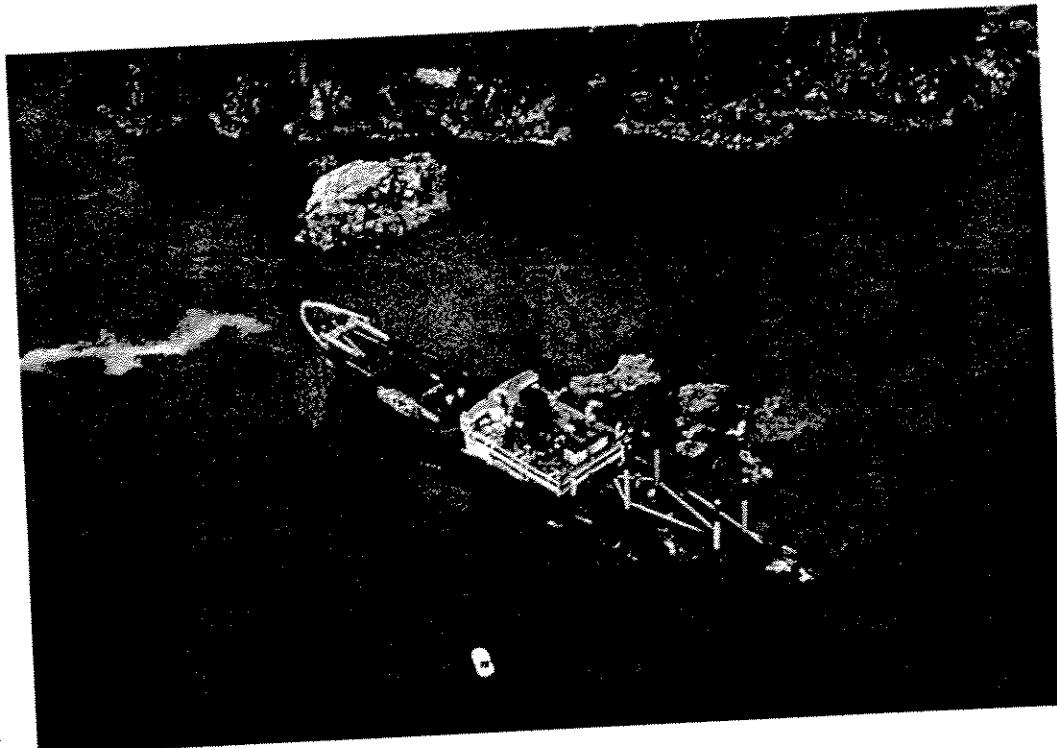


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PHYSICAL AND CHEMICAL STUDIES ON OIL SPILL DISPERSANTS: EFFECTIVENESS VARIATION WITH ENERGY

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SUMMARY

A study of the relationship between dispersant effectiveness and energy was performed in three different laboratory apparatus which use rotational motion to generate mixing energy. The stability of the resulting emulsions was gauged by measuring the amount of oil that remained in the water column over time.

The findings are that each oil/dispersant combination shows a unique threshold or onset to dispersion. The effectiveness goes up linearly with energy, expressed as flask rotational speed. Natural dispersion was also measured and shows similar behaviour to chemical dispersion except that the thresholds occur at a higher energy and effectiveness rises more slowly with increasing energy. Effectiveness (defined as the percentage of oil in the water column) rises rapidly to 100% with increasing energy for light oils treated with chemical dispersants. Heavier oils will disperse but to lesser effectiveness values.

Effectiveness varies significantly with quantity of dispersant amount. Stability of the resulting emulsion is affected by dispersant amount. Effectiveness can be viewed as a trade-off between energy, stability and dispersant quantity. As energy and dispersant quantity are increased, so is the effectiveness. Stability of the resulting emulsion is relatively independent of energy, but dependent on the amount of dispersant. High dispersion can be achieved using high energy and low dispersant amount, however, the resulting dispersion is less stable than one using more dispersant.

INTRODUCTION

Energy has been ascribed as the principle reason for the varying results of dispersant effectiveness results in the field and in the laboratory. Difficulties in varying or measuring this energy have left the variation of dispersion and energy largely unstudied. Energy is a complex topic.¹ Descriptions of what is meant by relevant energy to oil dispersion varies. One means to describe energy is by measuring the wavelength and amount of turbulence in the near surface.² Another definition is that of steepness of waves and their periods.³ Several discussions on the relationship between dispersion and energy have taken place, but little experimental work has been published.⁴⁻⁷ Fundamental literature on surfactants also does not propose energy relationships.^{8,9}

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Many different types of dispersant test procedures and apparatus are described in the literature. One estimate places this at 50 different tests or procedures.^{10,15} Little work has been done on determining the reason for the poor correlation between test results. Most of the investigators cite energy as being the most significant factor. The general conclusion has been that the differences in energy levels and the way these have been applied to the oil/water mixture result in effectiveness values that are unique.

