COMBUSTION PROMOTERS EVALUATION

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ABSTRACT

This study deals with the in-situ burning of oil slicks with the use of combustion promoters. It consists of a four-phase program. The intent of Phase I is to identify, utilizing controlled conditions, the most promising combustion promoters and to estimate the optimum promoter loadings. Phase II is to quantify the effect of the presence of slush ice on in-situ combustion with and without promoters, while Phase III is to quantify the possible effects of waves on oil combustion. Phase IV is to assess the feasibility of using combustion promoters to enable the combustion of unconfined slicks.

Extensive combustion experiments were undertaken in outdoor tanks with and without promoters for the cases under consideration. Standard ignition technique was used. Of the ten promoter tests in Phase I, Aerosil R972, Fibreperl and peat moss were selected for the subsequent phases. In Phase II, for thin slush ice condition, there is no sufficient advantage of using promoters over burning the oil alone to justify the purchase and distribution of the materials. However, great improvement is noted for thick slush ice condition. Combustion of unconfined slicks appears feasible with the use of a high bulk hydrophobic material.

1.0 INTRODUCTION

In the repertoire of oil spill cleanup techniques, in situ burning is an approach alternative to two other broad classes of treatment: skimming and emulsification. Skimming is usually the preferred approach in temperate climates because it removes the pollutant to a specialized disposal facility, but skimming is logistically difficult under Arctic conditions. Emulsification has been widely used at major spills such as the Torrey Canyon and to

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clean up last traces left after skimming. It disperses the pollutant into the water environment for biodegradation. Under suitable conditions it leaves virtually no undiluted residue. The burning approach, on the other hand, converts part of the pollutant to harmless materials (carbon dioxide and water vapour), disperses another fraction as smoke, and normally leaves a residue on the water.

In spite of this relatively crude cleanup performance, in situ burning is a promising approach for Arctic application because it might be possible to implement it from an aircraft under difficult environmental conditions. Ideally, igniters dropped from an aircraft would ignite and completely burn off the floating pollutant without any further intervention. Field experience (e.g. Torrey Canyon, 1967, Deslauriers et al, 1977) laboratory work (e.g. Abdelnour et al, 1977) and theory (Purves, 1977) show that this idea is unachievable in practice. Any turbulence greatly impedes ignition of a free-floating oil layer, and heat transfer to the cold water substrate cools the surface of the oil below the fire point once the fire has reduced the thickness to a few millimetres. It is these two problems that have motivated the development of promoters to improve combustion.

A wide variety of combustion promoters have been tested by various investigators (Frieberger et al, 1971; Tulley, 1976) in the laboratory under controlled conditions and in the field. Experience with the combustion promoters has been mixed. Inconsistant, sometimes even conflicting, results were reported. Freiberger and Byers performed a comparative study on the effectiveness of combustion promoters. They did not cover enough quantitative information of the tests, especially with respect to the test conditions, the conditions of the initial slicks and the residue after burn. Their application is, therefore, limited. As a result of this limited experience, Arctec has developed a quantitative comparative study of the effectiveness of combustion promoters using controlled burning tests.

2.0 RESEARCH PROGRAM

This study consisted of a four-phase program. A general description of each phase under consideration is discussed in the following subsections.

2.1 Phase I - Confined Oil Slicks

The intent of this phase is to identify, utilizing controlled conditions, the most promising combustion promoters and to estimate the optimum promoter loadings.

2.2 Phase II - Confined Slicks in Slush Ice

This phase is intended to quantify the effect of the presence of slush ice on in-situ oil combustion with and without promoters.

2.3 Phase III - Confined Slicks in Wave Conditions

The intent is to quantify the possible effect of waves on the combustion process with and without promoters.

2.4 Phase IV - Unconfined Oil Slicks

The aim is to assess the feasibility of using combustion promoters to enable the in-situ combustion of unconfined slicks.

During this study the following parameters were monitored:

- temperatures of air, water and oil
- wind speed
- preheat time
- flame spreading time
- combustion time
- volume and weight of residue remaining
- flame size
- smoke generation
- final size of unconfined slicks

The types of oil used in this test program were Bunker C, and one-day aged and seven-day aged crudes.

