

IN-SITU BURNING OF EMULSIONS: THE EFFECTS OF VARYING WATER CONTENT AND DEGREE OF EVAPORATION

by

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Abstract

A series of experiments has been conducted to study the effect of water content, evaporation, thickness of the emulsion layer and environmental factors on the burn efficiency of Statfjord crude oil and emulsions. The experiments were conducted on Spitsbergen, in basins excavated in sea ice.

This paper presents the results from the experiments and, in additions some preliminary results concerning the dynamics of burning emulsions, and the efficiency of conventional and novel igniters.

Water-in-oil emulsions with a water content of 40% could be burned. However, conventional gelled gasoline was not a very effective igniter. Ignition success was improved when gelled crude oil was used as an igniter. The results imply that, for practical in-situ burning, the igniter technology needs to be improved.

INTRODUCTION

In-situ burning of oil is considered to be one of the most promising techniques for rapid removal of large quantities of oil at sea, particularly in ice infested waters. Most research that has been done until now deals with burning of fresh or unemulsified oil (Fingas and Laroche 1990). However, some studies have dealt with in-situ burning of emulsions (e.g. Buist 1989; Buist and Potter 1983; Twardus 1980). Oil at sea tends to emulsify and after one day the water content can be as high as 70% (Daling and Johansen 1986). If in-situ burning is to be a practical and efficient measure against spilled oil at sea, more concern has to be given to the burning of emulsions. If emulsions can not be burned in-situ, burning will be limited by a response time of only a few hours. NOFO (Norwegian Clean Seas Organization) has initiated a program to improve oil spill contingency for ice infested waters, especially directed to the forthcoming oil drilling activities in the Barent Sea. As part of this program a project on in-situ burning is going on. The results presented in this paper are a portion of the results that were obtained during one project dealing with burning of emulsions.

The objective of this project was to study how burn efficiency is influenced by:

- 1) The degree of evaporation of unemulsified and emulsified oil;
- 2) Water content in emulsions;

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Canada, Environment Canada, Ottawa, Ontario, 547-559 pp, 1992.

- 3) The combined effect of the degree of evaporation and water content; and
- 4) Film thickness of fresh and emulsified oil.

MATERIALS AND METHODS

The experiments were conducted on the frozen fjord next to the SINTEF laboratory on Spitsbergen in late winter 1991 (April-May). The burn experiments were conducted in circular basins (4 m²) that were cut in sea ice in Van Mijenfjorden. To maintain a constant water level an overflow system was made for the basins (Figure 1). The results presented below were obtained in 25 test turns (Table 1).

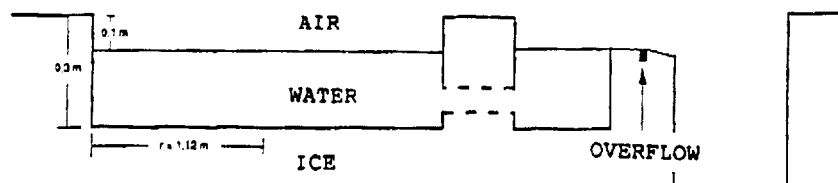


Figure 1. Overview of the constructed basins that were used in the experiments. The basins were evacuated in the sea ice, and comprised both a major test basin and an overflow system to maintain a constant water level.

Table 1. Summary of the experimental oil and emulsions burned.

Exp. Series	Oil Type	Water content (%)	Amount of oil/emulsion (liters)
I	Crude, 150+ - 300+	0	32
II	Crude, 150+ - 250+	0	32
III	Crude, 150+ - 250+	0	16
IV	Crude, 150+ - 250+	10	32
V	Crude, 150+ - 250+	20	32
VI	Crude, 150+ - 250+	40	32

Test oils

Oil from the Statoil refinery (Mongstad) was used in the experiments. The test oils comprised:

- a mixture of Statfjord and Gullfaks (4:1)
- 150+ (18% evaporated oil)
- 200+ (28% evaporated oil)
- 250+ (37.5% evaporated oil)
- 300+ (45.5% evaporated oil)

The weathered oils were characterized as mixtures of different petroleum products:

- heavy naphthalene (HN)
- kerosene (Kero)
- light gas oil (LGO)
- heavy gas oil (HGO)
- buffercut
- residue

The composition of the test oils are given in Table 2.

