

Comparative Laboratory-Scale Testing of Dispersant Effectiveness of 23 Crude Oils Using Four Different Testing Protocols*

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Abstract

A controlled laboratory study was conducted to measure the dispersion effectiveness of Corexit 9500 on 23 different crude oils. This study was a part of a larger project initiated by the Bureau of Safety and Environmental Enforcement (BSEE) testing 20 oils to compare the predictive value of laboratory dispersant effectiveness tests with their larger scale test conducted at Ohmsett, BSEE's national oil spill response test facility located in Leonardo, NJ. The test used in this study was the Baffled Flask Test (BFT), which is planned for adoption as EPA's official testing protocol for listing commercial dispersant products on the National Contingency Plan Product Schedule, replacing the current Swirling Flask Test (SFT) [1]. In addition, the results of 3 additional oils, the 2 used in the SFT and BFT as currently written plus another reference oil, are presented. The temperature used for the tests was 15°C, to match the temperature used at Ohmsett. The dispersion effectiveness ranged from 3.4% to 93%. The BFT is a laboratory test with results that are inversely correlated with oil viscosity and therefore has predictive value in the decision to use a dispersant in the event of a spill.

Keywords

Dispersion, Oil Spill, Dispersant, Crude Oil, Viscosity, Dispersion Effectiveness

*This document has been reviewed in accordance with US Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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1. Background and Introduction

Bench-scale Dispersant Effectiveness (DE) tests are routinely used around the world to evaluate the potential effectiveness of a dispersant product on standard oils or to study the effect of oil and dispersant type and environmental variables on dispersant effectiveness. In the United States, from the Code of Federal Regulations [1] dispersant products must achieve a measured effectiveness of 45% or greater for South Louisiana Crude (SLC) or Prudhoe Bay Crude (PBC) using the SFT in order to be placed on the US Environmental Protection Agency's (EPA's) National Contingency Plan (NCP) Product Schedule (NCPSP, or "the Schedule") [2] for possible use in an oil spill. However, the effectiveness values recorded in the various available laboratory tests do not necessarily relate closely to the expected effectiveness in the field [3], where natural dilution, weathering, emulsions, and other natural processes can occur. Attempts have been made to correlate the results of bench-scale tests to one another, but these attempts have met with limited success because each test is performed with different variables (mixing speed, oil type, degree of weathering or emulsification, temperature, etc.) that might affect performance [4] [5].

A dispersant consists of three types of chemicals: surfactants, solvents, and additives. The intended effect of adding dispersant as a countermeasure is to disperse the spilled oil in marine waters. Surfactants, the active ingredient in chemical dispersants, reduce the oil-water interfacial tension, promoting the formation of small oil droplets (<100 μm) that are less likely to re-coalesce [6], suspending oil droplets as a plume which is subjected to high rates of dilution. This action 1) reduces risk to shorelines and biota and 2) increases the surface area to volume ratio of oil droplets, enhancing oil biodegradation [7]-[9]. However, due to the chemical and physical interactions between spilled oils and the sea, an understanding of the behavior of released oil and impact of dispersants must be based upon empirical data.

Limited field data are available comparing bench-scale test results to field success [4] [10] [11]. In 2010, the Department of Interior's Bureau of Safety and Environmental Enforcement (BSEE) conducted a research project at Ohmsett, the national oil spill response test facility located in Leonardo, NJ. Its objective was to develop large-scale test tank dispersant effectiveness (DE) data on 20 crude and fuel oils using Corexit 9500 dispersant [4]. The Ohmsett facility used a pilot-scale batch wave tank to test oil dispersion under wave action. Oil was pumped onto the water surface through a manifold, followed by dispersant application. After 30 minutes of mixing by a breaking wave field, the floating, non-dispersed residual oil was collected and quantified to determine the volume of oil remaining.

BSEE initiated additional testing to be conducted in round robin-like fashion by various independent laboratories to compare various existing DE tests to determine which, if any, are predictive of the larger scale performance results from the Ohmsett wave tank. Laboratory tests performed were the BFT, the SFT, the Exxon Dispersant Effectiveness Test (Exdet) test, and the Warren Springs Laboratory (WSL) test. Fresh oils were tested in this laboratory study for reproducibility and repeatability purposes [4]. In the SFT procedure, a pre-mixed solution of crude oil and dispersant was added to a specially designed glass side-arm flask containing synthetic seawater. The contents of the flask were mixed on an orbital shaker and allowed to settle. The sample of dispersed oil in seawater was obtained by manually tilting and pouring an aliquot through the side-arm followed by extraction and subsequent measurement in the same manner as the BFT. The EXDET apparatus used a separatory funnel filled with seawater. The oil and dispersant were added at a dispersant: oil ratio (DOR) of 1:20 and mixed. An absorbant pad was added to absorb the non-dispersed oil. Oil was extracted from the water and pad followed by measurement on a spectrophotometer operating at a wavelength of 460 nm. The WSL apparatus, also a separatory funnel, was mixed by vertically rotating the funnels. After a short settling time, a sample was removed by opening the stopcock at the bottom, chloroform was used to extract the oil, and the oil was measured using a spectrophotometer at a wavelength of 580 nm.

This paper summarizes data from the BFT and compares it with results from the wave tank, the Exdet, and WSL tests. The BFT was originally developed by EPA's National Risk Management Research Laboratory (NRMRL) [12]-[14] to replace the SFT, which yielded large discrepancies in DE values. Specifically the SFT requires that the analyst manually tilt the flask to pour out the sample to be analyzed. This inadvertently reintroduces mixing of the contents, which differs from analyst to analyst, resulting in increased variability [13]. The improved BFT method, however, provides sufficient mixing energy for dispersion, akin to that observed in the field and better reproducibility [12] [15] [16]. Currently the BFT method is listed in the proposed decision rule amendments to the 40 CFR 300 for listing a commercial dispersant product on the NCPSP [17], providing better reproducibility and higher DE criteria with current reference oils.