3.0 COMBUSTION PROMOTERS

In general, a combustion promoter is defined as any organic or chemical material which is applied to oil to promote its combustion by sustaining combustion. The materials which serve to ignite or assist igniting of the oil slicks will not be considered as combustion promoters.

The combustion promoters which were examined during the Phase I tests can be categorized as follows:

a. Organic Fibres:

- Peat Moss - natural organic fibre
- Straw - natural organic fibre
- Wood Shavings - natural organic fibre

b. Inorganic Agents:

- Seabeads - celluated glass beads
- Vermiculite - expanded mineral
- Seawick - expoyamine resin and glass micro
- Aerosil R972 - silicon dioxide, surface treated with silane
- Cab-O-Sil M5 - silicon dioxide
- Tullanox 500 - silicon dioxide, surface treated

c. Mixed Agent (Organic/Inorganic):

- Fibreperl - expanded perlite (aluminum silicate) and cellulosic fibre

4.0 EXPERIMENTAL METHOD

4.1 Preparatory Work

The test crude was a light, sour Alberta crude which was obtained through BP Canada Limited. Two batches of crude oil were aged separately in a steam-jacketed, agitated mixing tank in ARCTEC's Laboratory. The aging was monitored by gas chromatography. The aged oil was then drummed off, sealed and stored at the test site.

The results of the gas chromatographic analysis for these two aged oils are given in Table 1. The physical properties are also included.

The viscosity measurement of the aged crude was undertaken with a General Electric Zaha Viscosimeter No. 2 at an outdoor temperature of $0^{o}C$. The viscosity of seven-day aged crude was three times that of the one-day aged crude.

4.2 Experimental Design

The test series took the form of a factorial screening experiment with four independent and ten dependent variables (eleven in Phase IV). Table 2 lays out the experimental design. Replicates of some promoters were also planned to estimate the possible effect of wind on air temperature and basic residual variance of the proposed methods.

Oil type, oil thickness, promoters and loadings were scheduled in random order prior to the test. This was intended to isolate the effects of small variations in the other parameters such as air temperature and wind speed at the time of data analysis. As a further control, the experiment organized partially-blind. This helped to prevent subconscious bias in the observations.

4.3 Test Procedures

All the combustion experiments were undertaken outdoors. Tests for Phase I - Confined Oil Slicks, and Phase II - Confined Slicks in Slush Ice, were conducted in four 1.22 x 1.22 x 1.22 metre deep metal tanks, while tests for Phase III - Confined Slicks in Wave Conditions, and Phase IV - Unconfined Oil Slicks, were carried out in a 6.1 x 1.22 x 0.91 metre deep metal tank.

Before each pour, the tanks were checked to ensure that they were free of ice and the water was agitated to maintain constant water temperature. The type and thickness of oil was poured according to the schedule. Promoters were then applied to the oil slick and the oil was then burned and observed. After burning, the residue was measured and sampled for future reference.

For Phase II - Confined Slicks in Slush Ice, the ice was added as required, to the open water to form an ice layer, and oil was then poured on top of the ice. The combination was then mixed up to form oiled slush.

For Phase III - Confined Slicks in Wave Conditions, the waves were generated by means of a hand-operated driver wedge at one end of the 6.1 x 1.22 x 0.91 metre deep wave tank. At the other end, a filter type beach was in place to serve as an absorber. A water spray boom was utilized to confine the oil slicks.

It was originally intended to straddle the trench with a spreading device for applying the promoters. Fertilizer spreaders, mulchers, seed drills, and manure spreaders were considered. It was decided instead to apply the promoters by hand. The loading for each cell was pre-weighed into a pail and broadcast as uniformly as possible by hand. This provided the greatest flexibility for uniform application of the wide range of materials under consideration. Otherwise, different equipment would have been required to apply peat moss and glass beads, and calibrated independently for each equipment/material combination. Hand application was an idealized process which did not represent the non-uniformity inherent in operational spreading although this effect was studied as part of the experimental design. Three loading levels selected for testing were accurately and precisely applied. The effect of non-uniform operational application was then estimated using the resulting data. Otherwise, application technique became another experiment parameter, seriously compromising the utility of the data. The three levels of promoter loading were 50%, 100% and 150% of the manufactureer's suggested dosage.