Table 2. Composition of the test oil used in the experiments, and for the mixing of emulsions.

Oil Type	HN	Kero	LCO	HGO	Buffercut	Residue
Crude	4.6	11.9	14.8	7.0	5.0	30.5
150+	6.2	16.1	20.1	9.5	6.8	41.3
200+	-	17.2	21.4	10.1	7.2	44.1
250+	-	-	25.8	12.2	8.7	53.3
300+	-	-	-	16.5	11.7	71.8

Physical and chemical properties

Oil density was determined with an Anton Paar densitometer, model DMA 35. Viscosity was measured with a Brookfield DV-II viscosimeter (Shear rate 10 s⁻¹, UL adapter). Distillation data were obtained from the Mongstad refinery. The physical and chemical properties of the oils are given in Table 3.

Table 3. Physical and chemical properties of the test oils used in the experiments and for mixing the emulsions.

Oil Type	Density (g/ml)	Visc. (13 °C) [cps]	Initial Boiling Point [°C]	Vol % Dist
Fresh crude	0.846	10.9	n/d*	-
150+	0.881	102	134	18
200+	0.883	87.7	193	28
250+	0.902	429	241	37.5
300+	0.921	n/d*	256	45

* n/d = not determined

Mixing of emulsions

Emulsions were made by mixing sea water and oil in the desired proportions. Maximum batches made each time were 64 liters. Oil and water were circulated through a gear pump (1450 rpm) until stable emulsions were created. Emulsion mixing time ranged from one to six hours depending on oil type and the amount of water.

RESULTS

Igniters

Initially, 400 ml of gelled gasoline (50 g Surefire/2000 ml gasoline) was used as an igniter. However, as the test burns proceeded, limitations with this mixture were found. In order to provide successful ignition of the most evaporated, and emulsified oils, alternative ignition sources were developed and tested. These were:

- gelled diesel
- liquid and gelled crude oil

Special attention was given to the gelled and liquid crude oil. Some measurements of flame temperature were done with a Termovision 400 Infrared Camera (Agema Infrared Systems AB), showing that crude oil burned with nearly twice the temperature of gasoline. The measured flame temperature for gasoline was about 1000°C, while for crude oil the temperature in the flames was approximately 2000°C. This may be due to the wider range of compounds in crude oils, particularly those with higher boiling points than found in the gasoline. Diesel gave a flame temperature in the middle between that found for gasoline and crude oil. In the burn tests gelled gasoline worked well with unemulsified oils but for the emulsions with 28% evaporation, and more than 20% water content, it was necessary to use gelled or liquid crude oil.

Burning of unemulsified oils

Three series of experiments with unemulsified oils were conducted (Table 1). In the experimental series I and II the initial film thickness was 8 mm, while in series III the thickness was 4 mm. Figures 2-6 present the results from these experiments.

Burn efficiency

Figure 2 gives the burn efficiency for the unemulsified oils. Burn efficiency was related to the degree of evaporation and the initial film thickness of the oils. In the two experimental series with 8 mm film thickness the burn efficiency for all the oils with evaporation of less than 45% ranged between 80 and 90%. In the burns with 45% evaporated oil the burn efficiency decreased to approximately 70%. In the experiments with 4 mm film thickness, oil burn efficiency was approximately 80% for the fresh crude and the 20% evaporated oils. For the 28 and 38% evaporated oil, the burn efficiency decreased to 70% and 30%.

Extinction film thickness

The extinction film thickness was estimated from the volume of residue and the oil-covered area at extinction. Estimated extinction film thickness for the three experimental series are given in Figure 3. Within each of the three experimental series the extinction film thickness tends to increase with increasing degree of evaporation.

