

RESEARCH ON A DISPERSING SOLUTION FOR BURNT CRUDE OILS: "AEGEAN SEA" OIL SPILL

J. R. Bergueiro, N. Morales, F. Dominguez
University of Balearic Islands, Chemical Engineering
Department
Carretera de Valldemossa Km 7.5 PALMA DE MALLORCA.
SPAIN

1. INTRODUCTION:

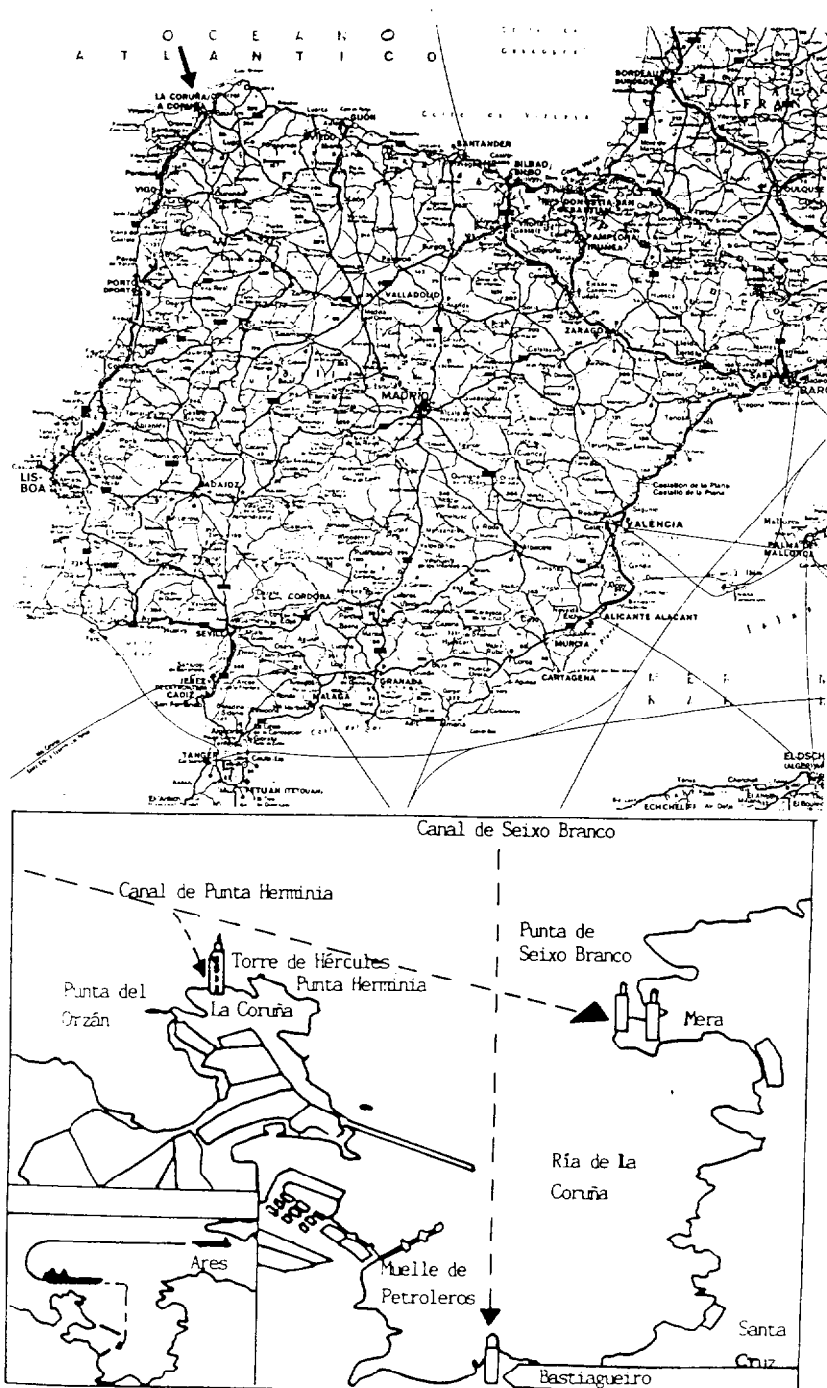
The oil tanker "Aegean Sea" arrived at the La Coruña coasts on 30th November 1992, and anchored at 0,30 hrs in the Estuary of Ares on 1st December. On 3rd December, round about 3,45 hrs, it set sail for the Repsol Terminal Port, which is situated in the port of La Coruña. The tanker sailed under unfavorable weather conditions, very strong winds about 90 km/h and direction 290°, and very rough seas. Due to this the tanker drew close to the Hercules Tower at low tide, it was thrown the cliffs at the bottom of the lighthouse (Plan I). Therefore, the tanker fell prow first and settled, while the stern swayed to and fro forced by the waves, subsequently breaking in two between tank numbers seven (7) and eight(8). It seems that the cause of the accident was due to the gale force winds, sometimes reaching as much as 100 km/h.