EXPERIMENTAL

Several rounds of experiments were conducted to determine the effect of varying energy. Several oils were used in these tests. Table I lists these oils and gives their basic physical properties. The dispersant used in this study is the Exxon product Corexit 9527 (abbreviated C9527 in some tables in this paper). All runs where dispersant was used, were performed with dispersant already mixed in the oil at a ratio of 1 to 25 by volume. This practice was adopted to achieve more repeatable results as determined in earlier experiments where both premixed and drop-wise addition were used.¹³ Saltwater was prepared with sodium chloride to 33 ‰ or degrees salinity. All tests were done at a temperature of 20°C. Apparatus, oil and water were left at these temperatures for at least 20 minutes before the beginning of each test to ensure thermal equilibrium. All tests were done in thermally-controlled chambers.

TABLE I
TEST OIL PROPERTIES

OIL	DESCRIPTION	KINEMATIC VISCOSITY (mm ² /sec at 15°C)	DENSITY (g/ml. at 15°C)
ASMB	ALBERTA SWEET MIXED BLEND	8	0.84
ARABIAN	ARAB BLEND	40	0.87
BUNKER C	LESS-VISCOUS BUNKER C	200	0.93
NORMAN WELLS	NORTHERN CANADIAN CRUDE	7	0.83
NORTH SLOPE	PRUDHOE BAY CRUDE	55	0.88

shaker consisting of a moving table. This shaker is capable of rotational speed variations from 50 to 450 with relatively good repeatability. The revolutions meter on the shaker is calibrated periodically with a tachometer to ensure accuracy. A pipette is used to remove a 30 ml. sample from the apparatus after the settling time.

Analysis for all four apparatus is performed by taking a sample of water from the test vessel after the run is complete, extracting the water with a solvent and measuring the absorbance at three visible wavelengths (370, 340, and 400), and then assigning effectiveness on the basis of a calibration curve. Calibration curves are prepared in a manner similar to the actual runs. Water is used in these calibration runs to ensure that extraction efficiency is compensated for and to compensate for the coloration addition of small water droplets.

EXPERIMENTAL RESULTS

Results of tests are shown in Table 2 and Figure 1. This figure illustrates the results of dozens of experiments. The findings are as follows: that dispersion increases very rapidly from a low value to nearly 80 to 100% and that natural dispersion onset occurs at an energy level higher than that for chemical dispersion, and finally that the natural dispersion curve has a lesser slope than that for chemical dispersion.

