous 5 years

Oily Wastewater Emulsion Publication Trends



BACKUP SLIDES

Publications

1. Daniels, G., Church, J., Chen, Y., Dutcher, C.S., Paynter, D.M., & Lundin, J.G. Effects of Surface Active Impurities on Surfactant Behavior at Fuel Oil-Water Interfaces. Langmuir. (In Preparation)
2. Diaz, D., Rodriguez, K., Church, J., Sarnyai, S., Lundin, J.G., Paynter, D.M., & Lee, W.H. Characterization of Simulated Shipboard Emulsion Stability Under Varying Environmental Conditions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. (In Preparation)
3. Park, C.Y., Diaz, D., Church, J., Lundin, J.G., Paynter, D.M. & Lee, W.H. Implementing Image Processing and Machine Learning for Predicting Bilgewater Emulsion Stability. Colloids and Surfaces A: Physicochemical and Engineering Aspects. (Submitted)
4. Church, J., Daniels, G.C., Lundin, J.G., Lee, W.H., & Paynter, D.M. Stabilization of Bilgewater Emulsions by Shipboard Oils. ACS ES&T Water 1 (8), 1745-1755.
5. Diaz, D., Church, J., Willner, M. R., Sarnyai, S., Lundin, J. G., Paynter, D. M., & Lee, W. H. (2020). Evaluation of Bilgewater Emulsion Stability Using Nondestructive Analytical Methods. Industrial & Engineering Chemistry Research, 60 (2), 1014-1025.
6. Church, J., Willner, M. R., Renfro, B.R., Chen, Y., Dutcher, C.S., Diaz, D., C Lee, W. H., Lundin, J.G., & Paynter, D. M. (2020). Impact of interfacial tension and critical micelle concentration on bilgewater oil separation. Journal of Water Process Engineering 39, 101684.
7. Son, J., Shen, Y., Paynter, D., Yu, X.Y. (2019). Surface Evolution of Synthetic Bilgewater Emulsion. Chemosphere 236, 124345.
8. Church, J., Lundin, J. G., Diaz, D., Mercado, D., Willner, M. R., Lee, W. H., & Paynter, D. M. (2019). Identification and characterization of bilgewater emulsions. Science of the Total Environment, 691, 981-995.

Presentations

1. Daniels, G., Church, J., Lundin, J.G., and Paynter, D.M. Identification and Role of Fuel Components on Bilgewater Emulsion Stability. *ACS National Meeting & Exposition*, Virtual, April 5-16, 2021.
2. Church, J., Daniels, G., Diaz, D., Willner, M.R., Park, C.Y., Rodriguez, K., Lundin, J.G., Lee, W.H., and Paynter, D.M., Emulsion Characterization Study for Improved Bilgewater Treatment and Management, *2020 SERDP/ESTCP Symposium*, Virtual, Dec. 1, 2020.
3. Park, C.Y., Diaz, D., Church, J., Rodriguez, K., Lundin, J.G., Paynter, D.M. & Lee, W.H. Implementing Image Processing and Machine Learning for Predicting Bilgewater Emulsion Stability. *2020 SERDP/ESTCP Symposium*, Virtual, Dec. 1, 2020.
4. Paynter, D.M. Emulsions Characterization Study for Improved Bilgewater Treatment and Management. Waste Reduction & Treatment in Armed Forces Vessels Webinar, June 12, 2020.
5. Church, J., Willner, M.R., Renfro, B.R., Chen, Y., Diaz, D., Lee, W.H., Dutcher, C.S., Lundin, J.G., Paynter, D.M. Impacts of Interfacial Tension and Critical Micelle Concentration on Emulsion Stability in Bilgewater. *259th ACS National Meeting & Exposition*, Philadelphia, PA, March. 22- 26, 2020. (Accepted/Cancelled due to COVID)
6. Church, J., Daniels, G.C., Willner, M.R., Lundin, J.G., Paynter, D.M. Impact of Fuel Additives on Oil-in-Water Emulsion Stability. *259th ACS National Meeting & Exposition*, Philadelphia, PA, March. 22- 26, 2020. (Accepted/Cancelled due to COVID)
7. Willner, M.R., Church, J., Lundin, J.G., Diaz, D., Lee, W.H., and Paynter, D.M., Emulsion Characterization Study for Improved Bilgewater Treatment and Management, *2019 SERDP/ESTCP Symposium*, Washington DC, Dec. 3–6, 2019.
8. Diaz, D., Willner, M.R., Church, J., Lundin, J.G., Diaz, D., and Paynter, D.M., and Lee, W.H. Nondestructive Stability Analysis and Characterization of Emulsions in the Presence of Suspended Solids, Salinity, and Surfactants. *2019 SERDP/ESTCP Symposium*, Washington DC, Dec. 3–6, 2019.
9. Willner, M., Church, J., Lundin, J., Diaz, D., Lee, W. H., & Paynter, D.. Structure-property relationship of commercial surfactants and bilgewater emulsions stability. *257th ACS National Meeting & Exposition*, Orlando, FL, Mar. 31–Apr. 4, 2019.
10. Willner, M.R., Church, J., Lundin, J.G., Diaz, D., Lee, W.H., and Paynter, D.M., Emulsion Characterization Study for Improved Bilgewater Treatment and Management, *2018 SERDP/ESTCP Symposium*, Washington DC, Nov. 27–29, 2018.

