

# THE EFFECTIVENESS OF FERROCENE IN REDUCING SMOKE EMISSION FROM BURNING CRUDE OIL.

J.B.A. Mitchell

Dept. of Physics, University of Western Ontario, London, Ontario, Canada, N6A 3K7.

## INTRODUCTION.

Oil spill cleanup is a difficult and expensive process that typically involves hundreds and even thousands of man-hours. It is frequently carried out under public scrutiny and has often prompted severe criticisms from environmentalists and concerned parties. An attractive method of clean-up is to simply ignite the oil and allow it to burn away. Such a technique would be rapid, would involve the minimum of personnel and be economical. A major concern would of course be to ensure that the conflagration would not represent a threat to personnel or property. This method is therefore best suited to spills occurring on open waters or in remote locations.

Studies by Brown and Goodman (1) have shown that oil spilled onto the ocean can be burned away efficiently provided that the combustion is initiated sufficiently soon after the spill has occurred and before wind and wave action have created an oil-water emulsion. A major problem however is the production of copious amounts of heavy smoke which is unsightly and in some cases environmentally damaging. This has mean't that oil combustion has been opposed by environmental groups as a viable clean-up method despite its efficiency.

Recent studies performed at the University of Western Ontario have shown that smoke emission from the combustion of crude oil can be reduced by as much as 90% by the addition of the compound ferrocene, to the fuel. These studies are described below.

## PROPERTIES OF FERROCENE.

Ferrocene is the common name for bis-cyclopentadienyl iron which has the chemical formula  $\text{FeC}_{10}\text{H}_{10}$  and the structure shown in figure 1. It is known as a sandwich compound for the iron atom is squeezed between two hydrocarbon rings. It was one of the first organometallic compounds to be synthesized and Wilkinson and Fischer received the Nobel Prize for Chemistry in 1973 for evaluating its structure. It is an orange, crystalline substance, insoluble in water but slightly soluble in hydrocarbon fuels to the extent of about 2% by weight. Most importantly for the application discussed here, it is

Environment Canada. Arctic and Marine Oil Spill Program Technical Seminar, 13th. June 6-8, 1990, Edmonton, Alberta, Canada, Environment Canada, Ottawa, Ontario, 75-85 pp, 1990.

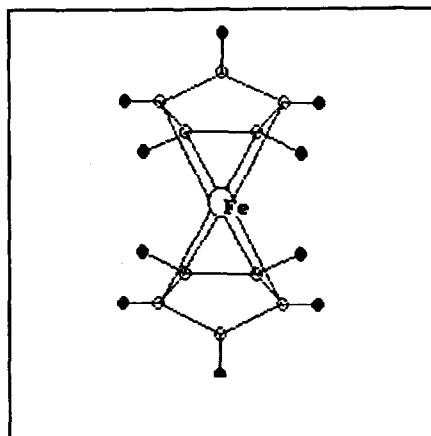


Figure 1. Structure of Ferrocene.

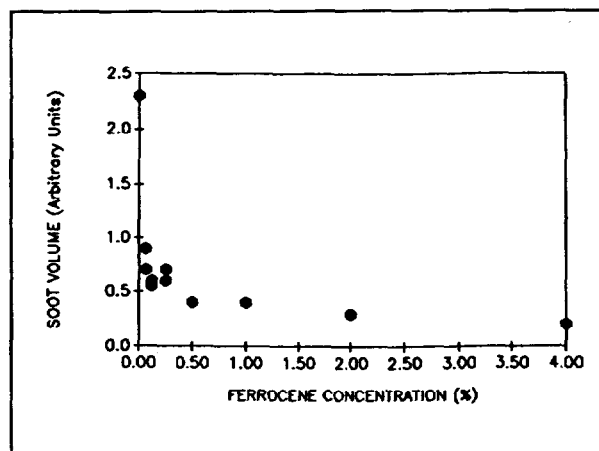


Figure 2. Collected soot volumes vs ferrocene concentration for samples of Norman Wells Oil.

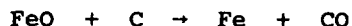
non-toxic although, as with any other finely divided compound, precautions must be taken to avoid inhaling it.

Howard and Kausch, (2) have described a number of studies in which premixed ferrocene/fuel mixtures were burned in a variety of engines and combustors and generally it was found that ferrocene was a very effective smoke inhibitor. It does however have a serious drawback in these applications and that is that iron oxide deposits, left behind in the combustion chambers, can lead to engine fouling. As a result it has not seen widespread usage except in specialized military applications involving short duration use.

#### MECHANISM FOR SOOT INHIBITION.

The exact mechanism for soot formation is not well understood. The transition from the gaseous to the solid state, which takes place on a millisecond timescale, involves very rapid chemical reactions and surface catalytic processes which have not been specifically identified. The general picture, however, is that fast chemical reactions produce large precursor molecules which then act as nucleation centers onto which carbon growth occurs. The young soot particles thus produced, collide with each other and agglomerate, forming larger, mature particles. Since combustion necessarily takes place in an oxidizing environment, the immature soot particles are susceptible to oxidative attack producing gaseous carbon oxides. A number of fuel additives which inhibit soot formation are known. Some, such as alkali salts, when sprayed into flames, alter the electrical charge of the young soot particles and decrease the agglomeration rate so that larger soot particles, which are more resistant to oxidative attack, do not form. Others, such as barium salts, appear to enhance the oxidation process by means that are not clearly identified. (Mitchell and Miller, 3).