Ignition was with a luminous acetylene flame from a welding torch. This gave a highly reproducible flame temperature, flame size and radiation from run to run. The torch was precisely adjusted to give a 10 cm luminous flame and was held centered over the cell to be ignited with the flame axis parallel to the surface and the flames just licking the oil/promoter mix.

4.4 Test Conditions

The combustion experiments were performed in an outdoor temperature range of $4^{O}C$ to $-23^{O}C$. The wind speed was ranged from calm to 30 km/hr. These conditions, although not exactly Arctic weather conditions, were rather severe.

5.0 RESULTS

5.1 Confined Slicks on Water

A total of 165 combustion experiments were conducted with and without combustion promoters. These included:

- 41 tests on 1 cm thick one-day aged crude
- 38 tests on lowest uniform one-day aged crude
- 37 tests on 1 cm thick seven-day aged crude
- 37 tests on lowest uniform seven-day aged crude
- 12 tests on 1 cm thick Bunker C.

Results of these experiments are given in Table 3. It should be noted that in this table, the percentage of burn in the case of unassisted burns, was the exact amount of oil burned away during the combustion process.
In other cases with combustion promoters, the percentage shown meant the completeness of cleanup of the burnt promoter residue without removing

the free-floating oil slicks.

Wood shavings were the first promoter to be rejected. It failed to burn the oil. It became waterlogged and submerged the oil; ignition and spreading of the flame were then extremely difficult. Straw and peat moss both gave almost complete burns. They are cheap and readily available. However, it was much easier to collect the peat moss residue than the heavy corbonaceous straw residue, therefore, straw was eliminated.

Cab-O-Sil M5, Tullanox 500 and Aerosil R972 are the same fumed materials except the first one is hydrophilic and the latter two are hydrophobic. Burning performance and the residue of these three promoters were similar. Since Cab-O-Sil M5 is hydrophilic and Tullanox 500 was unpleasant to use, Aerosil R972 was the best of the three.

Seabeads and vermiculite are very similar materials except vermiculite is cheaper and readily available. Materials were easy to apply; however, they are quite sensitive to the loading and the oil conditions. When oil was viscous, no reaction was noted, materials just sat on top of the oil. They submerged the oil slick and drew up water when loading became heavy; ignition and spreading of the flame was then very difficult.

Burning completeness can be improved by 10 to 15% with Seawick. It was believed that a greater coverage will be beneficial for effective burning. However, it was felt that there is no sufficient advantage over the use of other promoters to justify the purchase and distribution of the material.

Fibreperl gave the controlled and complete burns. Although it took longer for the flame to spread, it was not difficult to ignite. The material is non-sensitive to the uniformity of loading; a non-uniform loading was certainly beneficial to the spreading of the flame. Furthermore, after burning it formed a light buoyant cohesive mass; cleanup proved to be a very easy task.

It was from this basic evaluation that the following three materials were selected for the next three series of experiments:

1. Peat Moss - hydrophilic, combustible organic fibre
2. Aerosil R972 - hydrophobic, non-combustible fumed chemical
3. Fibreperl - hydrophobic, partially combustible sorbent.

5.2 Confined Slicks in Slush Ice

In this phase, it was planned to screen the experiments at three levels of slush ice/oil ratio. The ice loading was 1.5, 15 and 30 times that of the oil by volume. This involved 92 combustion experiments with and without promoters. The results are given in Table 4. The values in parentheses were the results of the confined slicks on water.

For the unassisted burns, higher percentages of reduction were achieved with smaller ice/oil ratio. In comparison with those burns on water, higher percentage of reduction was achieved with thin slush as a substrate than with water. It was believed that the ice somewhat hindered the flow of the warm oil and thus, reduced the heat transfer to the substrate. As the volume of slush ice increased, the effect of the slush ice became negative. The thick slush was thought to act as a large heat sink which effectively cooled the surface of the oil rapidly to below the fire point.

