# LAST FRENCH EXPERIMENTS IN ORDER TO EVALUATE THE BURNING POSSIBILITIES OF THREE WATER IN OIL EMULSIONS .

by

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## 1 . INTRODUCTION

### 1.1. Objectives of the study

The experimentations held in CEDRE in summer 1992, with the logistic and financial support of the FRENCH NAVY, followed a bibliographical study carried out in 1991, concerning the technical feasibility of the burning of oil slicks at sea.

The objectives were as follows :

- to acquire a know how in this field even at a mid scale
- to evaluate the various conclusions at which our bibliography led
- to obtain information about the burning initiators
- to dicuss the opportunity of using sorbents in order to promote the combustion ( wicking effect ).

### 1.2. Context

Besides the number of mid scale experiments or of real tentatives in case of oil spills at sea, the burning technique still makes a lot of Administrations reluctant or even sceptic. This attitude is mainly due to the fact that the field of application is not yet well known, without speaking of the air emissions of smoke, soots and gases.

Nevertheless, the burning technique could lead to many advantages if recovery and storage of large volumes of emulsions and sea water were taken into account, in terms of logistics.

### 1.3. Content of the study

The study gathers and analyses data in order to lead to a practical approach of the *in situ* burning of oil slicks at sea . To reach this clue, three crude oils have been choosen and were weathered in order to obtain emulsions representative of those found at sea, 24hours, 48hours, and 72 hours after their (spreading) spill.

The thickness of the slick was kept at 11 millimeters and the burning efficiency was measured by weighting the burning residues. The various results appear in efficiency curves and in combustion speed curves, versus the ageing of a given emulsion.

## 2. OPERATING PROCEDURE

### 2.1.Composition of the crude oils

The crude oils were obtained from a refinery ; they were made of blends from various pure crude oils ( table 1).

| N° 1 | | N° 2 | | N° 3 | |
|---|---|---|---|---|---|
| IRANIAN Heavy | 60 % | IRANIAN Heavy | 72 % | KITTIWAY | 63 % |
| ARABIAN Heavy | 21 % | ARABIAN Heavy | 15 % | ARABIAN Light | 33 % |
| ARABIAN Light | 15 % | OURAL | 10 % | OURAL | 4 % |
| MAYA | 2 % | MAYA | 3 % | | |
| OURAL | 2 % | | | | |

**Table 1 - Composition of the crudes**

Each crude showed individual properties , as described in table 2 .

| CRUDES | | N° 1 | N° 2 | N° 3 |
|---|---|---|---|---|
| **DENSITY (cP) 15° C** | | 0,8715 | 0,8648 | 0,8452 |
| **DISTILLATION (° C)** | | 16,87 | 13,23 | 7,93 |
| Distillation | 5 % | 68,3 | 73 | 55,1 |
| Distillation | 10 % | 100,2 | 89,8 | 76,4 |
| Distillation | 20 % | 162,7 | 158,9 | 121,4 |
| Distillation | 30 % | 217,2 | 212,2 | 167,7 |
| Distillation | 40 % | 276 | 263 | 217 |
| Asphaltenes (weight in %) | | 2,45 | 1,34 | 0,93 |

**Table 2 - Crudes properties**

## 2.2 . Preparation of the weathered crudes

### 2.2.1 . Ageing

The ageing of the crudes was achieved by agitating 120 liters of hydrocarbons in an outside pit . The agitation was maintained for a period of 24 H,48H, and 72H at outside temperatures, ranging between14 and 20 degrees Celsius, with a moderate sun .When sufficient time had elapsed, samples were taken , the remaining volume was measured and sea water added up to the final amount of water : 20%,30%, 40% .

To generate the emulsion, a centrifical pump was put in motion in a closed cycle for a period of two hours .

### 2.2.2.The burning trials

Each trial was implemented by using 20 liters of emulsion, spread on the surface of a 1.7m$^2$ of water. The tanks were almost full with water to avoid the reflection of the heat ( side effects ) .

Trials were carried out as described in table 3 :

| CRUDE N°1 | CRUDE N°2 et 3 |
|---|---|
| Fresh crude<br>Weathered crude without water<br>(24 h and 48 h)<br>Weathered 24 h : 20 % and 30 %<br>Weathered 48 h : 10 % and 20 % | Fresh crude<br>Weathered crude without water<br>(24 h, 48 and 72 h)<br>Weathered crude (24 h, 48 and 72 h)<br>with 40 % of water |

**Table 3 : description of the tested emulsions.**

The total number of trials was about fourty, without speaking of the preliminary tests performed in order to frame the parameters .