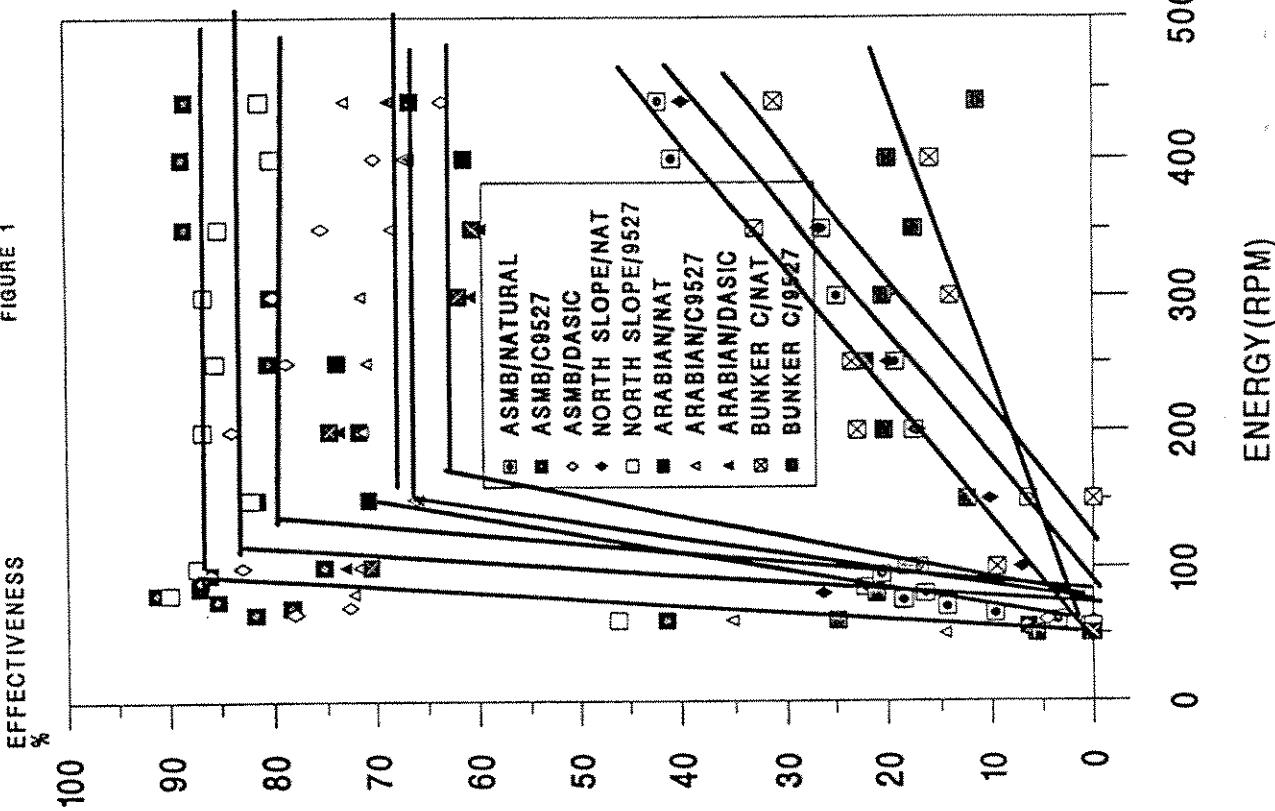
The energy is sufficient in the high energy apparatus to disperse Bunker C light. Tests on regular Bunker C did not yield dispersion chemically or naturally. During the natural dispersion runs and partially during the chemical runs, the Bunker C grouped into large droplets on the surface. This is indicative that the energy in the apparatus is insufficient to disperse this oil or that this oil is indispersible under normal conditions. Onsets of natural dispersion lag the chemical dispersion and the curves of natural dispersion have a lesser slope than those for chemical dispersion. In addition, the heavier oils tested do not go to as high a dispersion level as other oils. This is indicative that they are not as readily dispersable as the ASMB. Another trend observed is that the order of chemical and natural dispersion onsets for the oils tested, are the same and are similarly spaced with respect to energy. The effect of chemical dispersant is to decrease the onset of dispersion and increase the amount by a large factor.

Some preliminary work has been done on assessing the difference in dispersion at high and low energies. This work indicates that dispersions formed at lower energies are more stable. Experiments on the amount of oil that remains dispersed in the water column after 24 hours is about 60% for the high energy dispersion and 80% for the low energy dispersion. The difference may well be the amount of dispersant in the droplets. The preliminary results of these tests are illustrated in Figure 2. This figure shows only results from tests conducted using the dispersant Corexit 9527. Work on stability of the resulting emulsions continues.

An apparatus, called simply "the high energy test" in our laboratories, was developed to measure dispersion at very high energy levels. This vessel is square and of dimensions 30 cm. on all sides. The effect of the corners is to create high levels of turbulence. The volume of oil and water were 5 L and 0.25 mL to yield an oil-to-water ratio of 1:20,000. This ratio was shown in a previous paper to yield optimal results. The mixing time is 20 minutes and the settling time is 10 minutes before samples are taken. The mixing energy is supplied by a Brunswick

COMPOSITE DATA

FIGURE 1



GRPM	EFFECTIVENESS VALUES FOR FOUR OILS							
	ALBERTA SWEET BLEND	NORTH SLOPE	ARABIAN LIGHT	BUNKER C LIGHT	NATURAL	W/C9527	DASIC	NATURAL
440	42.0	88.2	63.4	39.7	81.0	114	73.2	68.7
400	40.7	88.6	70.1	20.0	80.0	19.9	67.2	66.6
350	26.2	88.4	75.4	26.5	86.0	17.5	68.5	69.7
300	24.8	80.1	79.9	20.0	86.5	20.4	71.6	60.7
250	19.2	80.4	78.7	19.8	85.4	22.1	71.0	60.7
200	17.5	81.8	83.9	17.2	86.7	20.3	71.4	73.7
150	6.4	81.6	70.5	10.2	82.1	12.4	66.4	65.9
100	17.1	75.3	82.9	7.0	87.3	18.2	71.9	73.2
90	20.6	86.1	86.0					9.5
85	22.2	87.1						70.6
80	20.6	87.0						
75	18.5	85.3	91.3	26.2	90.0	21.1	72.4	
70	14.4	78.3	81.7	72.8				
65	9.7	78.3						
60	3.6	41.4	41.4	78.0				
55	0.3	6.4	6.4		0.0	0.0		
50	0.0	0.0	0.0		0.0	0.0		