In all the experiments with fresh crude oil the extinction film thickness was between 0.6 and 0.7 mm. When the oil burned was 20% evaporated a slight increase in film thickness was found.

In the experiments with 8 mm initial film thickness and a 45% evaporated oil, the extinction film thickness was approximately 2.5 mm, the same thickness which was estimated for the burn with 4 mm initial film thickness and 40% evaporation.

Ignition time

The ignition time (i.e. time before the oil caught fire close to the igniter) is given in Figure 4. Fresh crude oil ignited instantaneously. When the oil was 18% evaporated or more, a delay in the ignition time was found. Except for the second experiment (with higher wind velocity - shown as open circles in Figure 4) with 37.5% evaporation and 8 mm initial film thickness all the oils were ignited after less than 90 seconds. For 4 mm initial film thickness ignition time was at the same level as for the 8 mm initial film thickness (Series I), for all the degrees of evaporation.

Flame spreading

The flame spreading is given in Figure 5. Except for the burn series conducted with high wind velocity, (open circles in Figure 5) evaporation results in reduced flame spreading rate. The flame spreading for fresh crude was approximately three times faster compared to the more evaporated oils.

Regression burn rate

The regression burn rate generally decreased with increasing degree of evaporation (Figure 6). In the burn with high wind velocity (open circles) this tendency was not clear. The burn rate for the fresh crude varied between 1.8 and 3 mm/min while for the evaporated oil, the burn rate was lower, between 1.2 and 2 mm/min.

Burning of emulsified oils

Three series of experiments with emulsified oils (10, 20 and 40% water content) were conducted (Table 1). In the experimental series IV and V the initial film thickness was 8 mm. In series VI (40% water) the thickness was increased to improve ignition success. Figures 7-11 present the results from these experiments.

Burn efficiency

Burn efficiency is given both as the percentage of emulsion removed (Figure 7) and the percentage of oil removed (Figure 8). The experiments with 10 and 20% water were done with an initial film thickness of 8 mm. In the burns with 10% water (closed dots), the burn efficiency was not affected by the degree of evaporation. The burn efficiency was approximately 90%. For the 20% emulsion (open dots), the burn efficiency was high, approximately 90%, when the oil from which the emulsion was made from either fresh oil, or 18% evaporated. For the 28 and 37.5% evaporated oil, the burn efficiencies decreased to about 80 and 60% respectively. The burn efficiencies for these emulsions (10 and 20% water), was approximately the same as that found for the unemulsified oil (Figure 2).

In the experiments with 40% water-in-oil emulsions (filled squares), attempts were made to ignite the oil with an initial film thickness of 8 mm, but only the emulsion made from fresh crude could be ignited. The emulsion with the 18% and 28% evaporation were ignited and burned when the initial thickness was increased to approximately 40 mm. The resulting burn efficiency was on the same level as that found for the 10 and 20% water emulsions. The emulsion with 37.5% evaporation ignited when the initial thickness was increased to 32 mm; however, the burning was not sustained and only a little part of the emulsion was removed.

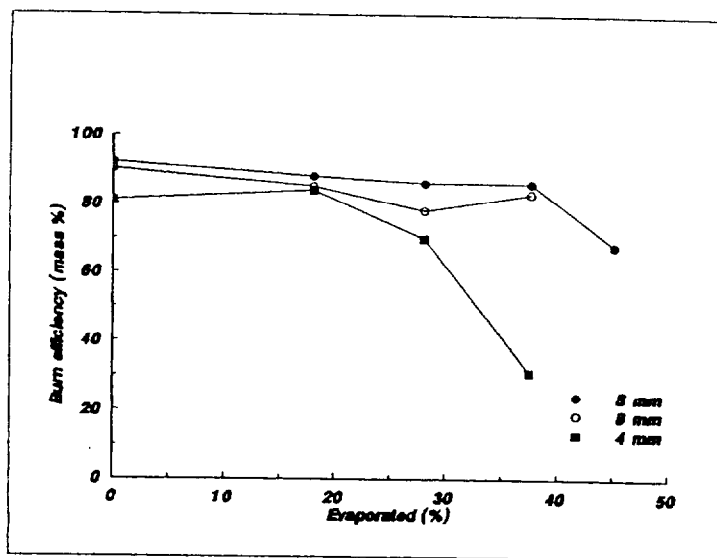


Figure 2: Burn efficiency of unemulsified oils plotted against the degree of evaporation

