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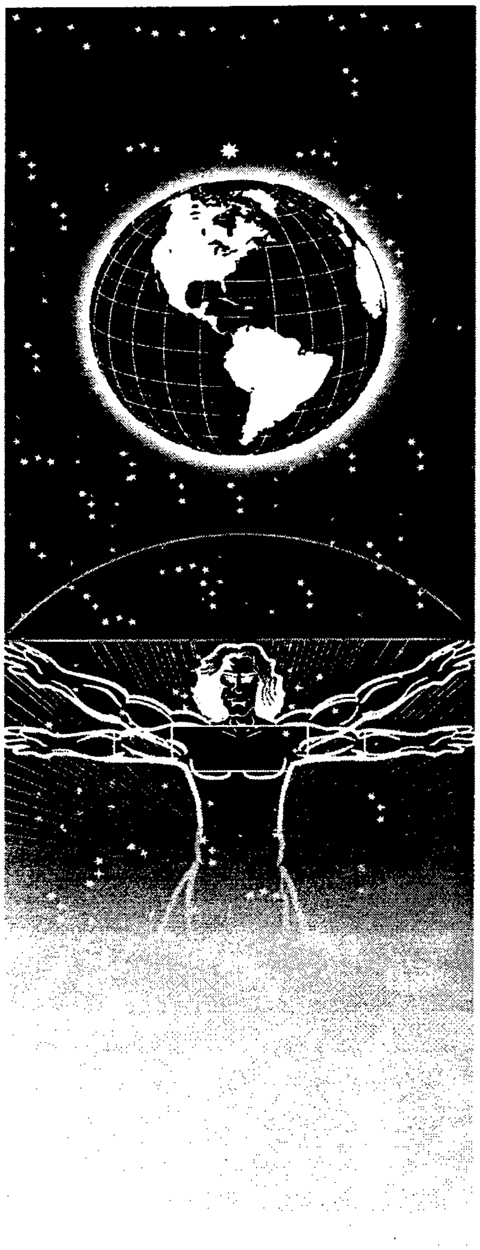

Novel System for the Decontamination of Firefighter Training Facility Wastes

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High foaming potential and chemical oxygen demand restricts discharge of firefighter training wastewaters. Innovative BioSystems designed a novel low energy bioreactor for application to firefighter training wastes. Jet A fuel concentrations went down. Concurrently, the butyl carbitol was transformed and more slowly degraded. In another reactor BTEX levels fell from initial values of 150 ppm to less than 4 ppm within 20 days. IBS AFFF at 0.3% concentration was degraded with surface tension measurements increasing from about 12 dynes/cm to over 30 dynes/cm within the first 10 days of degradation.

The IBS AFFF shows promise as a more degradable surfactant that should cause fewer problems in wastewater treatment facilities. Butyl carbitol is not a good choice as an AFFF co-solvent, and reducing the concentration in AFFF formulations would improve biodegradation and toxicity in degrading fuel components in firefighter training wastewaters.

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PREFACE

This report was prepared by Innovative BioSystems, Inc., 121 Sweet Avenue, Moscow, ID 83843-2386, under the Small Business Innovative Research contract no. F08637 94 C6023 for the U.S. Air Force, Armstrong Laboratory Environics Directorate (AL/EQ), 139 Barnes Drive, Suite 2, Tyndall Air Force Base, Florida 32403-5319.

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Executive Summary

Treatment and disposal of surfactant-laden waste waters is a significant problem at firefighter training facilities, as well as in real world use. The extremely high foaming potential and chemical oxygen demand of these waters restricts their discharge into sewage treatment plants. Improved treatment processes must be developed for aqueous firefighting foams, hydrocarbons, and their degradation byproducts.

Recent work by Innovative BioSystems, Inc. (IBS) scientists resulted in the design of a novel low energy bioreactor that is particularly adaptable for use with fire fighting waste water treatment without foaming. In this Phase I SBIR research contract, objectives included: 1. Testing treatment processes for firefighting waste waters using novel bench-scale reactors. 2. The degradability of firefighting wastes (such as petroleum hydrocarbons (including BTEX and jet fuel), SDS and other surfactants, currently used AFFF, and Innovative BioSystems, Inc.'s AFFF) by microbial enrichments.

Five bench-scale reactors were constructed, modeled after the novel bioreactor we developed in an earlier Navy SBIR. These reactors were computer controlled to allow aerobic operation and mixing without any detrimental foaming, and instrumented for measuring various parameters. These reactors were tested with bubbleless hollow fiber aerators and polyurethane bacterial immobilization supports. It was found that the AFFF reduced the efficiency of the hollow fiber oxygenators due to the very low breakthrough pressure differential needed to cause bubbles in the liquid side. However, the bubbleless oxygenators performed satisfactorily at the lower pressure.

Contaminated soil and water samples were gathered and enrichments were initiated for the degradation of AFFF, SDS, and fuels. These enrichments were monitored and modified to enrich for significant AFFF and fuel degradation, for nearly nine months. Following the enrichment process, subsamples of the enrichments were used to inoculate the bioreactors and degradation studies were performed using commercial AFFF, Jet A, IBS AFFF, and BTEX. The reactor contents were monitored by surface tension, GC and GC-MS for degradation quantation and the identification of breakdown intermediates.

Jet A fuel concentrations in the bioreactors went from 600 ppm to about 20 ppm within 20 days. Concurrently, the butyl carbitol was transformed and more slowly degraded. Even with only 0.3% commercial AFFF, the surface tension did not appreciably increase above 10 dynes/ cm until nearly forty days after degradation began. In another reactor BTEX levels fell from initial values of 150 ppm to less than 4 ppm within 20 days. IBS AFFF at 0.3% concentration was fairly rapidly degraded, with surface tension measurements increasing from about 12 dynes /cm to over 30 dynes/cm within the first 10 days of degradation.

The new IBS AFFF shows promise as a much more degradable surfactant that should cause many fewer problems in wastewater treatment facilities. Butyl carbitol is not a good choice as an AFFF co-solvent and anti-freeze and it would be preferable to significantly reduce the concentration in AFFF formulations for better biodegradation and less toxicity. The novel IBS bioreactor with bubbleless oxygenation is effective in degrading fuel components in firefighter wastewaters.