WP18-1114: Emulsion Characterization Study for Improved Bilgewater Treatment and Management

Performers

Ms. Danielle Paynter and Dr. Jared Church
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Dr. Jeffrey Lundin
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Technology Focus

Further current understanding of emulsion formation and stability through multiscale emulsion characterization and modeling analysis

Research Objectives

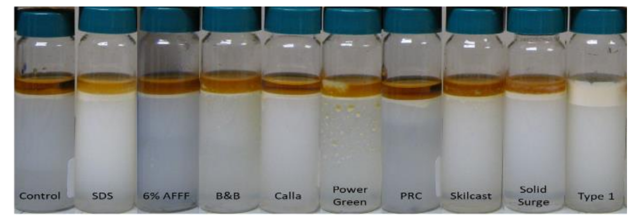
- *Identify surfactants likely to be found in Armed Forces bilges*
- *Characterize prepared and extracted bilgewater samples*
- *Provide analysis of emulsion stability trends shared with the community through peer-reviewed publications*

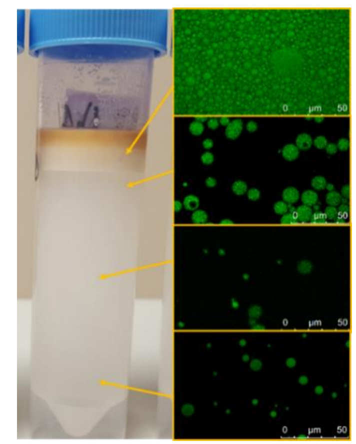
Project Progress and Results

- *Measured the impact of environmental factors on emulsion stability*
- *Determined the role of CMC in emulsion coalescence*
- *Investigated the impacts of fuel additives on emulsion stability*

Technology Transition

- *Development of emulsion stability trend database for Fleet application*
- *Development of surfactant stability model for Fleet application*
- *Recommend surfactants for reduced procurement or elimination*