2. Materials and Methods

2.1. General Approach

This study utilized the 20 oils distributed for the BSEE round robin plus three additional stock reference crude oils housed within the US EPA. The physical properties of those oils are summarized in **Table 1**, where crude type is described using two different definitions, one based on API gravity or density (light, medium, or heavy) and the other based on kinematic viscosity [very light, light, medium, and heavy].

The BFT protocol uses a 150-mL screw-cap trypsinizing flask (an Erlenmeyer flask with baffles), modified by the placement of a glass stopcock near its bottom so that a subsurface water sample can be removed without disturbing the surface oil layer (**Figure 1**). Synthetic seawater and oil are added to the flask, followed by addition of a dispersant directly onto the floating oil slick. The flask is placed on an orbital shaker to receive mo-

Table 1. List of oils and physical properties.

Crude Oil Name	Dynamic Viscosity ^A (cP at 15°C)	Measured Density ^A (g/cm ³ at 15°C)	Kinematic Viscosity ^B (cSt at 15°C)	API gravity ^C	Crude Category by API gravity ^C	Crude Category by kinematic viscosity ^D
Anadarko	10	0.906	11	24.37	Medium	Light
ANS (20% evaporated)	52	0.890	58	27.17	Medium	Light
ANS (fresh)	35	0.884	40	28.24	Medium	Light
BHP Billiton	388	0.924	420	21.32	Heavy	Medium
Doba	1955	0.918	2130	22.34	Medium	Heavy
Elly	9700	0.958	10,125	15.91	Heavy	Heavy
Endicott (18% evaporated)	516	0.922	560	21.67	Heavy	Heavy
Endicott (fresh)	120	0.896	134	26.11	Medium	Medium
Harmony	3588	0.942	3809	18.41	Heavy	Heavy
IFO 120	1440	0.948	1519	17.46	Heavy	Heavy
IFO 380	10,490	0.966	10,859	14.69	Heavy	Heavy
North Star	8	0.848	9	35.03	Light	Very Light
PER 038	2977	0.956	3114	16.22	Heavy	Heavy
PER 040	18,500	0.968	19,112	14.39	Heavy	Heavy
PXP 01	9400	0.951	9884	16.99	Heavy	Heavy
PXP 02	31,195	0.965	32,326	14.84	Heavy	Heavy
Rock	3290	0.957	3438	16.06	Heavy	Heavy
Terra Nova	380	0.867	438	31.39	Light	Medium
Venoco E-10	11,906	0.961	12,389	15.45	Heavy	Heavy
Venoco E-19	64	0.892	72	26.81	Medium	Light
Stock Reference oils. Prudhoe Bay and South Louisiana crudes are the ones listed in the SFT.						
South Louisiana	7	0.840	8	36.61	Light	Very Light
Arabian Light	14	0.864	16	31.95	Light	Light
Prudhoe Bay	39	0.894	44	26.46	Medium	Light

^AData from [4], for the first 20 oils and from [18] for the 3 reference oils. ^BKinematic viscosity is dynamic viscosity/density. ^CAPI degrees are unitless and were devised by the American Petroleum Institute and the National Institute of Standards and Technology. It is an inverse calculation using the density or specific gravity at 60°F (~15°C). The category definitions are as follows: Light crude has an API gravity higher than 31.1° (<0.87 g/cm³), medium crude has an API gravity between 22.3° and 31.1° (between 0.87 to 0.92 g/cm³), and heavy crude has an API gravity between 22.3° and 10.0° (0.92 to 1.0 g/cm³), and extra heavy crude has an API gravity <10.0° (>1.0 g/cm³) [19]; ^DThe category definitions are as follows: Very light crude has a viscosity < 10 cSt, light crude between 10 - 100 cSt, medium crude between 100 - 500 cSt, and heavy crude > 500 cSt. [20].



Figure 1. Photograph of the modified baffled trypsinizing flask.

derately turbulent mixing, equivalent to an energy dissipation rate of 0.163 W/kg water which is approximately 2 orders of magnitude greater than that obtainable in the SFT [11]. After a short quiescent period to allow non-dispersed oil to float back up to the water surface, a subsurface water sample is removed for liquid-liquid extraction and analysis by UV-visible absorption spectrophotometry.

2.2. Synthetic Seawater

“Instant Ocean”, an artificial seawater manufactured by Aquarium Systems of Mentor, OH, served as the exposure matrix for the study. Its concentration was 34 g/L Milli-Q water (final salinity = 34 ppt). **Table 2** provides a list of the ion compositions of the sea salt mixture. The saltwater solution was allowed to equilibrate to $15^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ in the constant temperature room.

2.3. Oil Extraction and Analysis

Dichloromethane (DCM, pesticide quality) was used for liquid-liquid extractions of oil from all seawater samples collected from the baffled flasks and during standards preparation. A Brinkmann Eppendorf repeater pipettor capable of dispensing 2 μL to 5 mL, depending on the tip selected, was used for dispensing the required amounts of the oil and the dispersant. Dispersed oil concentrations were measured in a Shimadzu Recording UV-VIS Spectrophotometer (Model UV-1800) using standard transmission-matched quartz 10-mm path length rectangular cells with PTFE cover. The same wavelengths, 340, 370, and 400 nm, from the original SFT protocol [21] were used.