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List of Abbreviations and Acronyms

AFFF Aquous film forming foam(s)
BTEX Benzene, toluene, ethylbenzene, xylene
CMC Critical micelle concentration
DEGMBE diethylene glycol monobutyl ether (butyl carbitol)
DOC Dissolved organic carbon
GC Gas chromatograph
GC-MS Gas chromatograph and mass spectrometer
IBS Innovative BioSystems, Inc.
OECD Organization for economic co-operation and development
SBIR Small business innovative research program
SDS Sodium dodecyl sulfate

Introduction

Treatment and disposal of surfactant-laden waters from firefighter training facilities is a significant problem. The extremely high foaming potential and chemical oxygen demand (COD) of these waters restricts the discharge into sewage treatment plants. These waters include surfactants, hydrocarbons, partially burned hydrocarbons, and other contaminants. The recommended method of firefighting waste disposal from 3M, for their Light Water® brand aqueous film forming foams (AFFF), is pre-treatment in an oil-water separator followed by metered discharge to a running sewer **(1)**. The discharge to the sewer should be at a level below 50 mg/L, and since the 3% AFFF contains 30,000 mg/L, a 600 fold dilution of the wastewaters would be required. This dilution is very difficult to attain at a training facility that may produce about 150,000 gallons per day **(2)**. To reduce the surfactant cost and increase the degradability, a surrogate AFFF (sodium dodecylbenzene sulfonate (SDS)) will likely be used, as often as possible, at firefighter training facilities **(2)**. The highly fluorinated surfactants used in producing AFFF are not rapidly biodegradable with only about 15% degraded at 7 days in the modified OECD screening test with DOC analysis **(3)**. Our laboratory is developing fluorinated and non-fluorinated surfactants for use as AFFFs that are more biodegradable.

1. 3M product environmental data "Light Water Brand AFFF waste disposal recommendations and hazard evaluation." St. Paul, Minn.
2. Philbrook, D., and J. S. Dang. 1992. Advanced fire fighting training facility wastewater treatability studies. *in* 47th Purdue Industrial Waste Conference Proceedings. Lewis Publishers, Chelsea, Mich.
3. 3M product environmental data "Light Water brand aqueous film forming foam concentrate FC-203CE." St. Paul, Minn.

Phase I Technical Objectives

1. **Optimize *Innovative BioSystems'* novel low-energy bioreactor for cultivation of an aerobic, polyurethane-immobilized, microbial population to degrade AFFF, SDS, and hydrocarbons.** The *IBS* bioreactor, described below, is designed to use

hydraulic processes for slurry formation and movement. The reactor handles slurried materials of various densities, being especially efficient with materials such as polyurethane cubes as microbial carriers. It can be operated in a flow-through mode, as a packed bed reactor, or as a batch reactor. It can function aerobically, microaerophylically, or anaerobically (or sequenced between those conditions in any order) without foaming. As the reactor is operated in the recycle mode, the flow of liquid up through the polyurethane cubes will bring new solution in contact with the immobilized bacteria and significantly reduce the mass-transfer limitations normally found in immobilized cell systems.

2. **Evaluate the biodegradation of: 1)** petroleum hydrocarbons including BTEX, and jet fuel; **2)** SDS and other surfactants; **3)** currently used AFFF; **4)** Innovative BioSystems' AFFF. These biodegradation studies will be carried out in our novel bioreactors and can be configured as respirometers for the analysis of oxygen uptake.

Enrichments

Enrichments were established from over 40 contaminated soil, contaminated water, and secondary sewage sludge samples. These samples were collected at a wide variety of AFFF contaminated sites including Tyndall AFB, Fairchild AFB, McCord AFB, Whidby Island NAS, Fort Lewis fire training facility, SeaTac fire training facility, and the North Bend fire training facility. A number of these samples were pooled together and added to minimal media containing yeast extract. A matrix of enrichments was set up containing commercial brands of AFFF at 0.3%, Jet A, or BTEX or a combination of these materials. The degradation was followed by the surface tension measurements (Figure 1) of the enrichment flasks and by monitoring the residual fuel. As the fuel component was degraded, additional material was added back into the enrichment flasks. At three months the enrichment flasks showed good removal of residual fuel and removal of the diethylene glycol monobutyl ether (DEGMBE; Butyl carbitol), used as an antifreeze and solubilizer in the 3M AFFF formulation. This fuel and DEGMBE removal, coupled with the excellent non-foaming operation of our reactors with the hollow fiber oxygenators, may be a significant breakthrough in pretreatment of the wastewater. By pretreating the firetraining wastewater to remove these two significant contaminants, there may be a very reasonable