At 9 o'clock in the morning the hull broke in two, due to the waves, but it was not a clean break. This brought about the first explosion and which started the fire, needless to say it spread quickly due to all the crude oil in the sea. After a short time, with the size of the fire growing, a huge black cloud was soon formed, with the hight of one kilometre and spreading all round the immediate area. Because of the crude oil it had a great amount of volatile elements, this began with a large stain of burning oil and later divided into smaller ones. Some of these were suffocated by the waves meanwhile the larger ones reached as far as Canabal, Seijo Blanco and Mera beaches which were affected the most.

The tanker was carrying 70000 Tm type Brent and 10000 Tm type Ninian crude oil when the accident happened. Due to the fire and the weather conditions, the oil arrived at the coast very worn and worse for wear it.

2. EXPERIMENTAL PART

The samples of oil mixtures were taken from the author (J.R. Bergueiro) in the Perbes Beach on 2nd January 1993, at the beginning by cleaning and restoring all beaches affected. Photographs I and II show the contamination on some beaches.



Plan 1.- Contamination place at La Coruña Harbour, Spain



Photograph I.- Contamination on Chanteiro beach



Photograph II.- Contamination on Perbes beach

To resolve the concentration of the dispersing during the biodegradation process, they followed the methods described in Prat & col.(1) and in the Standard Methods (2). To follow the oil degradation, the process used was the Standard Methods (3). The observations to study the emulsion influence were accomplished by shaking perfectly thermostatic cylinder tanks for 1 minute with 10 l. of sea water, 4.96 g of the oil mixture with different dispersant quantities BEEP ENERSPERSE 1990 and different vibrating speeds as shown in the Chart I.

Dispersant Quantity	Shaking Speed
(cc)	(rpm)
1	1000
1	3000
2	1000
2	3000
3	3000
4	3000
8	4000

Chart I. Quantities of BEEP ENERSPERSE 1990 and different vibrating speeds employed at the first emulsification studies.

In the most of the observations after one minute of shaking the quantity of oil, had not obtained the dispersion. Most of the dispersed oil was obtained shaking at the speed of 3000 r.p.m during 15 min, 4 c.c. of BEEP Enersperse 1990 with 4.96 g of oil mixtures and 10 l of sea water.

Nevertheless one hour after finishing the vibration, the quantity of dispersed oil was less than 0.001 g/l. What is showed was that the dispersion formed was completely instable.

At sight of the previous results it was accomplished new observations to obtain oil dispersal by vibration for 1 minute in a vibrating machine for testing pipes model REAX 2000 with a speed of 45 Hz with the following oil, dispersing and sea water quantities:

- Oil mixtures: 1 g
- Sea water: 30 g
- Dispersant: BEEP Enersperse 1990; 0.25, 0.5, 1, 2, 3, and 4g.
- Temperature: 20 °C

After 48 h, to see if the oil was dispersed and the sample was as follows:

- Sample nº 1.- The water had practically no oil, finding this floating on top.
- Sample nº 2.- The water had practically no oil, finding this floating on top, black and underneath the same amount in brown.
- Sample nº 3.- The same as sample N°2, but the brown emulsion was five times greater than the black.
- Sample nº 4.- The water as before did no have oil, formed with the rest a brown emulsion, but a volume nine times greater.
- Sample nº 5.- The oil was completely dispersed. Although it was noticed two types of emulsions, one floated on the water 3 times less in volume than the second which did not float. Both were separated by water wiht no oil, and both were color brown.
- Sample nº 6.- The oil was completely dispersed. Noting equal drops of water in the emulsion.