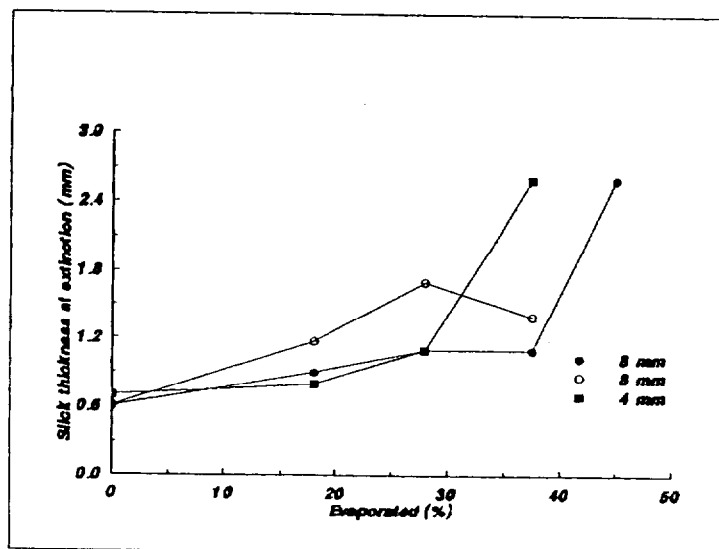


Figure 3: Extinction thickness of unemulsified oils plotted against the degree of evaporation

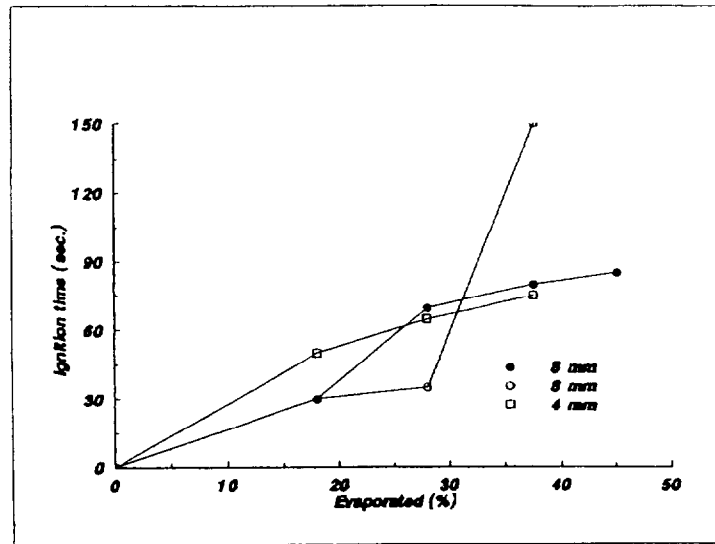


Figure 4: Ignition time of unemulsified oils plotted against the degree of evaporation