For a large ice/oil ratio, the improvement in combustion with the use of promoters, was obvious, but as there was considerable unmelted ice remaining after burning, the additional residue (remains of the combustion promoters) could increase the final cleanup effort. For a small ratio of the ice/oil mix, the oil reduction was not improved very much with the use of promoters. They, however, were ample enough to cleanup the unburnt slicks and the removal of these light buoyant residues proved to be an easy task.

5.3 Unconfined Slicks

A total of 29 combustion experiments were performed in a 6.1 x 1.22 x 0.91 metre deep steel tank. The test results are detailed in Table 5.

It is important to point out that the promoter loadings on the one-day aged crude were not sufficient to cover the entire slick surface in all cases. Therefore, the effectiveness of promoters was not completely clear. This demonstrated that a complete coverage of promoters on the slick surface was important.

Table 6 presents a summary of the test results on the seven-day aged crude. As noted, the effectiveness of the combustion promoters was obvious. It is important to point out that the oil spreading on water was rather uneven with the presence of promoters, particularly with Aerosil R972 and Fibreperl. The hydrophobic materials not only provided some cohesion on the oil slicks underneath, but also promoted combustion by wicking action. After burning, the free-floating slicks collected on the water for both promoters, were not more than 8%. The rest of the unburned portion was being held by the promoter residue in the form of cohesive mass. The light buoyant residues could be easily removed. On the other hand, although peat moss gave some improvement over the unassisted burns, the residues physically resembled liquid after burning. It did not justify the effort of distributing the material.

5.4 Confined Slicks in Wave Conditions

About one-third of the scheduled combustion experiments have been completed and testing is still in progress. The wave conditions used in this phase were 5 and 10 cm high of short wave length. The oil slick was confined by means of a fireproof water spray boom.

The effects of waves on the combustion process are not well understood. The waves tended to increase the heat transfer both to the water underneath, and to the air above. In particular, they tended to break up the slick into globs causing difficult spreading of fire and rapid extinction of the established fire.

From the test results there appears to be some advantage to using combustion promoters. They not only improved the burning completeness, but also provided a cohesive residue which was much easier to handle.

6.0 CONCLUSIONS

1. From the combustion experiments with the Bunker C, it was readily apparent that Bunker C will not support combustion either in its natural state or even with the aid of combustion promoters under the test conditions. However, it was found that combustion could be achieved when priming fuel such as gasoline, was used together with the combustion promoters.

2. In calm conditions, with a confined slick, decrease in residue does not normally justify the effort of distributing and recovering promoters.

3. In waves, heavy slush ice and with unconfined slick, promoters can significantly improve the completeness of in-situ burns.

4. Low density, high absorptive capacity for oil, hydrophobicity, combuctibility and large particle size are desirable promoter attributes.

5. In most conditions, Fibreperl proved the best of the promoters tested. It tended to form cohesive, easily handled residue.

7.0 RECOMMENDATIONS

The results continue to support the recommendation that in-situ burning is a promising component of Arctic oilspill response.

Tests indicate that development of a technique for distribution of these combustion promoters over the slick surface is essential. Another development effort in connection with the use of combustion promoters should be directed towards removing the residue after burning, as the residues formed by various promoters are rather different.

REFERENCES

The Torrey Canyon; Cabinet Office Report of the Committee of Scientists on the Scientific and Technological Aspects of the Torrey Canyon Disaster; Her Majesty's Stationary Office, London, 1967.

Deslauriers, P., Martin, S., Monson, B. and B. Baxter, "The Physical and Chemical Behaviour of the Bouchard #65 Oil Spill in the Ice Covered Waters of Buzzards Bay", submitted to OCSEAP, National Oceanic and Atmospheric Admin., Boulder, Colo., June 1977.

Abdelnour, R., Nawwar, A., Hildebrand, P. and W. Purves, "Novel Countermeasures for an Arctic Offshore Well Blowout", Environment Canada Economic and Technical Review Report EPS-3-EC-77-14.

Frieberger, A. and J. Byers, "Burning Agents for Oil Spill Cleanup", Proceedings of Joint Conference on Prevention and Control of Oil Spills, Washington, D.C., June 1971.