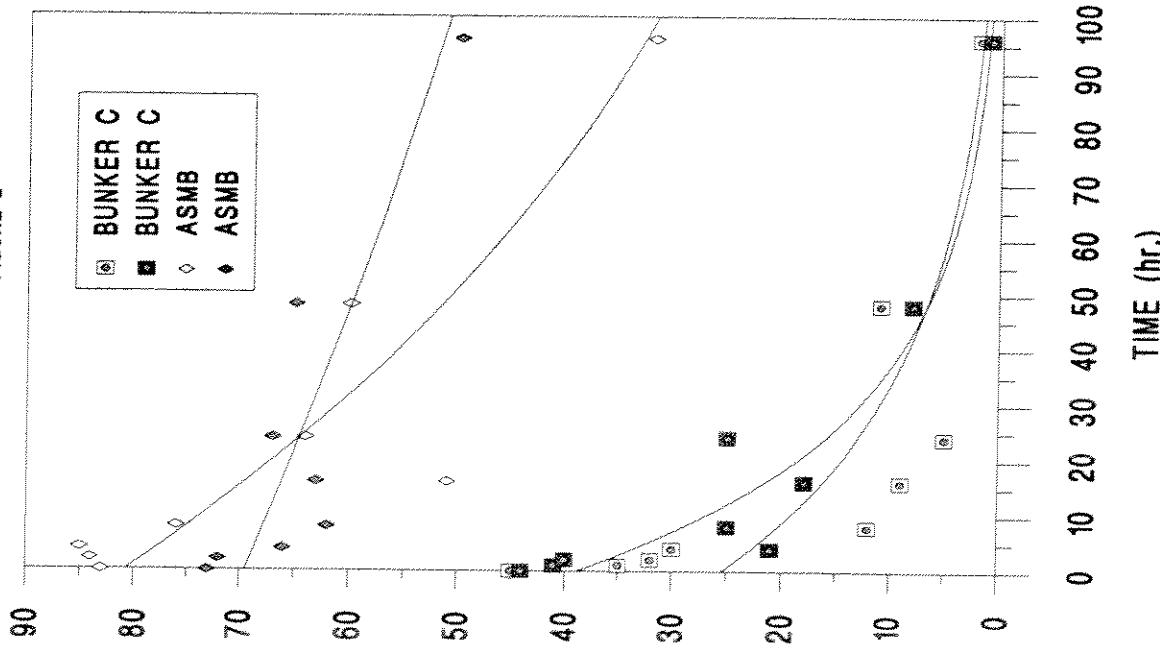
LEGEND W/C9527 = WITH DISPERSANT CORREXIT 9627

TABLE 2 EFFECTIVENESS VALUES FOR FOUR OILS

STABILITY MEASUREMENTS ON TWO OILS WITH COREXIT 9527

OIL REMAINING IN
THE WATER %

FIGURE 2



SUMMARY AND CONCLUSIONS

Chemical dispersion increases with energy in a linear fashion until a maximum is reached. For light oils this maximum is about 85%. For heavier oils this is about 65%. The dispersion curve is very steep, that is only a small amount of energy causes a large amount of change in dispersion. There exists an energy threshold below which little dispersion occurs. Chemical dispersion curves for different oils appear to be parallel. This may be indicative that the mechanism is fixed and only the threshold varies.

Natural dispersion is analogous to chemical dispersion except that the onset occurs at a higher energy and the increase with energy is much less. Initial work has also been conducted on particle stability. This shows that there may be differences in the stability of dispersions at low and high energies. The difference does not appear in droplet size, but is probably due to the lesser amount of dispersant in those droplets formed at high energy. This lesser dispersant amount is simply a result of forming many more droplets at high energy with the same amount of dispersant.

The major question these experiments raise is how the energy in these tests relates to that at sea. There are a few observations which indicate that most typical sea energies actually occur at the low end of the energy spectrum shown in the test data presented here. In one test at sea, ASMB and Bunker C light were observed to start dispersing naturally around Beaufort 6.²⁰ The EKOFISK BRAVO oil was observed to disperse naturally at sea states around Beaufort 5 or 6.²¹ It is recognized that turbulent energy is the important factor for dispersion. Technology does not exist at this time to measure this type of energy at sea and in the laboratory. There may be potential for this in the future with laser doppler or hot wire instruments.

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