The effectiveness of the dispersant Beep Enersperse 1990 was confronted with the very gluish mixtures, compared with mixing Fuel Oil N°1 and 0.5 c.c. of dispersant. The variation with the time of the concentration, once finished the vibration is shown in Chart II.

Time	FUEL-OIL Concentration	percentage of emulsion
(h)	(g of FUEL- Oil /l de dissolution)	%
0	0.880	88.0
1	0.470	47.0
2	0.361	36.1
3	0.290	29.0
8	0.135	13.5
24	0.087	0.870
48	0.055	0.055

Chart II.- Variation with the time of the concentration of FUEL-OIL, finished the vibration

The following experiences were guided to study the demission by biodegradation of hydrocarbon mixtures with sea water absent but present Beep Enersperse 1990 (sample N°1 & sample N°2) and present mineral salts M9 . The other class of observations were guided to study the demission of dispersant used for the dispersal of the hydrocarbon mixtures. All the samples were inoculated with commercial microorganisms by the name of "PUTIDOIL" and kept 42 days in a thermostatic reacher at 20 °C with stirring of 200 r.p.m.

The oil quantity made by de biodegrading microorganisms are shown in chart III.

Time (days)	Concen- tration Sample N°1 (g/l)	Biodegra- dation Sample N°1 (%)	Concen- tration Sample N°2 (g/l)	Biodegra- dacion Sample N°2 (%)
0	4,2675	0,00	4,2675	0,00
13	1,4300	60,00	1,2105	71,64
20	1,4200	60,28	1,1986	71,91
28	1,0000	72,03	0,9500	77,44
34	0,9800	72,59	0,9300	78,21
42	0,7000	80,42	0,5000	88,28

Chart III. Variation of the oil concentration pending the biodegradation experience. Sample N°1 has no any dispersing agent. Sample II has the Beep Enersperse 1990.

The disposal percentage variation of the dispersant Beep Enersperse 1990 in time operation is shown in Chart IV.

Time (h)	Disposal %
24	12.60
48	18.83
72	25.20
144	37.56
192	43.90
240	46.91
312	53.17
384	59.35
480	71.87
672	93.76
686	93.98

Chart IV. Percentage variation of amounts of Beep Enersperse 1990

3. CONCLUSIONS

According to the previous results we concluded the stable emulsion format of very old hydrocarbon mixtures from combustion oil was in actual conditions very difficult. In other words, by means of shaking at low speed you can not obtain good emulsions at the level of the laboratory systems to supply energy to the mixture. Which is very difficult technically in the middle of the sea. Nevertheless the disposal of the oil mentioned by means of the product "Putidoil" is very high. Although this disposal grows with the presence of the dispersant. Also the disposal of the dispersant is just as effective with this type of microorganism.

These authors are now studying biodegradation of hydrocarbon mixtures from contaminated sands on the beaches. The disposal microorganisms kinds are PUTIDOIL and three *Pseudomonas* Stubs ssp.

4.-BIBLIOGRAPHY

1.- PRAT, A. Análisis de tensioactivos en formulaciones. En "Formulación y aplicaciones de sistemas con tensioactivos. Modulo IV" Universidad de Barcelona., Barcelona.pp 1-63. 1991

2.- AMERICAN PUBLIC HEALTH ASSOCIATION. Standard methods for the examination of water and wastewater. (17th Edition.) (5540D) Washington. pp 5.64-5.67.1989.

3.- AMERICAN PUBLIC HEALTH ASSOCIATION. Standard methods for the examination of water and wastewater. (17th Edition.) 5.43-5.44. Washington 5.43-5.44.1989. (5520B)

5.- Acknowledgment.

The authors wish to thank the collaboration given for the fulfillment of the work to QM UNICOM in Barcelona and the people D. Jordi Vila and D. Emilio Lecuona.

Environment Canada. Arctic and Marine Oil Spill Program Technical Seminar, 16th. Volume 2. June 7-9, 1993, Edmonton, Alberta, Canada, Environment Canada, Ottawa, Ontario, 1065-1071 pp, 1993.