Purves, W., "Techniques for Igniting and Burning Oil in Arctic Ice", submitted to Environment Canada, February 1977.

Anonymous, "Major Oil Slick Burned by Cabot", Industrial Chemistry, p. 509, April 8, 1970.

Conpal, B., "Use of Peat Moss in Controlled Combustion Technique", submitted to Environment Protection Service, Hull, Quebec, June 1972, pp 3-5, 18.

Conpal, B., "Controlled Combustion Tests Carried Out near Rimouski", Report EPS-4-EC-76-2.

Tulley, P.R., "Removal of Floating Oil Slicks by the Controlled Combustion Technique", Billerica Laboratories, Cabot Corp., Boston, Mass. 1976.

Sittig, M., "Oil Spill Prevention and Removal Handbook", Noyes Data Corp., New York, 1974, pp 434-449.

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TABLE 1

RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS
AND PHYSICAL ANALYSIS OF CRUDE OIL
(FINAL SAMPLES)

	% LESS THAN C_{10}	% LESS THAN C_6	DENSITY	FLASH POINT °C
RECEIVED CRUDE	26.37	14.26	0.8396	18
ONE-DAY AGED CRUDE (Batch 1)	-	2.41	0.8540	24
SEVEN-DAY AGED CRUDE (Batch 2)	9.94	-	0.8789	39

TABLE 2

EXPERIMENTAL DESIGN

INDEPENDENT VARIABLES	PARAMETERS	DEPENDENT VARIABLES
Promoter Type	Air Temperature	Volume of Residue
Loading	Wind Speed	Weight of Residue
Oil Type	Water Temperature	% Oil in Residue
Oil Thickness		Oil Remaining after Cleanup
	Slush Thickness	Preheat Time
	Wave Height	Flame Spreading Time
		Burn Time
		Final Diameter
		Flame Size
		Smoke Generation
		Nature of Residue

TABLE 3

PHASE I: COMPLETENESS OF BURNS ON CONFINED OIL SLICKS

(F = Failure)

	LOADING RATE	LOADING (%)	A1C (10 mm)	A1C (3 mm)	A7C (10 mm)	A7C (3 mm)	BUNKER C (10 mm)
Unassisted	-	-	85, 90	75	80	75	F
Wood Chips (62% Moisture)	2.9 kg/m^2	50	90	F, F	30	F	
		100	F, F	F	F, F	F, F	F
		150	20	F	F	F	
Dry Wood Chips	1.22 kg/m^2	70		100			
		100	100	100			
		200			F	F	
Straw	1/5 by weight	50	98	95	98	98	
		100	98	98	98	98	
		150	98	95	98	95	F
Peat Moss (56% moisture)	1/10 by weight	25	95				
		50	98	95		98	
		100	100	100	98	100	F
		150	98	95	F	100	
Aerosil R972	1/10 by weight	50	100	90	95	80	
		100	100	95	F	95	F
		150	100	100	F	100	
Tullanox 500	1/10 by weight	50	100	100	98	80	
		100	100, 100	92, 90	100, 98	90, 90	F
		150	100	98	F	95	
Cab-O-Sil M5	1/10 by weight	50	100	95	100	80	F
		100	100	85	100	98	
		150	100	95	F	85	
Seawick	2 pads/m^2	50	92	80	84	F	
		100	85,88,92	84, 85	90, 90	80, 80	F
		150	91	84	90	80	
Seabeads	0.5 kg/m^2	50	100	100	98	100	F
		100	95, 100	100, 98	F, 95	85, 95	
		150	90	100	F	F	
Vermiculite	0.2 kg/m^2	50	95	90	98	85	
		100	100, 100	100, 98	95, 90	F, 85	F
		150	100	95	30	F	
Fibreperl	1/7 by weight	50	100	100		100	F
		100	100	100	100, 100	100	
		150	100	100	100	100	

TABLE 4

COMPLETENESS OF BURNS OF OIL IN SLUSH ICE

	ICE LOADING BY VOLUME		
	1.5	15	30
PEAT MOSS	85	88	83
AEROSIL	90	90	90
FIBREPERL	96	98	95
UNASSISTED	94 (85)	87 (85)	70 (75)