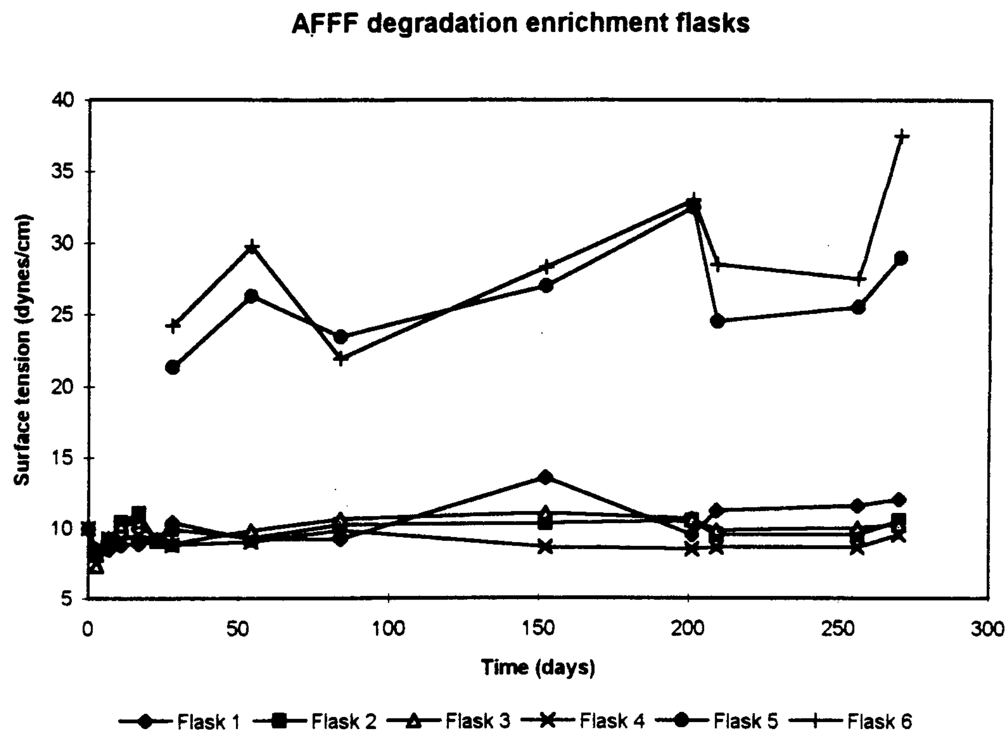


Figure 1. AFFF degradation enrichment flasks.
Flask 1: odd number enrichment samples, 3-M AFFF, Jet A.
Flask 2: odd number enrichment samples, Chub National AFFF, Jet A.
Flask 3: even number enrichment samples, Chub National AFFF, Jet A.
Flask 4: even number enrichment samples, 3-M AFFF, Jet A.
Flask 5: odd number enrichment samples, SDS, Jet A.
Flask 6: even number enrichment samples, SDS.

chemical/physical treatment to remove the fluorinated surfactants if the further enrichment processes are not successful in biodegrading these fluorinated compounds. Enrichment flasks 1 and 2 contained half gram subsamples from half of the collected samples and flasks 3 and 4 contained subsamples from the remaining half of the collected samples. All flasks contained 200 ml of phosphate buffer at pH 7 and 1000 mg / liter of varying combinations of AFFF, SDS, and Jet A. Flasks 2 and 3 had Chub National brand AFFF and flasks 1 and 4 had 3M brand AFFF. The three substrates (AFFF, SDS, Jet A) were added as they became depleted to enrich for degrading organisms. The Jet A was added as depleted in a portion of the enrichments so the only significant carbon sources in the remaining enrichments would be the surfactants Enrichment flasks 5 and 6 are enrichments for SDS degrading organisms without jet A or with jet A respectively. This was in hope of allowing the growth of a consortium of organisms would be efficient surfactant degraders Later during this research, as many as 20 combinations of enrichments were established. Samples were taken from these enrichment flasks and were used to seed the new bioreactors after they were completed.

Construction of Reactors

We completed the construction of five reactors and they were operated for nearly six months during the testing and degradation experiments We have received bubbleless membrane oxygenators from two companies to compare performance in our first reactor and have seen excellent oxygenation without any foaming of the AFFF solutions in the reactor. Figure 2 is the photo of one of the bench-scale novel bioreactors in operation with the

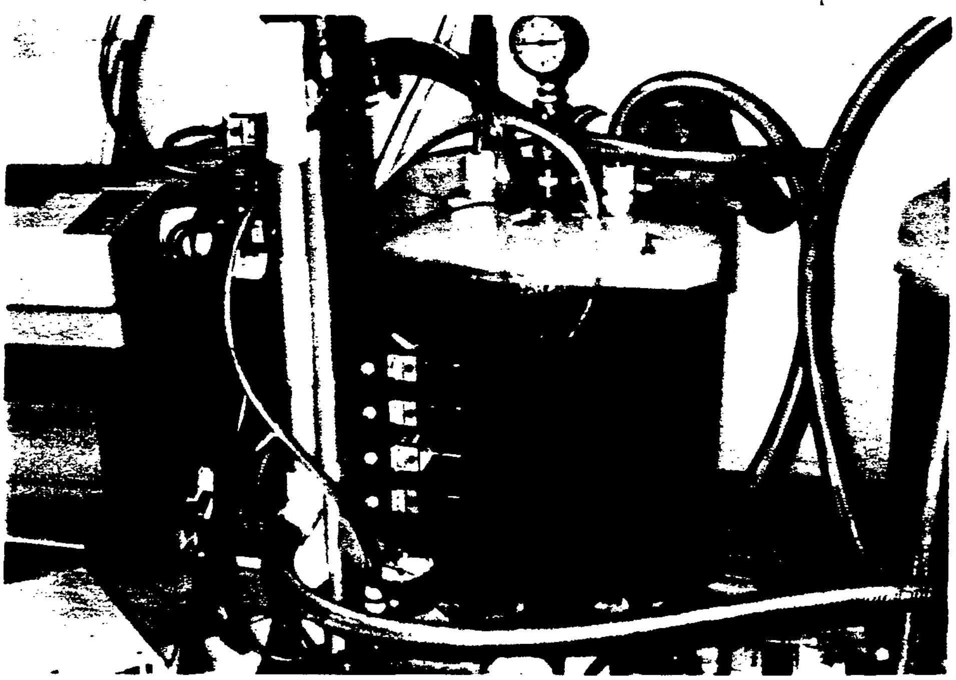


Figure 2 Photo of bench-scale bioreactor in bubbleless operation with 0 3% AFFF

bubbleless oxygenation device and control solenoids shown. The ability to operate these reactors in a high capacity aerobic mode without any foaming, to degrade the fuel and DEGMBE, could very well be a significant advancement in the treatment of firefighter training wastewaters The reactors were seeded with samples from the enrichment flasks and enrichments continued. Later, degradation studies of the BTEX, jet fuel, and DEGMBE in the reactors with different AFFF solutions were completed.

Control System

We optimized the software configuration for the control and operation of the reactors by the data system. We selected Strawberry Tree data collection boards ACPC12/16 and the Workbench PC software for computer data collection and control of the reactors. This system worked well for cycling the reactor pumps and collecting data from pH, redox, and dissolved oxygen electrodes to monitor the system operation. We also set up a du Nouy ring tensiometer with the Strawberry Tree system in conjunction with our analytical balance that works well and have been using it for the surface and interfacial tension measurements. Figure 3 is a screen capture of the control system for the reactors and surface tension tests. The switches control various functions and the chart labeled "CH2 Dissolved O2 # 1" is a plot of redox potential at about +240 mV and the dissolved oxygen at about 4.5 to 6.0 mg/l with the reactor operating in water circulation only mode.