2.4. Oil Standards Procedure

Stock solutions in DCM were prepared for each oil with and without dispersant by combining 2 mL oil with 18 mL DCM. A volume of 80 μL Corexit 9500 was added to the oil-dispersant stock solutions to give a DOR of 1:25 (4% dispersant in oil). Stock solution concentrations were determined by mass measurements after each addition and subsequent density determination. To generate a 6-point calibration curve, a specific volume of the stock standard solution was added to 30 mL synthetic seawater in a 125 mL separatory funnel. These stock solution volumes were adjusted so that the absorbance readings fell within the linear dynamic range (LDR) of the spectrophotometer. Triplicate liquid/liquid extractions of samples were then performed by using 5 mL of DCM for each extraction and adjusting the final extract to 20 or 25 mL (adjusted to maintain the LDR).

2.5. Baffled Flask Test Procedure

To 120 mL of synthetic seawater in the baffled flask, 100 μL oil was pipetted directly onto the seawater surface with an Eppendorf repeater pipettor (set at stop 1 using a 5 mL tip). A volume of 4 μL of dispersant was pipetted onto the center of the oil slick (pipettor set at stop 2 using a 100- μL tip), taking care that the dispersant contacted

Table 2. Major ion composition of Instant Ocean™ Synthetic Sea Salts.

Major Ion	Salt Composition, % total weight	Salt Composition at 34 ppt Salinity, mg/L
Chloride (Cl ⁻)	47.470	18,740
Sodium (Na ⁺)	26.280	10,454
Sulfate (SO ₄ ²⁻)	6.600	2631
Magnesium (Mg ²⁺)	3.230	1256
Calcium (Ca ²⁺)	1.013	400
Potassium (K ⁺)	1.015	401
Bicarbonate (HCO ₃ ⁻)	0.491	194
Boron (B ³⁺)	0.015	6
Strontium (Sr ²⁺)	0.001	7.5
Solids Total	86.11%	34,090
Water	13.88	--
Total	99.99%	--

the oil before the water. This resulted in a DOR of 1:25, the DOR originally used in our standard BFT protocol (Sorral *et al.*, 2004a) and close to the average DOR reported in the BSEE Ohmsett report (~1:30) and the Exdet and WSL tests (DOR = 1:20). The flask was mixed on an orbital shaker (New Brunswick G24 shaker incubator with an orbital diameter of approximately 2.5 cm) set at a rotation speed of 200 rpm ($\pm 10\%$) for 10 ± 0.5 min. At the end of the mixing period, the flask was removed from the shaker and allowed to remain stationary for a quiescent period of 10 ± 0.25 minutes. A 30 mL sample volume was collected without disturbing the flask contents in a 50 mL graduated cylinder by opening the stopcock at the bottom of the baffled flask after first discarding the first 2 mL of sample exiting the stopcock. The sample was transferred into a 125 mL separatory funnel and extracted 3 times with 5 mL fresh DCM. For analysis the extract was adjusted to a final volume of 20 or 25 mL (some oils required dilution in volumetric flasks in order to conform to the LDR of the spectrophotometer). Each of the four replicates was analyzed separately such that mixing and settling times were exactly the same for all. In addition to the 4 replicate dispersant/oil/seawater mixtures, 4 additional replicate oil/seawater mixtures with no dispersant and 4 replicate method blanks (seawater alone for quality control purposes) were also analyzed.

2.6. Analysis of Extracts

Although a recording spectrophotometer capable of measuring absorbance at multiple wavelengths was used, the standard the SFT/BFT protocol was followed by recording the absorbance at three discrete wavelengths of 340, 370, and 400 nm and calculating the Area (A) under the absorbance vs. wavelength curve by applying the trapezoidal rule according to Equation (1):

$$A = \frac{(Ab_{340} + Ab_{370}) \times 30}{2} + \frac{(Ab_{370} + Ab_{400}) \times 30}{2} \quad (1)$$

where: Ab = the absorbance reading at a particular wavelength

The area count (Y) for the calibration standards was used to determine the slope (m) where X is the oil concentration (mg/L) in the calibration standard. This area count was used to calculate the Total Oil Dispersed (OD_T) and then the percentage of oil dispersed (%OD), based on the ratio of oil dispersed in the test system to the total oil added to the system, as given in Equations (2) and (3):

$$OD_T \text{ (mg)} = \frac{A}{m} \times D \times V_{DCM} \times \frac{V_T}{V_E} \quad (2)$$

where:

D = Dilution factor (as necessary to keep measurement in the LDR)

V_{DCM} = Volume of DCM extract, mL,
 V_T = total volume of seawater in flask, mL,
 V_E = volume of seawater extracted, mL, and

$$\%OD_d \text{ or } \%OD_c = \frac{OD_T}{\rho_{oil} \times V_{oil}} \times 100 \quad (3)$$

where:

$\%OD_d$ or $\%OD_c$ = %oil dispersed by chemical dispersant (d) or control, mechanical mixing alone (c),

ρ_{oil} = density of the specific test oil, mg/L, and

V_{oil} = volume (mL) of oil added to test flask

The dispersion effectiveness (DE) value that is reported is the lower 95% confidence level ($LCL95$) of the 4 independent replicates. Equation (4) summarizes the calculation of the $LCL95$:

$$LCL95_d \text{ or } LCL95_c = \bar{x} - t_{n-1,1-\alpha} \left(\frac{s}{\sqrt{n}} \right) \quad (4)$$

where:

$LCL95$ = lower 95% confidence level for chemically dispersed oil (d) and physically dispersed oil (c),

\bar{x} = mean dispersion effectiveness of the $n = 4$ replicates,

s = standard deviation, and

$t_{n-1,1-\alpha} = 100 \times (1 - \alpha)$ th percentile from the t-distribution with $n-1$ degrees of freedom.

For four replicates, = 2.35, where $\alpha = 0.05$.