## 2.2.3. Parameters evaluated

### *2.2.3.1. Combustion initiator*

We tried two initiaters and a flame generator available on the market :

- Gas-oil, gelled with a gelling agent,
- A blended chemical, specially designed by a manufacturer,
- A granulate, spontaneously reactive with water.

The rate of use was 5% of the volume of emulsion to be burnt.

3.

A. Gelled diesel oil

The powder was blended with diesel oil after a strong agitation at a concentration of 10 grams per liter of diesel, and after a gelling time of 20 minutes, the gel was spread on a surface of approximately 400 $cm^2$ . For some emulsions, difficult to set on fire, the gel was spread regularly around the surface of the pit .The flame was brought by a burning torch.

B. Liquid blend of chemicals

A few chemicals were blended on scene with an appropriate device brought by the supplier, and spread on the slick surface in thin droplets thanks to a pressurized chambre and through nozzles.

C. Solid granulate, used as a flame producer

This granulate reacts with water in producing a bright flame . It is conditioned in small plastic bags, located in a sealed box full of an hydrophobic powder .Before throwing the bag into the water, the operator has to cut the plastic bag. Special care must be taken when handling this product outside.

### 2.2.3.2. Influence of oil sorbents on the burning efficiency

To evaluate the wicking effects of sorbents on the burning efficiency, we used various types of oil sorbents such as :

- polypropylene in bulk
- peat derivated
- phenolic foam
- hydrophob vegetal fibre

The sorbent was used at a rate of 1/1 and our trials did not take into account the emission of nocive gazes, specially in the case of the phenolic foam.

2.2.3.3. Measurements

The folowing measurements were made :

- ignition time
- burning time
- weight of residue, determined by absorbtion on sorbents sheets
- wind
- qualitative aspects:smoke, aspect of the burning residues.

## 3. RESULTS

### 3.1. Combustion of the non emulsified crudes

3.1.1. Efficiency

The evolution of the ageing of the crudes is given by the measurement of the density (figure 1).The flash point of the three crudes was always below 100 ° Celsius, even after 72 hours ageing.

Figure 2 describes the evolution of the efficiency of the burning *versus* the ageing of the crude.The effect of the initiators did not show any significant differences and the speed of combustion decreases after 24 hours ageing, to reach a constant value, around 50 grams per second(figure 2).

The average efficiency remained around 90% .The results obtained by the crude N°2 seemed a bit erratic .The dispersion of the results is probably due to the turbulent wind which was blowing at the moment of the experiment (figure 3).

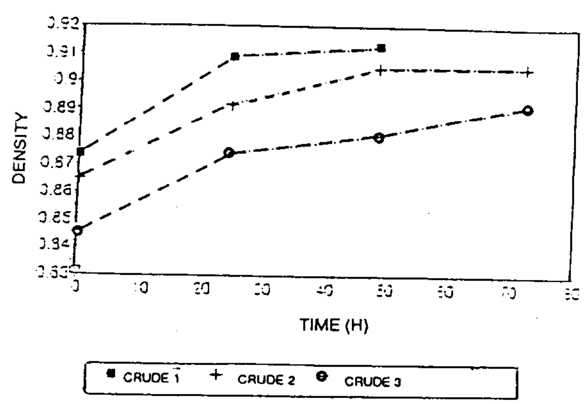


**Fig. 1 - Density *versus* ageing**

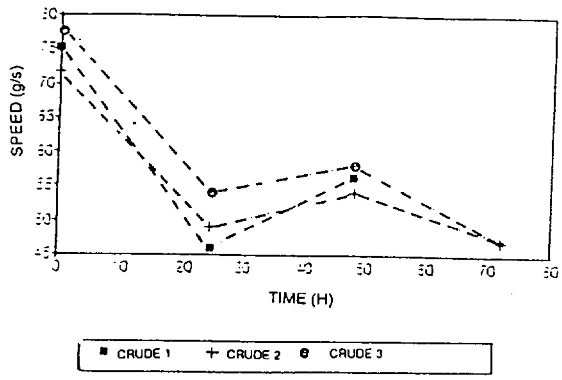


Fig. 2 - Speed of combustion of unemulsified crudes

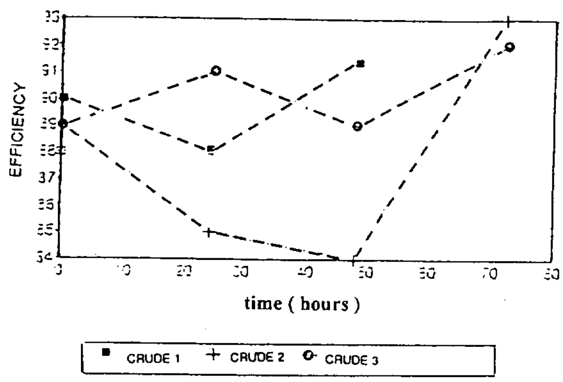


Fig. 3 - Burning efficiency of unemulsified crudes

## 3.2 Combustion of the emulsified crudes

### 3.2.1. Efficiency

⇒ **Crude 1**

The heaviest crude, crude 1,after 24 hours, is caracterized by a dramatic fall of the efficiency when adding more than 20% of water. The efficiency falls from 94% to 13% (figure 4 ).