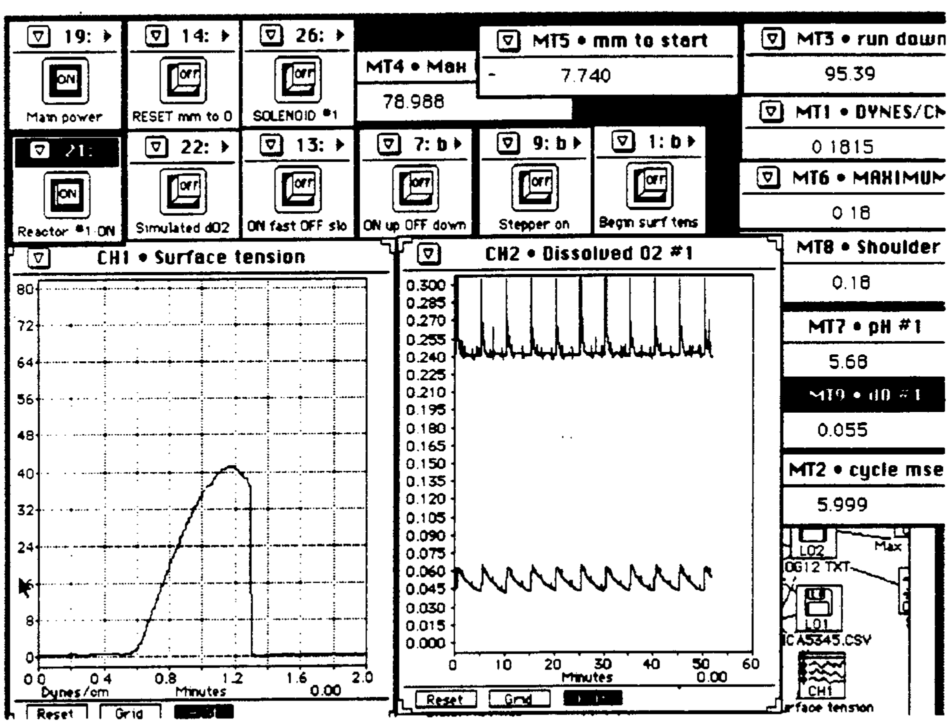


Figure 3. Data collection interface.

The data is also being stored in files for later analysis. Stored data can be retrieved over our network while the control system is still operating the reactors and collecting additional data.

IBS Surfactants and AFFF

In the synthesis of fluorinated and non-fluorinated surfactants, we continued our testing of the surface tension and filming properties. About 30 individual surfactants have been synthesized and their properties measured. Figure 4 shows the critical micelle concentration (CMC) graphs of four different surfactants by themselves. We also gathered data for mixed surfactants that show surface tensions of less than 10 dynes/cm.

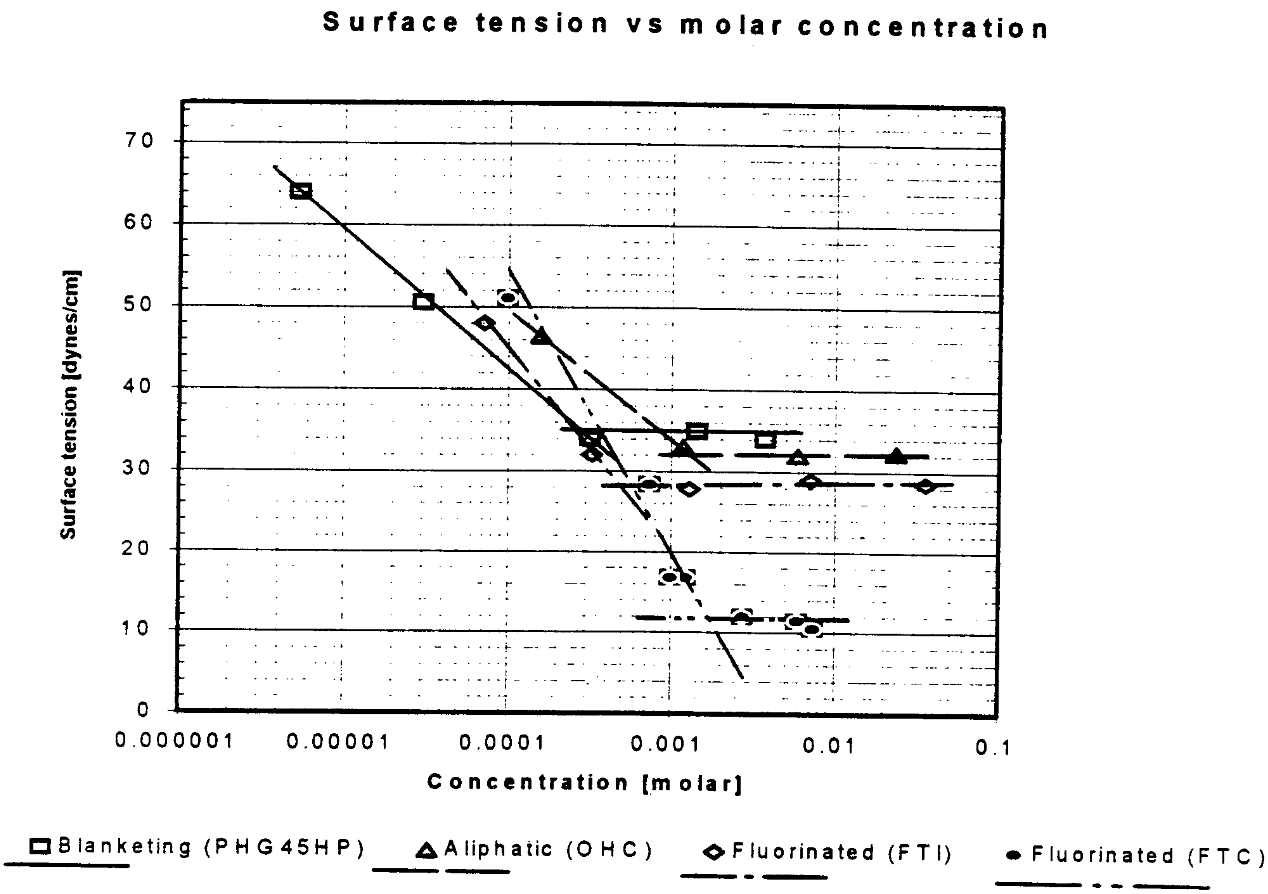


Figure 4. Surface tension vs. molar concentration.

We determined the spreading coefficient and interfacial surface tension between the best individual and mixed surfactants. Figure 5 is a screen capture of the interfacial tension for our surfactant D-62 and cyclohexane (6.2 dynes/cm) and the surface tension of cyclohexane (20.8 dynes/cm) from our tensiometer.