2.7. Statistical Analysis

Prior to conducting the statistical comparisons, the four replicates within a given treatment were subjected to an outlier test, the Grubb's Test or Maximum Normal Residual test [22], and if an outlier ($p < 0.05$) was detected, an additional replicate was analyzed to maintain the required four replicates.

3. Results and Discussion

For the 23 oils tested, viscosity was well correlated with density, demonstrated by **Figure 2** where \log_{10} of the dynamic viscosity is plotted as a function of oil density. The figure confirms that viscosity increases with density [23], and the relationship is good as denoted by the coefficient of determination ($r^2 = 0.83$).

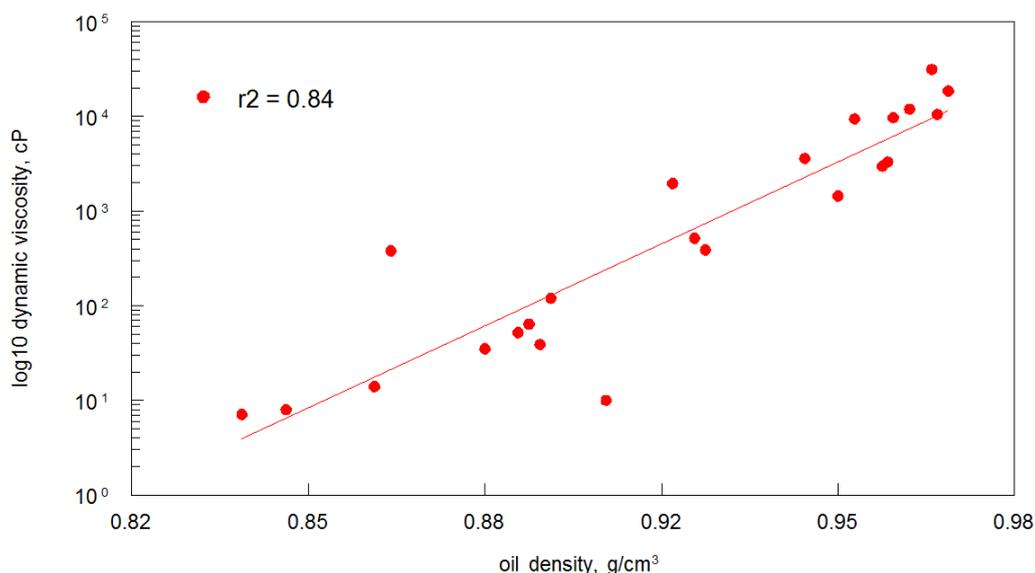


Figure 2. Dynamic viscosity as a function of oil density for the 23 crude oils.

Results of the dispersion experiments were tabulated for all 23 oils in **Table 3** along with the kinematic viscosity (dynamic viscosity/density). The table summarizes the kinematic viscosity, the average % oil dispersed by chemical dispersant (*LCL95d*) or control without dispersant (*LCL95c*). Results are sorted in descending order by the BFT's *LCL95d*.

Table 3 indicates that DE as expressed by the *LCL95d* appears to be inversely proportional to viscosity, both dynamic and kinematic, (although the correlation is non-linear), with less viscous, lighter oils being more easily dispersed than the heavier, more viscous oils. This relationship would likely also be true if all the oils had been previously weathered or emulsified, but this was outside the scope of the study objectives. This is illustrated in **Figure 3**, where the lower 95% confidence level of DE (with and without Corexit 9500) for the 23 test oils are sorted in descending order by *LCL95d*. The *LCL95d* or *c* formula adjusts for variability, hence error bars are not necessary. In general, effectiveness of dispersion was inversely proportional to viscosity, as the oils farther to the right in the figure are higher viscosity oils than those on the left side of the histogram. All oils categorized as very light-light based on kinematic viscosity exhibited DE between 57.86% and 94.65% when treated with chemical dispersant, compared to the controls which were less than 11%. Medium oils treated with dispersant exhibited DE between 54.95% and 75.91%, with controls less than 2.2%. The bulk of heavy oils had less than 50% DE with dispersant.

Table 3. Results sorted in descending order by dispersant effectiveness (*LCL95d*).

Test Oil	Kinematic Viscosity, cSt	Avg % oil dispersed, $\overline{\%OD}_d$	<i>LCL95d</i>	Avg % oil dispersed in controls, $\overline{\%OD}_c$	<i>LCL95c</i>
Arabian Light	16	96.50	94.65	1.88	1.22
Anadarko	11	100*	87.12	14.96	10.76
South Louisiana	8	93.81	85.76	8.42	5.64
North Star	9	87.84	82.37	10.87	0.60
Terra Nova	438	81.00	75.91	3.57	2.20
ANS Fresh	40	76.33	74.00	5.08	4.59
Endicott Fresh	134	80.01	72.47	4.15	2.32
Endicott, 18% evaporated	560	71.97	68.24	5.32	1.51
Prudhoe Bay	44	71.16	66.41	2.43	1.76
IFO 120	1519	73.11	65.88	5.58	3.31
ANS, 20% evaporated	58	78.44	64.93	4.19	3.46
Venoco E-19	72	70.88	57.86	2.28	1.87
BHP Billiton	420	58.14	54.95	5.51	3.93
Doba	2130	55.09	51.03	5.64	4.52
Rock	3438	50.46	44.74	2.50	1.72
PER038	3114	53.89	37.97	2.97	1.63
IFO 380	10,859	40.44	26.93	4.34	2.02
Venoco E-10	12,389	31.52	26.42	1.50	1.31
Elly	10,125	31.34	24.14	0.95	0.74
PER040	19,112	31.56	21.34	0.61	0.24
Harmony	3809	32.28	19.78	1.69	0.83
PXP01	9884	11.12	4.67	0.72	0.56
PXP02	32,326	7.04	3.88	0.99	0.46

*Analytical results were >100%, due to difficulties with this transparent oil.