TABLE 5

PHASE IV: UNCONFINED SLICKS

PROMOTER	LOADING	A1 CRUDE (2.5 L)			A7 CRUDE (4.5 L)			BUNKER C
		% BURN	INITIAL SIZE	FINAL SIZE	% BURN	INITIAL SIZE	FINAL SIZE	
UNASSISTED	-	25	1.98	3.10	50	1.07	2.90	F
		30	0.91	3.66	30	0.91	2.74	
FIBREPERL	50	50	1.07	2.74	65	1.16	2.44	
	100	50	1.83	2.60	70	1.07	2.90	
		60	1.07	2.44	67	0.91	3.20	
	150	50	1.22	3.05	80	0.91	2.90	
AEROSIL R972	50	40	1.07	2.74	65	1.07	1.52	
	100	30	1.16	2.13	70	0.91	2.44	
		40	1.22	3.66	55	0.91	2.44	
	150	45	1.52	2.74	40	1.07	3.05	
PEAT MOSS	50	30	1.37	3.35	40	1.07	4.88	
	100	40	1.22	3.05	50	0.91	2.74	
		35	1.22	3.66	40	0.91	3.66	
	150	40	1.07	3.05	50	1.07	3.05	

TABLE 6

COMPLETENESS OF BURNS OF UNCONFINED SLICKS

	% COMBUSTION	SIZE INCREASE (LENGTH)
PEAT MOSS	45	450%
AEROSIL	68	220%
FIBREPERL	73	275%
UNASSISTED	35	300%

DISCUSSION

Q. Did any of the residues tend to have a density heavier than water after the burn?

A. We did see some residues that would sink among the organic materials which would become waterlogged and take the oil with them. That is the only case.

Q. For example?

A. Wood chips and straw. The peat moss I don't think ever did that.

Q. The burning is getting me a little bit worried. I was at an oil spill in Portugal where most of the oil from that tank explosion did burn and I understand that over 50% of the people in Portugal were actually in the hospital for more than two weeks. Has this side been looked into?

A. We didn't do any smoke measurements in these experiments here. That certainly has been one of the problems. Another case where they tried to burn was by Buzzards Bay and the original story I heard was that they had to discontinue the burning because the smoke was going to the houses nearby but certainly it does generate a lot of smoke. I would hope that in the arctic environment this would be less of a problem in terms of choking people nearby. You would have to make some provision for people who have to work there. Dr. Mackay presented some results last year about the effects of that smoke in terms of damage to the wildlife in the area and so on but he would be better to speak to that particular point.

Q. I was worried about the toxic value, rather than just the smoke, of the gases in the smoke.

A. I think Dr. Mackay would be the man to say something about that. I haven't done any tests in that area but there is certainly lots of smoke.

Comments from Dr. Mackay:

The conclusion of the work that we did was that you wouldn't want to stand inside a plume of smoke from an oil fire up to a distance of a few kilometers from the burn itself, but beyond that it wasn't much worse than conditions are in a place like Ottawa.

Comment By W. Purves:

While we are on the subject and just in case people want to go out and try this themselves, there are clear warnings on the bags of many of these commercial materials, to say that when you are working with it you should work with dust masks. When we started out weighing the materials to do the tests, after the 325th burn some people got tired of wearing their dust mask, and got sick from breathing these fumes. So if you decided to get involved with some of these commercial materials, be careful.

Q. I have two questions, one do you see processing of these residues to recover the burning promoter as being economically or technically feasible at this stage, and two, would such recovery be practical in terms of the cost of recovery.

A. Many of the promoters are partially consumed and end up as an ash. I would say that in the arctic environment the idea of trying to recover the promoters is probably unreasonable and there is no economic mechanism established whereby the guy who bought the promoter can get his money back. There are a lot of problems there. The cost is probably pretty important. Let me just give you a few examples, from the ones that we tested. The peat moss is a few cents a pound. The man who buys a few tons is going to do considerably better. Fibre perl, which we thought, was one of the best is about 60 cents a pound. You are talking about flying a half-inch layer over acres and acres of oil and some of the others run up to $5.50 a pound.