The new IBS alternative AFFF formulation was tested by a number of screening methods as an AFFF formulation both with regard to its fire extinguishing (Table 1) and degradation characteristics (Figure 5). Surface tension measurements of our surfactants (Figures 3 and 4) and film forming tests done comparing our AFFF formulation to a commercial AFFF formulation both demonstrated very similar fire extinguishing properties (Table 1).

Table 1. AFFF screening test comparison.

Test description	IBS AFFF	Commercial AFFF
Film formation and spreading	15 seconds	24 seconds
Seal	>60 seconds	>60 seconds
Burnback resistance	9 seconds	6 seconds
Resistance to agitation	190 seconds	100 seconds flashing
Aqueous emulsion	emulsion	emulsion

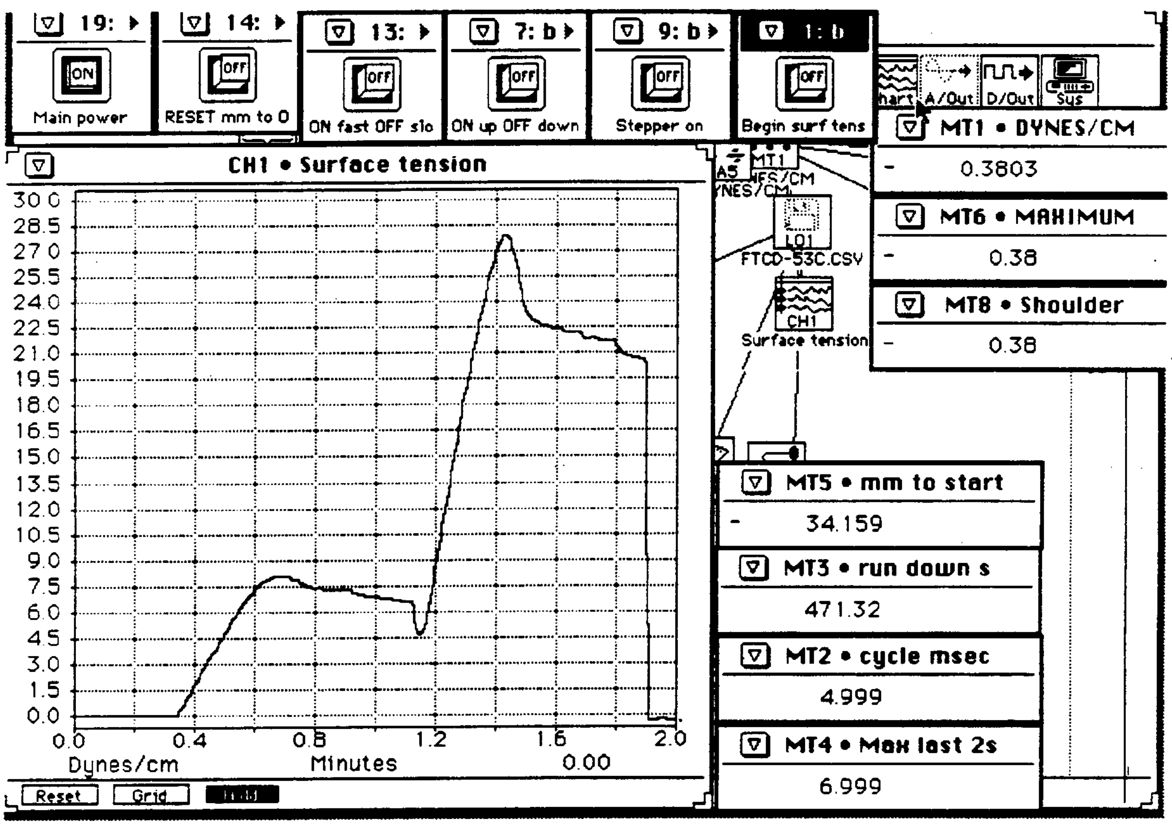


Figure 5. Screen capture of interfacial and surface tension.