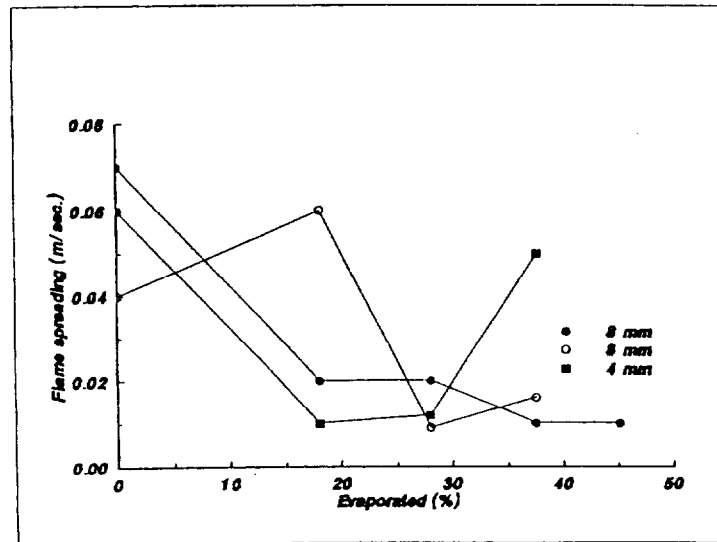


Figure 5: Flame spreading rate of unemulsified oils plotted against the degree of evaporation

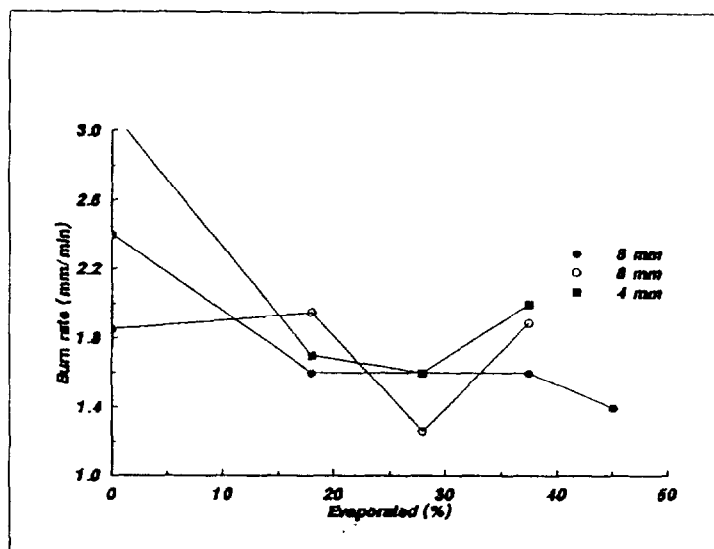


Figure 6: Regression burn rate of unemulsified oils plotted against the degree of evaporation

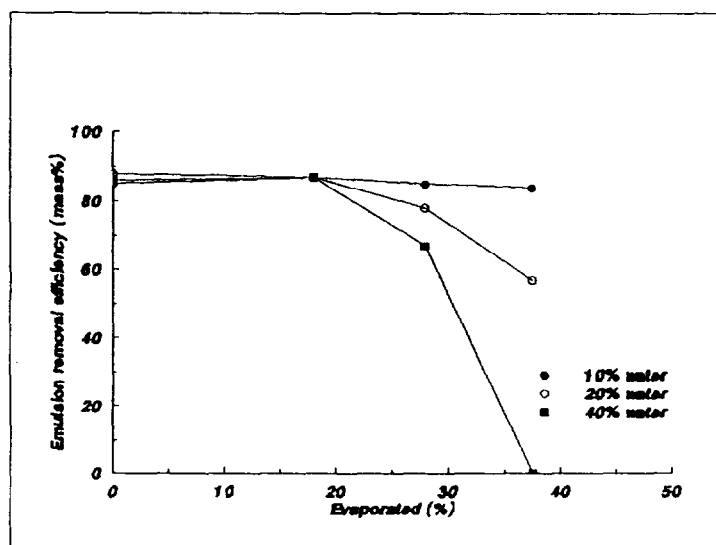


Figure 7: Burn efficiency of emulsified oils plotted against the degree of evaporation and based on the removal of the emulsion