Dispersion Effectiveness of the test oils with chemical dispersant vary depending on the test method used (Figure 4) using LCL95d from Figure 3). DE data are sorted in descending order according to the BFT results with the addition of the other test method results for the 20 oils. For light and medium oils, the BFT yielded higher DE compared to the WSL test. However, for some heavy, viscous oils (eg. Rock, Elly or PXP01), WSL yielded higher DE than the BFT method. Overall, the Ohmsett and Exdet tests resulted in higher DE regardless of oil viscosity. Large variations in the reported DE can be attributed to differences in aspects of test design, such as mixing energy, settling/surfacing time and oil collection from tanks or flasks [5] [20]. For example the low mixing energy of the WSL, biases the DE low compared to the other tests, whereas the high mixing and reduced wall effects of the tank in the Ohmsett test biases the DE high compared to the BFT. What these results do not demonstrate though are reproducibility issues associated with specific tests, where the BFT has been previously shown to exhibit the highest reproducibility [8]-[10]. The correlation among the four different methods of measuring DE was low.

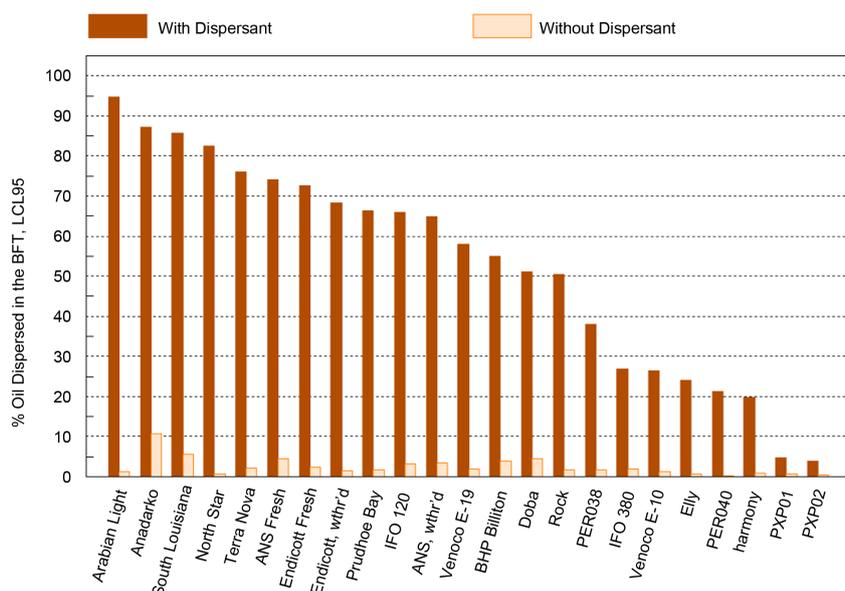


Figure 3. LCL95 for the 23 oils with and without Corexit 9500.

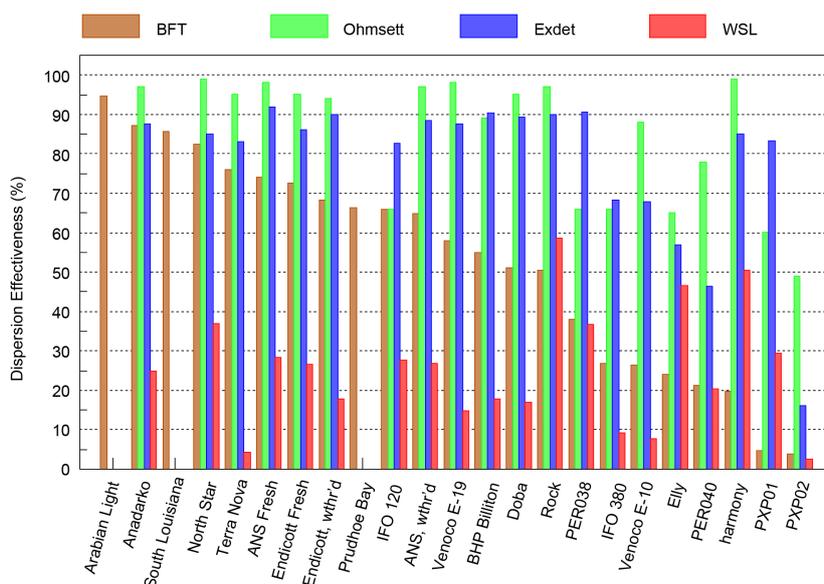


Figure 4. Comparison of DE results (LCL95d for BFT).

An attempt was made to correlate the BFT DE with the other three tests as illustrated in **Figure 5**, which plots the BFT vs. WSL, Ohmsett, and Exdet tests in terms of DE. No correlation was found with the WSL test. The Ohmsett and EXDET test showed a slight correlation. The scatter was high in all cases, as denoted by the low r^2 values. The y-intercepts were also high (63.6% for Ohmsett, and 55.6% for EXDET), which suggests that the low DE values for the higher viscosity oils measured by the BFT were not detected accurately by the other three methods. In other words, the BFT data showed low DE values for the high viscosity oils relative to the lower viscosity oils, but the other methods were unable to distinguish DE as a function of oil viscosity (see **Figure 4**).