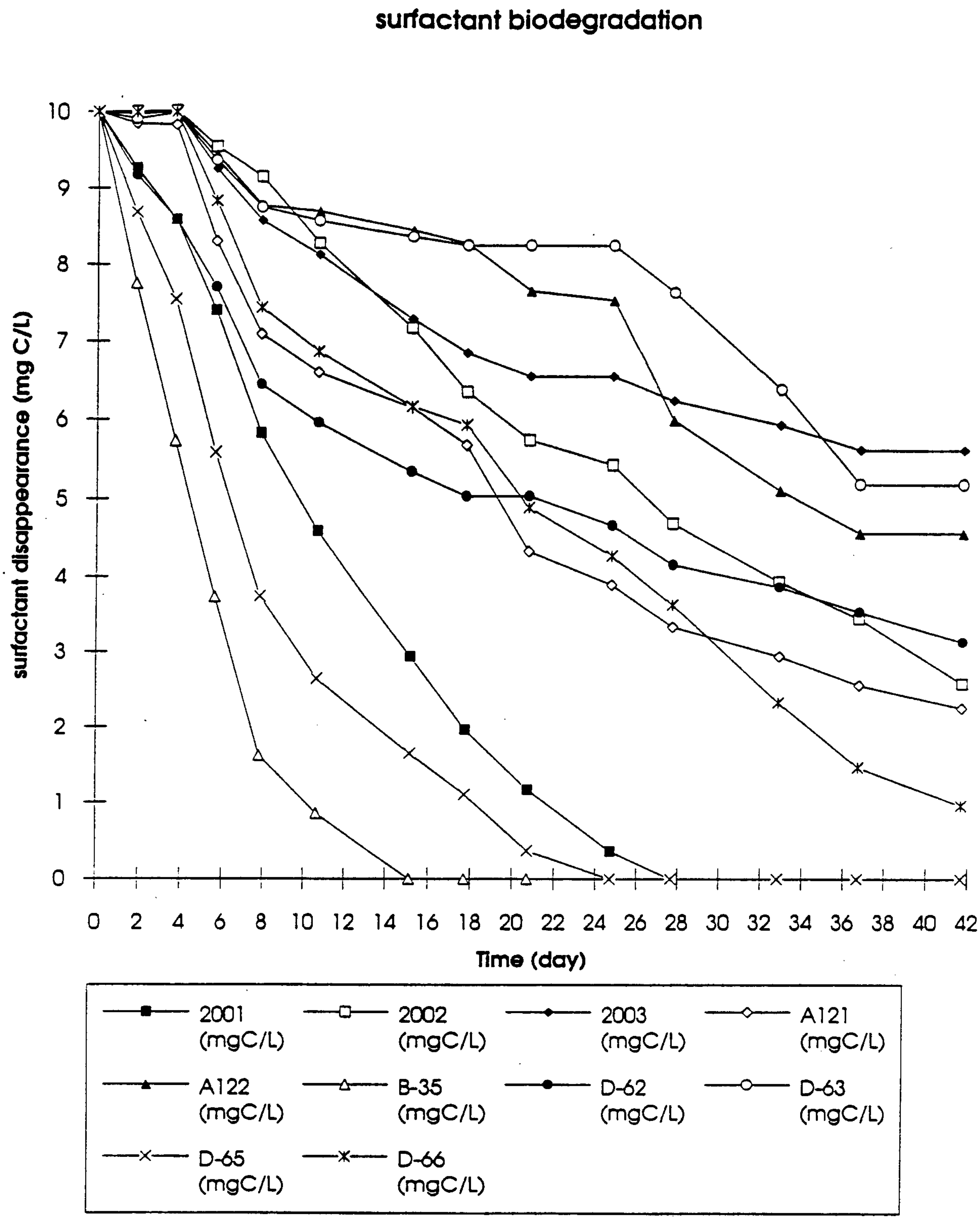


Figure 6. Individual IBS surfactant biodegradation.

The enhanced degradability testing of these new IBS surfactants as pure compounds was completed. Figure 6 is a plot of the mineralization of a selected group of nine of our new surfactants and one readily degradable surfactant as a comparison. The four fluorinated surfactants are A-121, A-122, D-62, and D-63 and all the rest in Figure 6 are non-fluorinated surfactants. This biodegradation procedure is based on a non-acclimated seed of municipal sludge. Degradation of 60% of the carbon within 28 days is considered "readily degradable". For new compounds that are not normally found in the municipal wastewater, the test can be used with a 30 day acclimated seed and followed by monitoring of the degradation. We chose to use non-acclimated seed, even though our new type of surfactant molecules are not in wastewater, because we wanted to assess the ease of cleavage of the new hydrolyzable linker bonds in the IBS AFFF surfactants. The results from this degradation study demonstrate that two of the IBS fluorinated surfactants are readily degradable and it is likely that the lag on the others are from the non-acclimated seed. This demonstrated that the new IBS AFFF should more degradable in a much shorter time than the currently used AFFF formulations. The enzymatic vulnerability of the linking component in these new surfactants demonstrates the potential for their use in firefighter training facilities and in actual fire situations.

Fuel Component Degradation Results

Bioreactors containing enrichments were spiked with 600 ppm of Jet A fuel and 0.3% commercial AFFF concentrate. This is a ten-fold dilution of the normally produced AFFF solution and much higher than the currently recommended 600 fold dilution. The total Jet A concentration was rapidly reduced as shown by Figure 7.

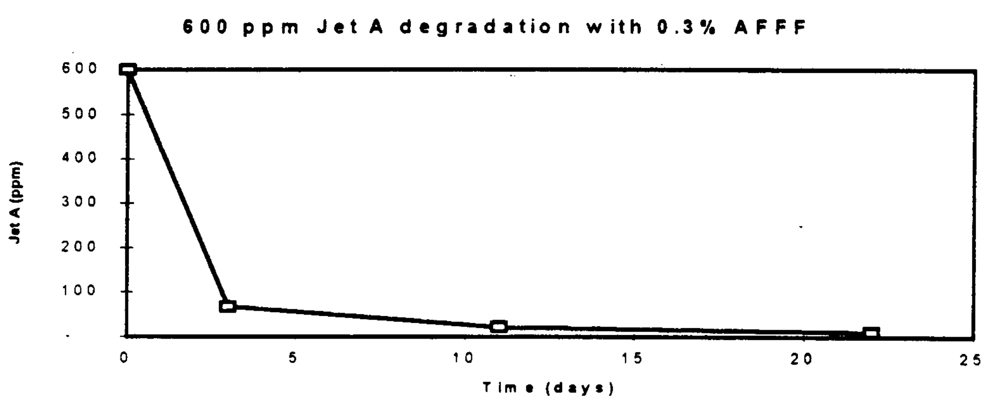


Figure 7. Jet A degradation with 0.3% AFFF.

When the individual Jet A components were monitored, there was some slower degradation of the higher chain length compounds, as seen in Figure 8. In Figure 8 all peak areas have been normalized to 100% of the initial value. Any degradation is seen as a reduction in peak area as the sample time increases. The summation of all the separate peak areas totaled together is shown on right side of Figure 8.