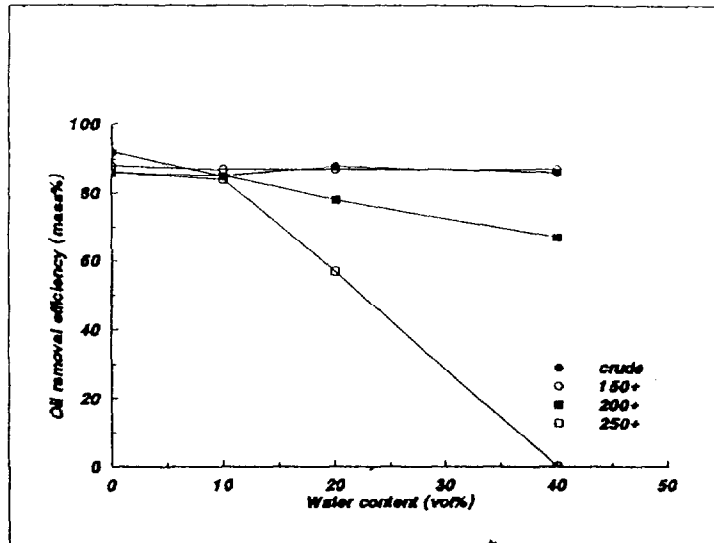


Figure 8: Burn efficiency of emulsified oils plotted against the water content of the emulsion and based on the removal of the oil

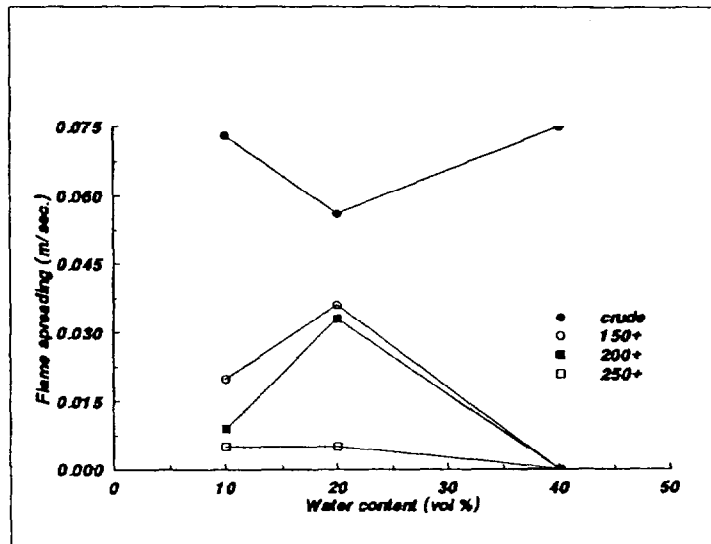


Figure 9: Flame spreading of emulsified oils plotted against the water content of the emulsion

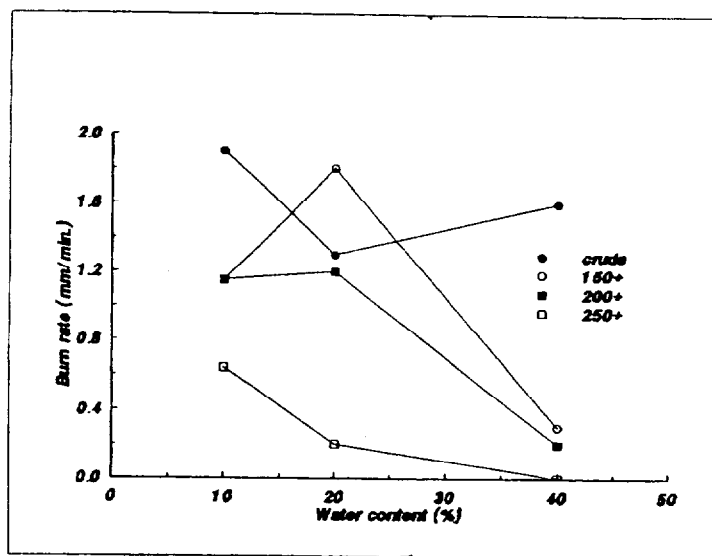


Figure 10: Regression burn rate of emulsified oils plotted against the water content of the emulsion