In regards to the Ohmsett wave tank test, the dispersed oil measurement was calculated by subtracting the mass of non-dispersed oil, collected by skimming the floating oil on the surface, from the known amount of total oil added to the system. This method does not account for losses of oil due to adhesion to surfaces (booms, walls of the tank, etc.), which may have contributed to significant measurement error. Since the mixing energy input for the BFT equates to that of a moderately energetic sea state [11], it is possible that the other methods (Exdet, and WSL) did not produce mixing energy conditions sufficient for adequate DE to occur in the presence of a product (Corexit 9500) widely known to be a good dispersant. In addition to mixing energy, differences in test design might account for differences observed between the BFT and the other test methods. As compared to the BFT results, the wave tank and the EXDET tests appeared to overestimate DE for the heavier oils, while the WSL test under-reported for the lighter oils. Bias may result if the sorbent pad in the EXDET and Ohmsett test is unable to sorb all the heavy oil, leaving a residual undispersed oil that would be measured and misinterpreted as dispersed oil. Since we did not conduct those measurements ourselves, but are only comparing our results to the findings of others, we can only speculate the reasons for the differences noted.

When it was clear that DE was moderately dependent on oil viscosity and density, additional plots were constructed for further study. When *LCL95d* was plotted as a non-linear function of kinematic viscosity (**Figure 6**), the data conformed to an approximate 1st order relationship with an r^2 of 0.85. Thus, the higher the viscosity, the lower was the dispersibility. This result was not unexpected since viscosity should affect DE due to the resistance to interfacial tension change in the presence of a surfactant.

Reference 24 reported that results indicating that most high energy tests (the Mackay, the Labofina (also known as the WSL), and the oscillating hoop) produce unique dispersant effectiveness results that correlate poorly with the physical properties of the oil. However, our laboratory BFT (**Figure 6**) agrees with previous research from field studies showing that dispersibility of oil is inversely proportional to viscosity [3] [6] [24] [25].

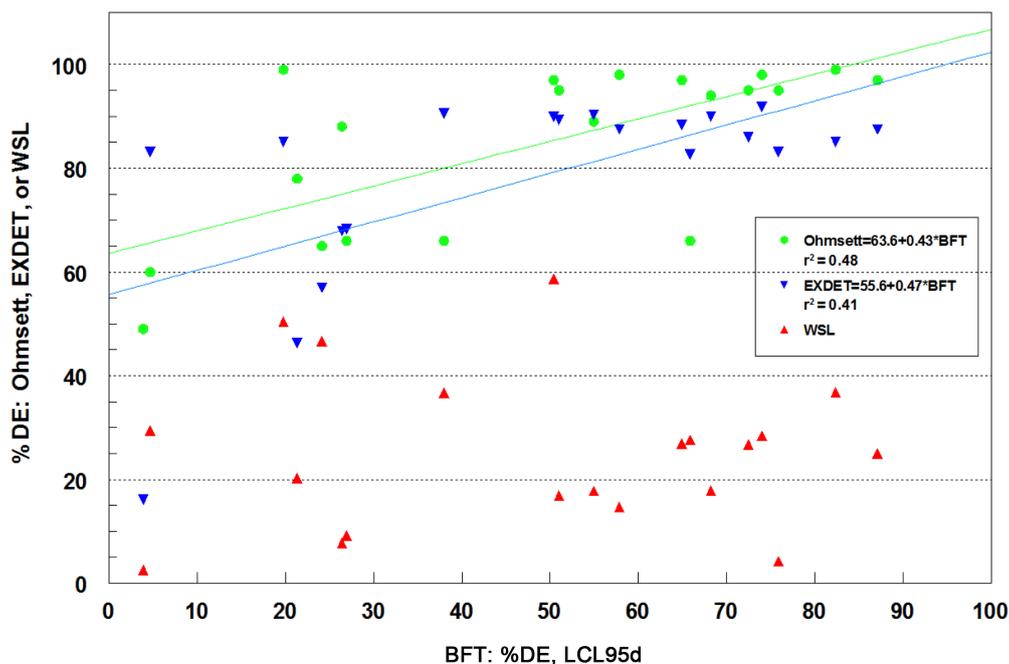


Figure 5. Correlation between the BFT vs Ohmsett, EXDET, and WSL.

A correlation for DE with the paraffin content of heavier oils has been reported [26]. There are instances where oils of similar viscosity disperse quite differently. Long-chain linear paraffins have been suspected of resisting dispersion by their cohesive nature [25]. Utilizing gas chromatograph/mass spectrometer (GC/MS) measurements, they calculated the ratio of total normal paraffin content (SIM mode, ion 57) to total oil (scan mode, total ion chromatogram (TIC) and found a negative correlation whereby the higher the saturate concentration, the lower the DE. Following their method, the ratios for the oils in our study were calculated in duplicate and illustrated in **Figure 7**. No correlation was found for viscous oils (>1000 cSt). The most striking observation is found in analyzing the oils with DE > 30%. The results for Anadarko crude (circled) were omitted due to its uniqueness as an almost transparent oil with a very high PAH content. The regression of the subset, oils with DE > 30% minus Anadarko, gives an $R^2 = 0.57$ and shows a positive correlation between paraffin content and DE. So high saturate concentrations may be a limiting factor in dispersibility for lower viscosity crude oils.

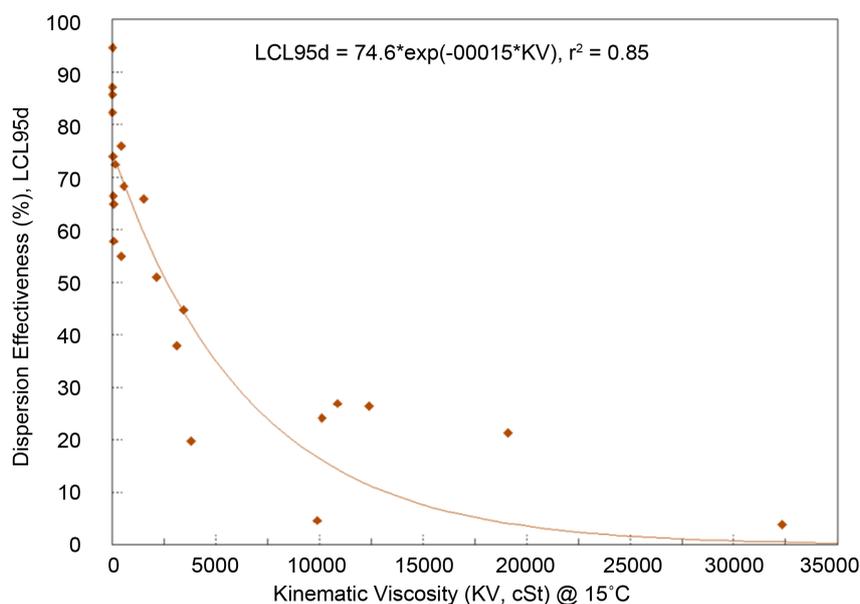


Figure 6. LCL95d as a function of kinematic viscosity (cSt) at 15°C.