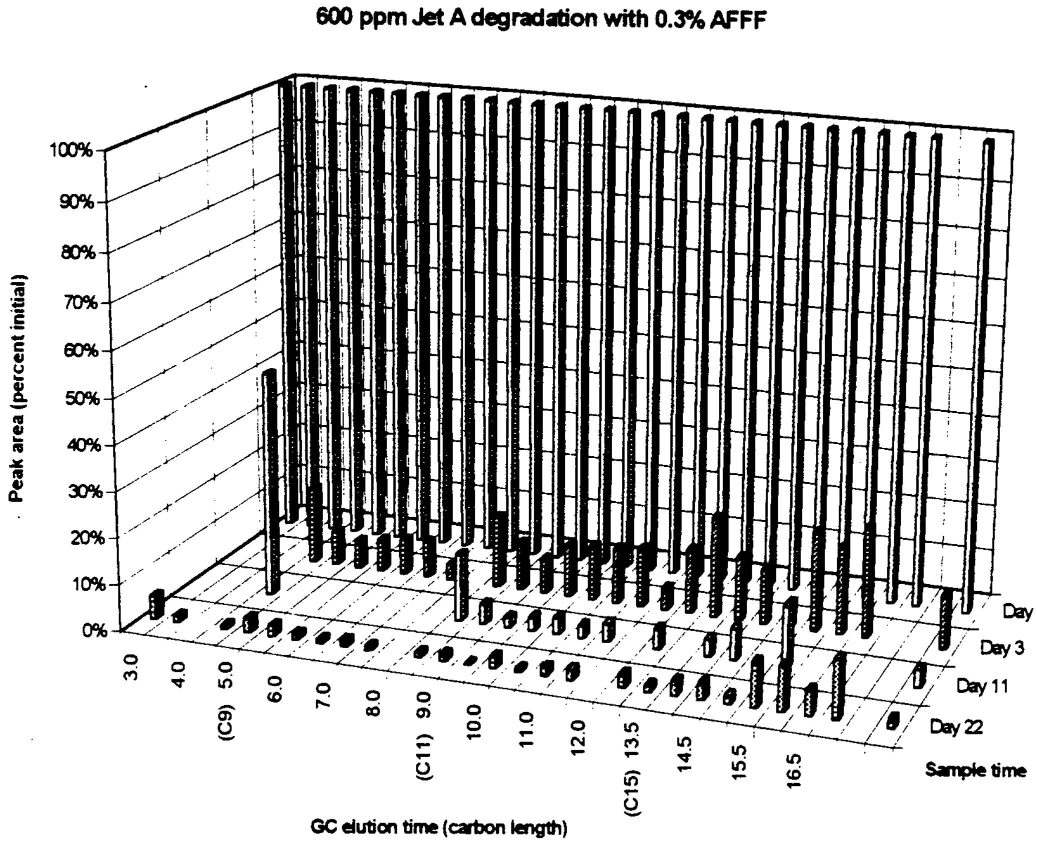


Figure 8. Individual Jet A component degradation.

Sample time is the number of days after the 600 ppm Jet A and 0.3% AFFF were added.

GC elution time is in minutes and based on standards injected: 5 minutes coresponds to a 9 carbon chain length, 9 minutes to 11 carbon length, and 13.5 minutes to 15 carbon length compounds.

All peak areas within the GC elution time periods were summed to determine the 100 % peak area for that specific elution time period at time zero.

In another bench-scale bioreactor, BTEX components were added at 150 ppm each with 0.3% AFFF. This reactor was operated as a closed system with only a small amount of headspace vented during hollow-fiber purging to decrease any release of volatiles to the atmosphere from the reactor. Figure 9 is a plot of the individual BTEX components over time in the reactor.

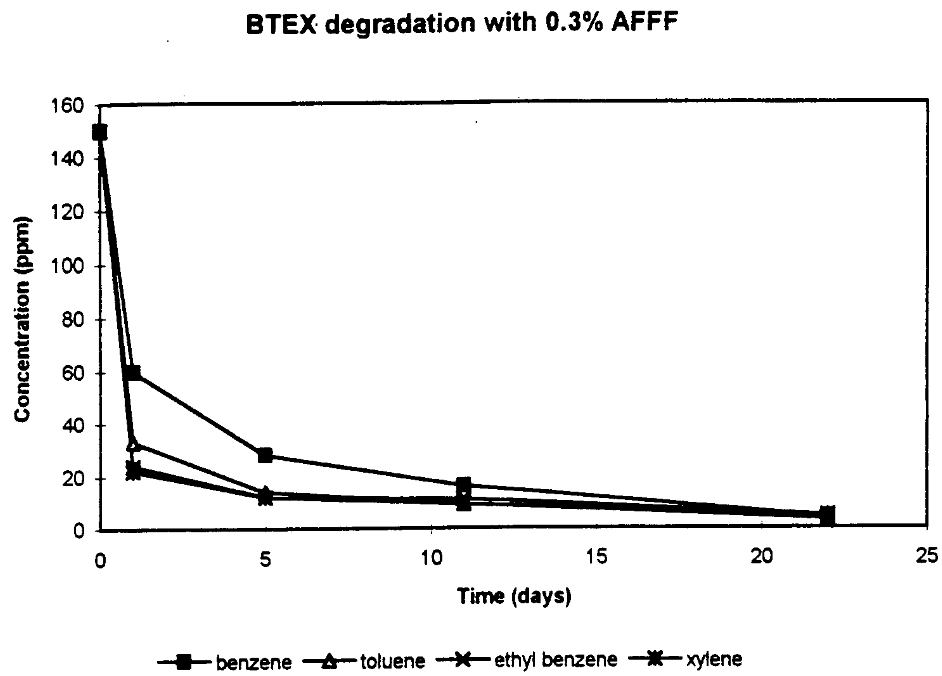
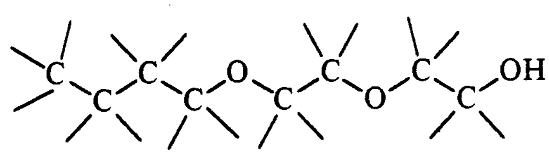


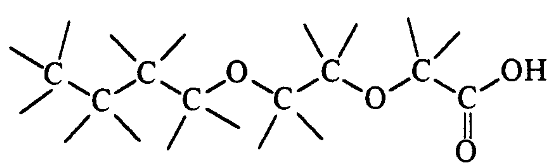
Figure 9. BTEX removal with 0.3% AFFF.

AFFF Solvent Degradation Rates

The major organic solvent of most AFFF formulations is DEGMBE. This solvent has a structure as follows:



We found that the 2-(2-butoxyethoxy)ethanol was fairly rapidly removed but rather than degraded, it was transformed to 2-(2-butoxyethoxy)acetate by the addition of a double bonded oxygen. These results were confirmed by GC-MS. The structure of the transformed product is shown as follows:



This intermediate had not been significantly degraded within 20 days after initial degradation began. Figure 10 shows the actual peak area of the DEGMBE and its transformation product during the first eleven days of degradation. Peak area data from day 22 is not shown in Figure 10 due to the very low Jet A concentrations and the need to concentrate the sample for quantitation of the Jet A compounds. What the GC data shows is a very large peak at 12.8 minutes and a relative increase in the peak area of the 8.0 minute peak. GC-MS was not able to confirm the identity of the second intermediate at 8.0 minutes.