⇒ **Crude 2 and 3**

To observe a drop of efficiency, we had to wait 72 hours with 40% of water (figure 5 ).

### 3.2.2. Speed of combustion

The decrease in the speed of combustion is a direct and linear fonction of the ageing and of the amount of water(figure 6 and 7 ).

Crude N°1 : after 48 hours we obtained a speed of combustion ranging from 40 g/s (25 g/s.m² or 1,6 mm/mn) for 20% of water to 15 g/s (9 g/s.m² or 0,8 mm/mn )for 40% of water.

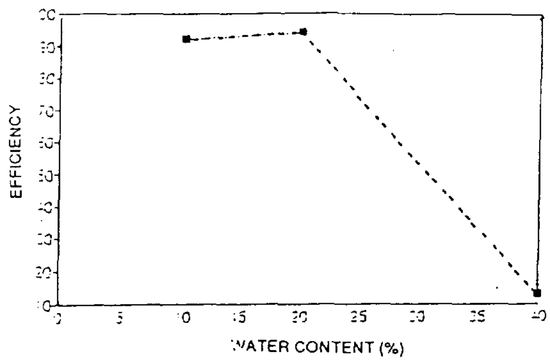


Fig. 4 - Burning efficiency of various emulsions of crude N°1 after 48 hours ageing

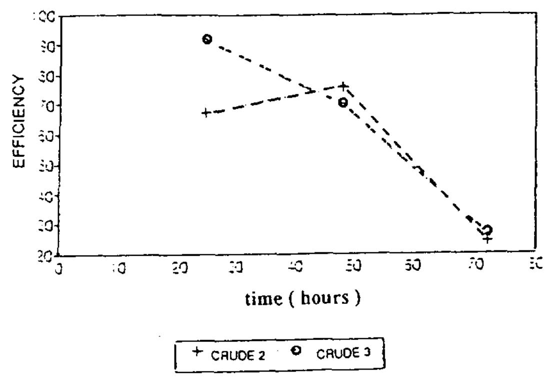


Fig. 5 - Burning efficiency of a 40% water in oil emulsion of crudes 2 and 3

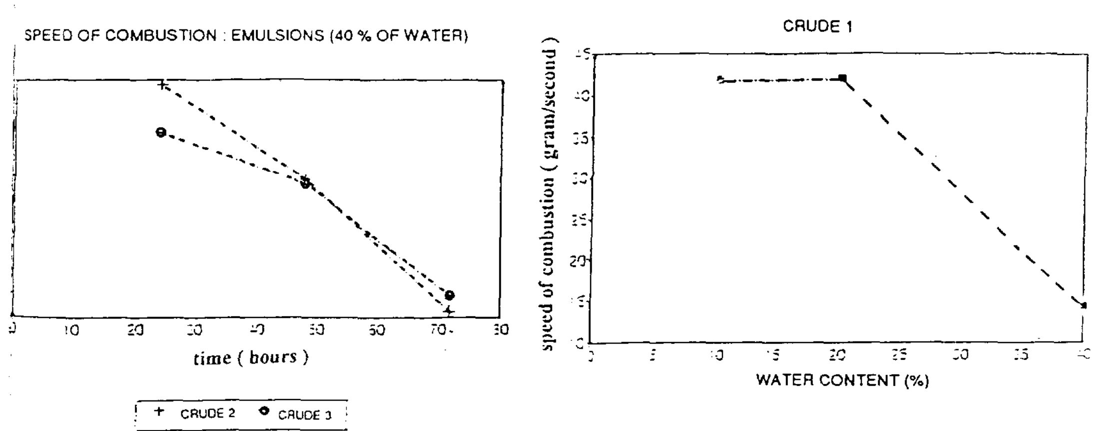


Fig.6 and 7 - Speed of combustion of water in oil emulsions

For crudes 2 and 3, containing 40 % of water, it varied from about 32 g/s after 24 hours (19g/s.m² or 1,2 mm/mn ) to 15 g/s after 72 hours (9g/s.m² or 0,6 mm/mn ).