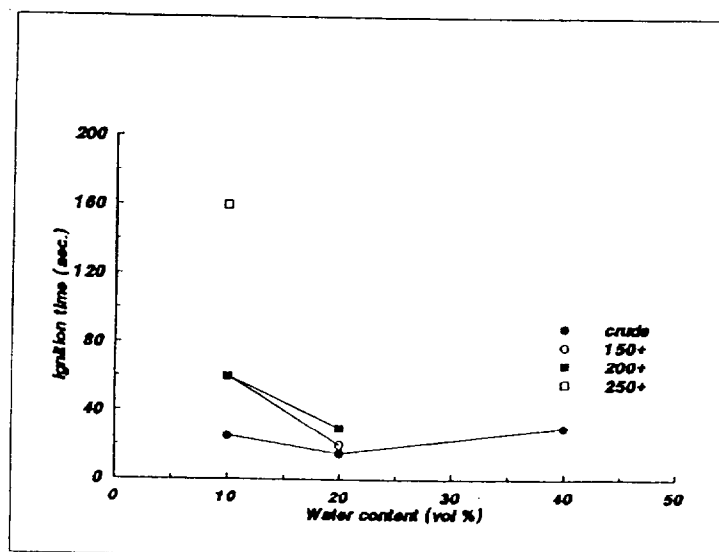


Figure 11: Ignition time of emulsified oils plotted against the water content of the emulsion

Flame spreading

The flame spreading rate (Figure 9) decreased when the degree of evaporation of the emulsions increased, and when the water content increased. For the emulsions made from fresh crude oil, the flame spreading was much faster than for the emulsions made from evaporated oils, i.e. approximately four times faster than for the emulsions made from 18 and 28% evaporated oil. The flame spreading of the 37.5% evaporated oil was very slow, and close to zero, when the water content was 40%.

Regression burn rate

The regression burn rate (expressed as mm of emulsion removed per minute) for the emulsions is given in Figure 10. The rate for the emulsions made from fresh crude oil varied between 1.3 and 2.0 mm/min. Both the 18% and 28% evaporated emulsions with water content up to 20% burned with rates on the same level. Emulsions blended from the same two oils, but with 40% water, and all the emulsions made from 37.5% evaporated oil, had much lower burning rates, in the range slightly above zero up to 0.6 mm/min.

Ignition time

The ignition time for the emulsions is given in Figure 11. The ignition time increased with increasing degree of evaporation. The emulsion made from crude oil ignited after approximately 25-30 seconds. The ignition time for the 18% and 28% evaporated oil with 10 and 20% water was longer, up to about 60 seconds. It was not possible to ignite the emulsions made from the 18 and 28% evaporated oils with 40% water content with the gelled gasoline.

DISCUSSION

In-situ burning of emulsions differs from burning of unemulsified oil. The controlling process seems to be the removal of the water in the emulsions. We can assume two different modes for this:

- By boiling the water out; or,
- By breaking the emulsion thermally or chemically.

In our studies we have no indications that the emulsion is broken thermally, and the process outlined is thus based on observations that water is evaporated from the emulsion layer. When the water is boiled out, oil is released and forms a layer on top of the emulsion layer. The amount of oil that is released and the rate of release probably depend on the water content of the emulsion. With higher water contents, the amount of heat required to leave a certain amount of oil, increases. If the water content is f_w , then the amount of oil that can be released (f_o), is $1-f_w$. The required heat for the release of f_o , is thus the heat required to evaporate f_w from the emulsion. When the oil layer is created on the emulsion layer, the oil will be volatilized by the radiated heat and when its temperature reaches the fire point of the oil it will ignite. The temperature in the oil depends both on the added heat, and the thermal properties of the oil, emulsion and the underlying water. If the thermal conductivity of emulsions is lower than for water, the oil layer required on the top of the emulsion layer may be thinner than that necessary to ignite the same oil directly on water.

In order to ignite an emulsion, the igniter needs to have certain properties:

- It must burn long enough, and with enough heat to create an oil layer on top of the

- emulsion, which is thick enough to burn and then ignite the layer.
- Ignite oil in an area that is big enough to ensure a self sustained burn.