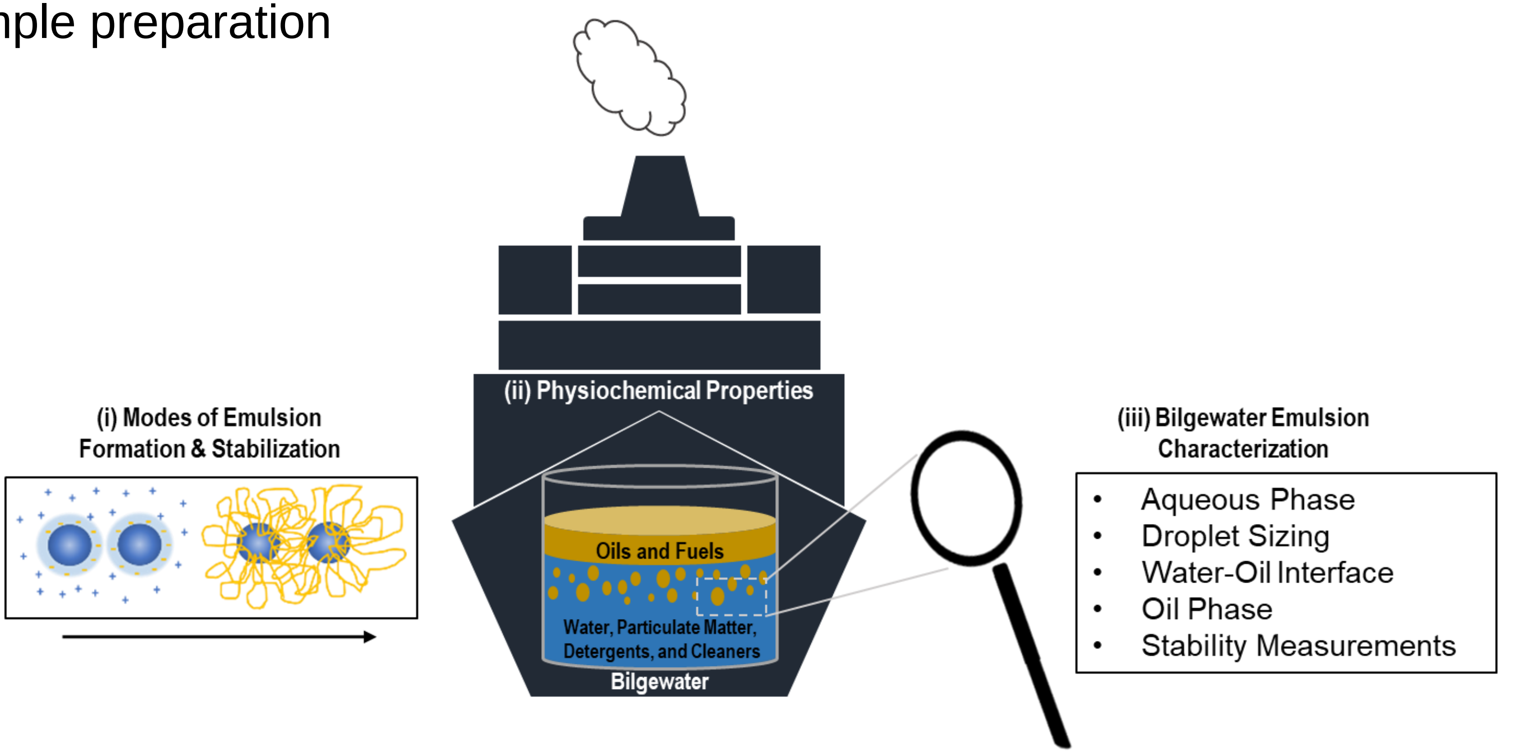




Technical Approach

<u>Task 1:</u> Scoping Study for Review of Armed Forces Vessels Oil-in-Water Emulsions

- Conduct literature and regulation review
- Use Navy procurement information for basis of surfactant identification
  - ♦ Navy procurement data mined for top surfactants procured by volume
  - ♦ NSWCCD standard challenge mixture
- Publish review article on emulsion characterization techniques, equipment needed, and sample preparation



Technical Approach

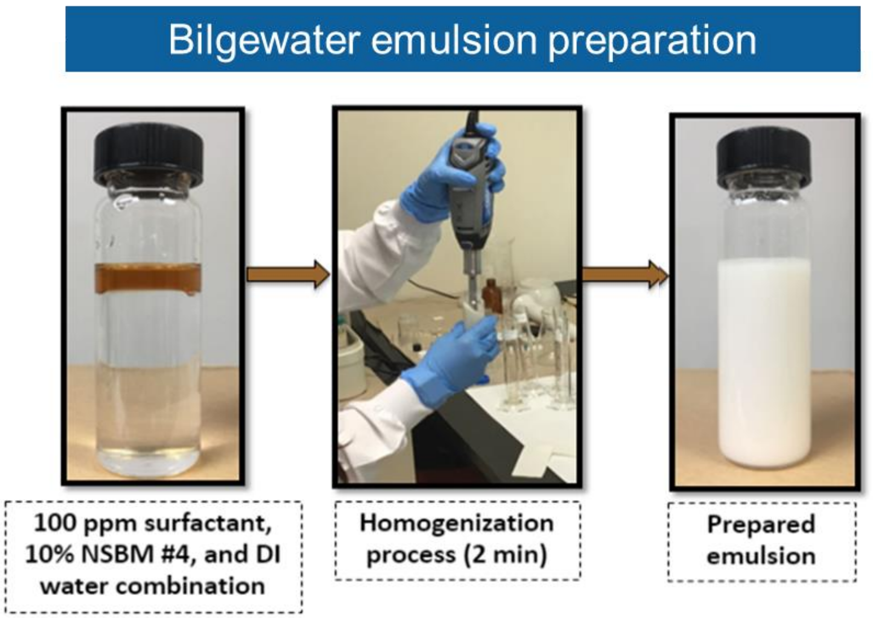
Task 2: Characterization of Bilgewater Emulsions