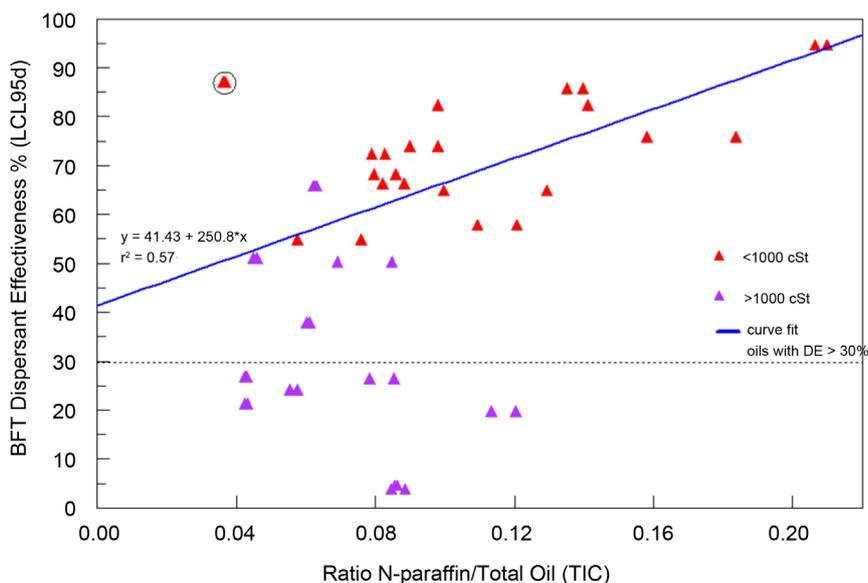


Figure 7. %DE as a function of paraffin content.

4. Conclusions

This study was undertaken to characterize dispersion effectiveness for a variety of oils (fresh or slightly weathered) covering a range of viscosities and densities. DE results with the BFT were compared with three other procedures, the WSL and Exdet laboratory tests and the Ohmsett pilot test. In addition to the 20 oils tested by the other labs, Arabian Light crude and the two standard EPA reference oils (SLC and PBC) currently used in EPA's SFT and BFT were included. These additional oils are light and medium crude oils, according to their reported API gravity (Table 1). The kinematic viscosities and API gravities of the 23 oils tested ranged from 8 to 32,326 cSt and 14.39° to 36.61° API, respectively. Expectedly, DE was inversely proportional to oil viscosity and directly proportional to API gravity (density). The Baffled Flask Test provides a good indication of the dispersibility of oil based on mixing energy. Neither the WSL test nor the EXDET test produced results comparable to the BFT in terms of predicting dispersibility as a function of the viscosity or API gravity properties of the oil. A modest correlation between the BFT and the Ohmsett and EXDET tests were found, but the high y-intercept value suggested that those tests might be positively biased when reporting results compared to BFT.

There is a critical need for an improved method of evaluating DE in commercial dispersant products prior to their listing on the National Contingency Plan Product Schedule. Such testing aides the federal government on-scene coordinators and the responsible parties in determining viability of dispersant products and decision making during oil spills. The Baffled Flask Test is a laboratory test in which oil dispersibility is inversely correlated with viscosity. Our findings also demonstrated that both paraffin content and viscosity can be predictors of Dispersion Effectiveness. These results strengthen the case for the use of the BFT as a standard DE test of oil spill chemical dispersants in the Federal Register proposed decision rule.

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References

- [1] 40CFR Appendix C To Part 300—Swirling Flask Dispersant Effectiveness Test, Revised Standard Dispersant Toxicity Test, and Bioremediation Agent Effectiveness Test. (7-1-03 Edition)
http://www.epa.gov/oem/docs/oil/cfr/appendix_c.pdf
- [2] National Contingency Plan (NCP) Subpart J—Product Schedule.
<http://www.epa.gov/emergencies/content/ncp/index.htm>
- [3] Colcomb, K., Salt, D., Peddar, M. and Lewis, A. (2005) Determination of the Limiting Oil Viscosity for Chemical Dispersion at Sea. *Proceedings, 2005 International Oil Spill Conference*, **2005**, 53-58.
<http://dx.doi.org/10.7901/2169-3358-2005-1-53>
- [4] SL Ross Environmental Research (2011) Comparison of Large Scale (Ohmsett) and Small Scale Dispersant Effectiveness Test results, Report for US Department of the Interior, Bureau of Ocean Energy Management, Regulation, and Enforcement, Herndon, Va.
- [5] Clark, J., Becker, K., Venosa, A. and Lewis, A. (2005) Assessing Dispersant Effectiveness for Heavy Fuel Oils Using Small-Scale Laboratory Tests. *Proceedings, 2005 International Oil Spill Conference*, **2005**, 59-63.
<http://dx.doi.org/10.7901/2169-3358-2005-1-59>
- [6] Li, M. and Garrett, C. (1998) The Relationship between Oil Droplet Size and Upper Ocean Turbulence. *Marine Pollution Bulletin*, **36**, 961-970. [http://dx.doi.org/10.1016/S0025-326X\(98\)00096-4](http://dx.doi.org/10.1016/S0025-326X(98)00096-4)
- [7] Venosa, A.D. and Zhu, X. (2003) Biodegradation of Crude Oil Contaminating Marine Shorelines and Freshwater Wetlands. *Spill Science & Technology Bulletin*, **8**, 163-178. [http://dx.doi.org/10.1016/S1353-2561\(03\)00019-7](http://dx.doi.org/10.1016/S1353-2561(03)00019-7)
- [8] NRC, National Research Council (2005) Understanding Oil Spill Dispersants: Efficacy and Effects. National Academies Press, Washington DC.
- [9] Venosa, A.D. and Holder, E.L. (2007) Biodegradability of Dispersed Crude Oil at Two Different Temperatures. *Ma-*