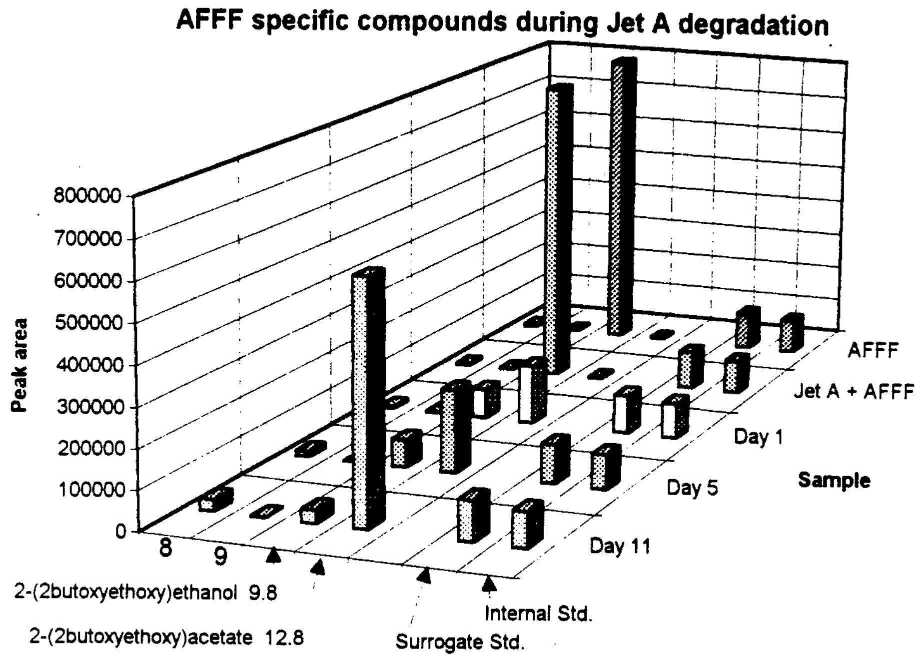


Figure 10. AFFF specific compounds.

AFFF Surface Tension Results

Surface tension measurements were made on bioreactor contents with both commercial AFFF and IBS AFFF formulations. These were plotted in Figure 11 over the course of about 50 days. The drastic difference in the surface tension increase is readily apparent when comparing the two different AFFF formulations.

The rapid increase in the IBS AFFF surface tension is an advantage since after the AFFF has performed its fire fighting function, low surface tension is not wanted. The very low surface tension of commercial AFFF is detrimental to degradation of the waste waters

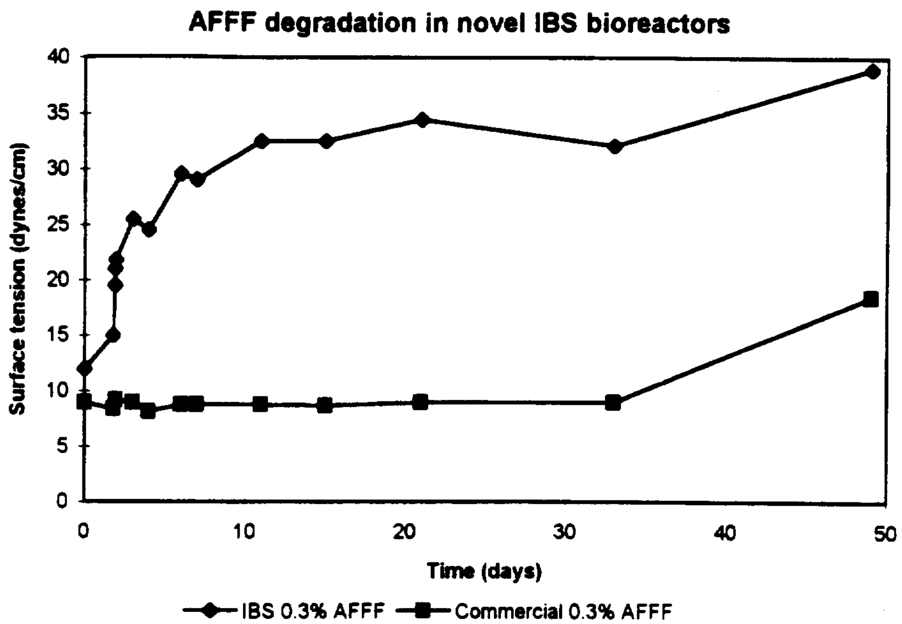


Figure 11 Surface tension of reactor contents during degradation.

and harmful to waste water treatment facilities in a number of ways including the significant foaming problems that can occur if large dilutions are not done.

Problems Encountered

There were a number of difficulties encountered during the course of this research project. One initial difficulty was the failure of four of the five water circulation pumps in our reactors. We contacted the manufacturer after the third failure within one week and they immediately shipped us six replacement pumps. These were installed and only one of them has failed. We do not see this as a reactor design flaw but more of a component failure that is being addressed by the pump manufacturer.

A significant problem was the extreme difficulty in producing enrichment cultures that were able to degrade the commercial AFFF surfactants. The surfactant degradation would have allowed the surface tension to significantly increase and this would greatly reduce the disposal problems. Even after nearly nine months there was not significant increase of the surface tension in the commercial AFFF enrichments. However, in the novel bioreactors, there was some significant increase about 40 days later.

It was found that the AFFF reduced the efficiency of the hollow fiber oxygenators due to the very low breakthrough pressure differential needed to cause bubbles in the liquid side. However, the bubbleless oxygenators performed satisfactorily at the lower pressure. Normally the manufactures recommend between 20 and 80 psi pressure differential between the air and liquid side of the fiber, but with the AFFF in solution, pressure differentials had to remain below 5 psi.

The contract analytical lab had some difficulty in analyzing for fuel components due to the large surfactant effects. They found through analyzing matrix and matrix spike samples that liquid/liquid extraction was not at all effective and solid phase sample extraction devices worked reasonably well. Internal and surrogate standards are very important but they also can have problems due to solubility and the limited time they are in solution. These effects are not easy to account for.

Conclusions

Jet A fuel concentrations in the bioreactors went from 600 ppm to about 20 ppm within 20 days. Concurrently, the butyl carbitol was transformed from an alcohol to an acid and more slowly degraded. Even with only 0.3% commercial AFFF, the surface tension did not appreciably increase above 10 dynes/ cm until nearly forty days after degradation began. In another reactor BTEX levels fell from initial values of 150 ppm each to less than 4 ppm within 20 days. IBS AFFF at 0.3% concentration was fairly rapidly degraded with surface tension measurements increasing from about 12 dynes /cm to over 30 dynes/cm within the first 10 days of degradation.

The new IBS AFFF shows promise as a much more degradable surfactant that should cause many fewer problems in wastewater treatment facilities while still performing as an excellent AFFF. Butyl carbitol is not a good choice as an AFFF co-solvent and anti-freeze, and it would be preferable to significantly reduce the concentration in AFFF formulations for better biodegradation and less toxicity. The novel IBS bioreactor with bubbleless oxygenation is effective in degrading fuel components in firefighter wastewaters.