In terms of ignition success, all the unemulsified oils (fresh crude to 45% evaporation) could be easily ignited with the available gelled gasoline technology. As long as the initial film thickness is high, i.e. approximately 8 mm, the oils will burn with an efficiency of 70 - 90%. For the most evaporated oils, low initial film thickness gives efficiencies below this (e.g. 37.5% evaporation, 4 mm film thickness burned with only 30% efficiency).

Emulsions can be burned; however, for oils evaporated more than 18%, and with a water content of more than 20%, the gelled gasoline is insufficient as an igniter. Gelled or liquid crude oil proved to be a better igniter for the emulsions. With crude oil it was possible to ignite emulsions with 40% water, and 28% evaporation provided that the initial film thickness was high enough. Successful ignition and burning of oils and emulsions required good flame spreading. With heavy oils and emulsion this is only possible if the igniter either itself covers an area that is big enough to continue burning, or somehow promotes flame spreading across the slick surface.

CONCLUSIONS

- 1) Ignition time for unemulsified crude oil, increases with increasing degree of evaporative loss. Fresh crude ignited instantaneously while the most evaporated oils needed more than one minute to be ignited.
- 2) For unemulsified oils the flame spreading rate decreases as the evaporative loss increases.
- 3) The regression burn rate decreased as the evaporative loss increased, and varied between 3 and 1.5 mm/min.
- 4) Burn efficiencies for oils with maximum 37.5% evaporation were on the same level (approx. 90%). With higher evaporative loss and low initial film thickness, burn efficiency was drastically reduced.
- 5) The extinction film thickness increased with increasing evaporative loss and varied between 0.6 (fresh crude oil) and 2.8 mm (45.5% evaporated).
- 6) Ignition time for emulsified oil increases with the degree of evaporative loss of the oils from which the emulsions were made.
- 7) When the water content varied between 10 and 40% the emulsions made from fresh crude were ignited after approximately 25 seconds. Emulsified 18% evaporated and 28% evaporated fractions were more difficult to ignite. The emulsified 18% evaporated fraction (40% water) could not be ignited with gelled gasoline without increasing the film thickness to approximately 40 mm. The emulsified 28% evaporated fraction (40%) did not ignite with gasoline but did with gelled crude oil. It was not possible to ignite the emulsified 37.5% evaporated with 40% water.
- 8) For the emulsions the flame spreading rate decreased with increasing degree of evaporation in the parent oil and with increasing water content. When the emulsions were made from fresh crude oil no relation between flame spreading and water content was found. For evaporated oil with 40% water content the flame spreading rate was approximately zero.
- 9) The emulsions with the lowest water content and the lowest degree of evaporation had higher burning rates than the more heavy emulsions.
- 10) For the removal of emulsions the effect of evaporation was greatest when the water content was high (40%); between 70 and 90% of the emulsion was removed when the degree of evaporation was up to 30%. Only 12% was removed when the degree of evaporation was 40%.
- 11) Emulsions can be ignited and burned; however, gelled gasoline is not the best igniter; a system that burns longer, hotter and spreads to cover a larger area would be an improvement.

Acknowledgements

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REFERENCES

Buist, I. 1989. "Disposal of Spilled Hibernia Crude Oils and Emulsions. In-situ Burning and the "Swirlfire Burner". Proc. 12th AMOP Tech. Seminar.

Buist, I., S. Potter. 1983. "Fate and Behaviour of Water-in-Oil Emulsions in Ice". Proc. 6th AMOP Tech. Seminar.

Daling, P. and Johansen, Ø. 1986. "Effektivitet av dispergeringsmidler på oljesøl til havs - En håndbok for Statens Forurensningstilsyn". Oceanografisk senter, Trondheim. 60p. (In Norwegian).

Fingas, M. and Laroche, N. 1990. "An Introduction to in-situ burning of oil spills". Spill Technology Newsletter 15(4): 1-11.

Twardus, E.M. 1980. "A study to evaluate the combustibility and other chemical properties of aged oils and emulsions". Energetex Engineering, EE-5.