## 3.3. Influence of the combustion initiator

### 3.3.1. Gelled diesel

The gelling agent is easily blended with the diesel oil but its handling needs a sheltered area due to the effects of the wind transport of this light powder .
The flame produced is easily smothered by a wind over 10 m/s if the crude is emulsified .

### 3.3.2. Blended chemical

The chemicals which were proposed to us did not give any improvement in the combustion processes of emulsifed crudes, compared to gelled diesel, even used at a rate of 10% of the emulsion.

Whereas diesel is easily available on board ships, there could be a logistic problem with a chemical specially designed for initiating the burning, specially when 10% of initiator is needed, compared with the volume of the emulsion to be burned .

The table 4 summaries these observations:

| GELLED DIESEL | BLEND OF CHEMICAL |
|---|---|
| - 5 % of the volume of emulsion<br>- The praparation needs a strong agitation (max. 10 g/l of diesel)<br>- Absorption of the residues gives satisfaction | - 10 % of the volum of emulsion<br>- Efficiency 20 % over that of blend diesel<br>- Inefficient on strong emulsions<br>- Need a preparation on scene<br>- The spraying nozzles are often plugged<br>- Absorption of residues difficult to obtain |

**Table 4 :comparison of combustion initiators**

## 3.3. Use of sorbents as combustion promoters

The trials were performed on crude N°3, aged 48hours with 40% of water.

The results are presented in table 5 :

| | phenolic foam | peat derivative | polypropylene | vegetal fibre | no sorbent |
|---|---|---|---|---|---|
| Ignition time (mn) | 10 | | | | 2 |
| combustion time (mn) | 42 | no combustion | No combustion of the emulsion | no combustion | 9 |
| combustion speed | 2,8 g/s.m$^2$ | | | | 15 g/s.m$^2$ |
| residues (mm) | 4,2 | | | | 3,6 |

Table 5 : evaluation of the sorbents contribution to the combustion of emulsions

## 4. ANALYSIS OF THE RESULTS

The *in situ* burning of fresh crudes differs from that of aged and emulsified crudes  The quantity of water in the emulsion and the stability of this one are the parameters that govern the combustion processes

The demulsification of the emulsion is achieved by :

→breaking the emulsion
→boiling of the water

The initiator's job is to burn during enough time to create, on the emulsion, a layer of crude thick enough to avoid the transmission of the heat to the water

Another mission of the initiator is to evaporate the lighter parts of the demulsified crude and to put the fire in this gas layer

With no water, for the fresh or aged crudes, in the tests conditions, the efficiency varies between 80% and 90%  The ageing only affects the flame propagation and the speed of combustion.

Emulsions can be burnt, depending on the crude composition and the amount of water.

The medium crudes tested can contain up to 40% of water  for a maximum ageing time of 48 hours.

The heavier crudes, richer in asphaltenes, are more difficult to burn and the combustion is very poor over 20% of water for 48 hours aged emulsions.

## 5. CONCLUSIONS

Our experiments led to a few conclusions which can be taken as guide-lines in case of considering the use of the *in situ* burning to combat a pollution at sea.

**Non emulsified** crudes should not give any burning problems if the thickness of the surface layer is sufficient and the wind lower than 10m/s ; however, the **emulsified crudes** could lead to serious difficulties to be ignited.

We can consider that, for a medium crude, the maximum ageing time is aroud 48 hours with an amount of water of 40%.

A heavy crude, rich in asphaltene should not burn after 48 hours with only 20% of water.

In these conditions, the cases where the *in situ* burning can be applicable are very limited from an operational point of view, if we consider the high speed of emulsification of a great number of crudes .For that reason, it is foundamental to gather information on the tendancy of the crudes to form emulsions with sea water and to appreciate the corresponding emulsion's stability.

One way of future investigation could be to evaluate the possibilities of burning a cargo of crude in order to avoid a greater impact on the environment than that induced by floating residues and atmospheric emissions.

Nevererthеless, in case of choosing this technique, diesel is a good initiator, in a gelled form for easier handling and behaviour at the surface of the slick.

For logistic reasons, and availability on the site, a special chemical is not recommended except if its strong efficiency has been proven at a low rate of use.

In taking into account the danger of using the granulate flame initiator, specially at sea, chemicals reactive with sea water have to be banished.

The operationals have rather to use gas and fuses for instance.

Environment Canada. Arctic and Marine Oil Spill Program Technical Seminar, 16th. Volume 2. June 7-9, 1993, Edmonton, Alberta, Canada, Environment Canada, Ottawa, Ontario, 823-832 pp, 1993.