- rine Pollution Bulletin*, **54**, 545-553. <http://dx.doi.org/10.1016/j.marpolbul.2006.12.013>
- [10] Trudel, B.K., Belore, R.C., Lewis, A., Guarino, A. and Mullins, J. (2005) Determining the Viscosity Limits for Effective Chemical Dispersion: Relating Ohmsett Results to Those from Test At-Sea. *Proceedings, 2005 International Oil Spill Conference*, **2005**, 71-76. <http://dx.doi.org/10.7901/2169-3358-2005-1-71>
- [11] Daling, P.S. and Lichtenthaler, R.G. (1986) Chemical Dispersion of Oil. Comparison of the Effectiveness Results Obtained in Laboratory and Small-Scale Field Tests. *Oil & Chemical Pollution*, **3**, 19-35. [http://dx.doi.org/10.1016/S0269-8579\(86\)80011-9](http://dx.doi.org/10.1016/S0269-8579(86)80011-9)
- [12] Venosa, A.D., King, D.W. and Sorial, G.A. (2002) The Baffled Flask Test for Dispersant Effectiveness: A Round Robin Evaluation of Reproducibility and Repeatability. *Spill Science & Technology Bulletin*, **7**, 299-308. [http://dx.doi.org/10.1016/S1353-2561\(02\)00072-5](http://dx.doi.org/10.1016/S1353-2561(02)00072-5)
- [13] Sorial, G.A., Venosa, A.D., Miller, K.M., Holder, E.L. and King, D.W. (2004a) Oil Spill Dispersant Effectiveness Protocol—Part I. Impact of Operational Variables. *Journal of Environmental Engineering (ASCE)*, **130**, 1073-1084. [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(2004\)130:10\(1073\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(2004)130:10(1073))
- [14] Sorial, G.A., Venosa, A.D., Miller, K.M., Holder, E.L. and King, D.W. (2004b) Oil Spill Dispersant Effectiveness Protocol—Part II. Performance of the Revised Protocol. *Journal of Environmental Engineering (ASCE)*, **130**, 1085-1093. [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(2004\)130:10\(1085\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(2004)130:10(1085))
- [15] Kaku, V.J., Boufadel, M.C. and Venosa, A.D. (2006) Evaluation of Mixing Energy in Laboratory Flasks Used for Dispersant Effectiveness Testing. *Journal of Environmental Engineering*, **132**, 93-101. [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(2006\)132:1\(93\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(2006)132:1(93))
- [16] Kaku, V.J., Boufadel, M.C. and Weaver, J.W. (2010) Scaling Exponents of Structure Functions in an Eccentrically Rotating Flask. *Advances in Theoretical and Applied Mechanics*, **3**, 233-252.
- [17] Environmental Protection Agency (2015) National Oil and Hazardous Substances Pollution Contingency Plan (2015) Proposed Rule. 80 FR 3380, January 22, 2015.
- [18] Environment Canada. Spills Technology Databases. http://www.etc-cte.ec.gc.ca/databases/spills_e.html
- [19] API Gravity. <http://www.petroleum.co.uk>
- [20] Fingas, M.F., Stoodley, R. and Laroche, N. (1990) Effectiveness Testing of Spill-Treating Agents. *Oil & Chemical Pollution*, **7**, 337-348. [http://dx.doi.org/10.1016/S0269-8579\(05\)80048-6](http://dx.doi.org/10.1016/S0269-8579(05)80048-6)
- [21] Fingas, M.F., Hughes, K.A. and Schweitzer, M.A. (1987) Dispersant Testing at The Environmental Emergencies Technology Division. *Proceedings of the Tenth Arctic Marine Oil Spill Program Technical Seminar*, Edmonton, 9-11 June 1987, 343-356.
- [22] Grubbs, F. (1969) Sample Criteria for Testing Outlying Observations. *Annals of Mathematical Statistics*, **21**, 27-58.
- [23] Jokuty, P. (2001) Properties of Crude Oil and Oil Products (Not Just another Pretty Database). *Proceedings of the 2001 International Oil Spill Conference*, Tampa, 26-29 March 2001, 975-981.
- [24] Fink, J. (2011) Oil Spill Treating Agents. In: *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids*, Elsevier Gulf Professional Publishing, Amsterdam, 625-646.
- [25] Lessard, R.R. and Demarco, G. (2000) The Significance of Oil Spill Dispersants. *Spill Science & Technology Bulletin*, **7**, 299-308. [http://dx.doi.org/10.1016/s1353-2561\(99\)00061-4](http://dx.doi.org/10.1016/s1353-2561(99)00061-4)
- [26] Canevari, G., Calcavecchio, P., Lessard, R.R., Becker, K.W. and Fiocco, R.J. (2001) Key Parameters Affecting the Dispersion of Viscous Oil. *Proceedings of the 2001 International Oil Spill Conference*, 479-483.