Prepare synthetic emulsion samples

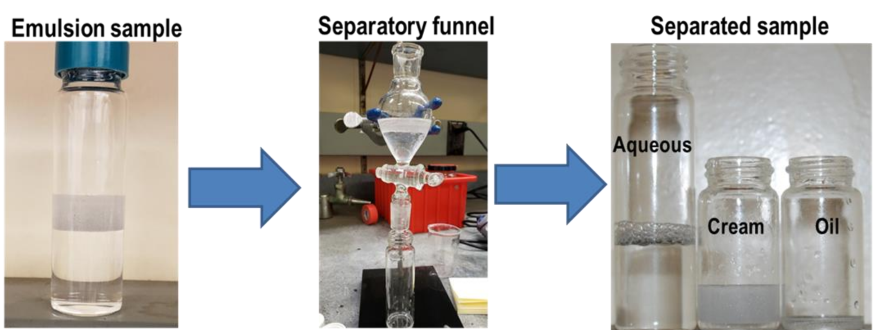
- > 1,000 emulsion experiments
  - Various types of cleaners/ surfactants
  - Various surfactants concentrations
  - Various oil types and concentration
  - Different homogenization intensities
  - Different environmental conditions

Analyze Emulsion Samples:

- Visual observations
- Macrophase Oil separation
- Turbidity
- Droplet Size Distribution
- Creaming Rate



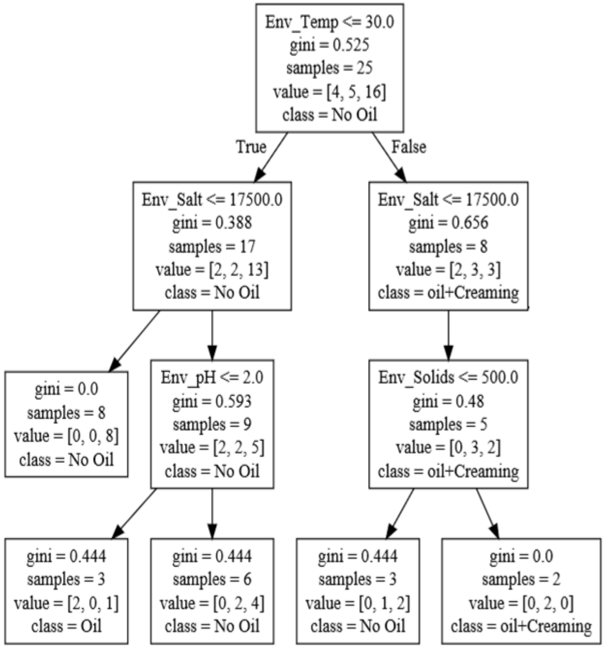
Macrophase Oil Separation



Technical Approach

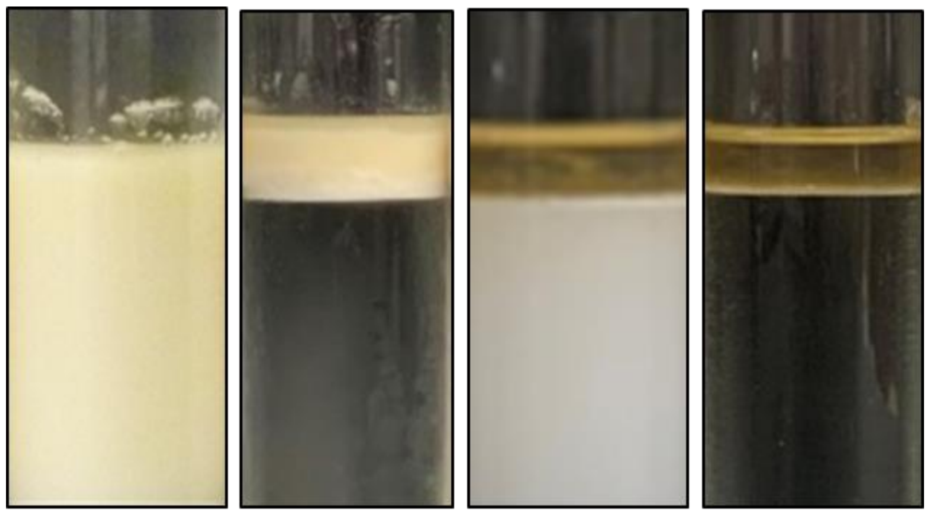
<u>Task 3:</u> Data Analysis, Interpretation and Publication

- Perform data analysis and correlate chemical, thermodynamic and physical properties of known surfactants to bilgewater samples using traditional and modeling data analysis methods
  - ♦ Decision tree or random forest models
  - ♦ Model outputs include phase diagrams and optimal emulsion breaking conditions
  - ♦ Model validation for investigated bilgewater system possible through proposed analytical characterization results and physical observations



- Build emulsion database which correlates known surfactant chemicals to emulsion concentration, stability mechanism and strength, including notes on effect of time, temperature and salinity
- Publish emulsion stability database and a series of peer reviewed journal articles

Types of emulsion stability



Kinetic and Coalescence Stability | Coalescence Stability | Kinetic Stability | Unstable