Ferrocene action however, is believed to be different. Studies by Ritrievi et al, (4), indicate that when a ferrocene/fuel mixture is burned, the ferrocene is rapidly oxidized to form small iron oxide particles which act as nucleation centres. Carbon condenses out of the flame onto these particles to form young soot particles. The carbon is however, subsequently oxidized via reactions such as:-



In this way, the solid carbonaceous particles are converted back to the gas phase and so smoke emission is reduced.

## EFFECTIVENESS OF FERROCENE WITH CRUDE OIL.

As mentioned above, the main drawback to ferrocene usage is the fact that iron oxide particulates are formed during its combustion and these have deleterious effects on the operation of practical combustors. This, however, is not a problem for the oil spill application. Iron oxides are emitted into the atmosphere but they are non-toxic and are produced in much less quantities than soot particles. A series of studies was initiated therefore to determine the effectiveness of ferrocene addition in combatting smoke emission from crude oil combustion. The majority of these studies were conducted using Norman Wells Crude Oil supplied by ESSO Resources Canada Ltd.

A typical experiment involved burning a premixed ferrocene/crude oil sample in a ceramic crucible and collecting the emitted particulates on a glass-fibre filter attached to a vacuum pump. Following the burn, the soot volume was measured. All tests were conducted using equal weights of oil/additive samples and the results obtained are comparative, rather than absolute, in nature. Figure 2 shows a plot of soot volume collected versus ferrocene concentration. It can be seen that indeed, ferrocene is very effective, producing up to a 90% reduction in particulate emission. It is also evident that only small concentrations of ferrocene need be used.

Tests were also performed on other crude oils, supplied by Environment Canada and the tabulated results are shown in TABLE I.

TABLE I.

Soot production from the combustion of various oils with and without the addition of ferrocene.

Oil Sample	Ferrocene Concentration (% by Wt)	Soot Volume (ml)	% Reduction
Norman Wells	0	2.3	0
Norman Wells	4	0.2	91
Norman Wells	2	0.3	87

Oil Sample	Ferrocene Concentration (% by Wt)	Soot Volume (ml)	% Reduction
Norman Wells	0	2.3	0
Alberta Sweet Mix, (ASM).	0	1.2	0
ASM	2	0.2	83
ASM	0	1.2	0
ASM	2	0.35	71
Prudhoe Bay	0	1.6	0
Prudhoe Bay	2	0.1	94
Prudhoe Bay	0	1.6	0
Prudhoe Bay	2	0.25	84

These results show that ferrocene is a very useful soot inhibitor across the spectrum of crude oils. Since the intended application for this compound is the combustion of oil spills over water, tests were performed in which samples of oil and an oil/ferrocene mixture floating on water were burned in a crucible and the soot collected. This test is much less definitive for as is well known, Evans et al. (5), the combustion of oil floating in water involves a violent burning phase which terminates in extinction and so, in a small scale apparatus, it is difficult to control the burn time. Again however, our results, (shown in Table II), indicate that ferrocene produces very effective soot inhibition in this case.

TABLE II

Soot Volumes produced from the combustion of oil samples burned on their own and floating on water.

Sample	Soot Volume (ml)
15g Norman Wells Oil	2.3
15g Norman Wells Oil/4% Ferrocene	0.2
10g Norman Wells on Water	1

Sample	Soot Volume (ml)
10g Norman Wells/4% Ferrocene on Water	0.25

#### A STUDY OF OTHER IRON COMPOUNDS.

The tests described above were all performed using pre-mixed ferrocene/oil samples. For use in an oil spill on water application, however, a method must be devised for introducing the additive into the spill. This is not straightforward for ferrocene does not dissolve rapidly in oil and, being more dense than seawater, if added directly in solid form, quickly sinks through the oil layer into the underlying water.

Since it is believed that iron is the active ingredient of ferrocene, it was postulated that perhaps other compounds with more suitable physical properties may be equally effective. A number of compounds were identified which were insoluble in water but soluble in oil. Two of these were examined. These were iron stearate and iron 2-ethylhexanoate. The former is a light powder which rapidly dissolves in oil, the latter is a liquid with a density less than that of water. Tests were performed on both these compounds but unfortunately, as indicated in Table III, neither was particularly effective in inhibiting soot emissions.

TABLE III.

Soot volumes collected from tests using different iron additives.

Additive.	Concentration (% by Wt).	Soot Volume (ml).
Oil only.	-	2.3
Ferrocene.	4	0.2
Iron Stearate.	4	1.4
Iron 2-Ethyl Hexanoate.	2	1.6

A number of surface analytical tests were performed on soot samples arising from the combustion of ferrocene/oil, iron stearate/oil and iron 2-ethyl hexanoate/oil samples. Energy dispersive x-ray analysis, (EDX) showed that in

fact, while iron was a significant constituent of soot collected from a ferrocene/oil burn, it was entirely absent from soot collected in the other two cases, (See figure 3). This shows that ferrocene owes its effectiveness to its ability to introduce iron into the combustion environment. The reason for this is not well established but it could be due to the fact that ferrocene sublimates when heated. Auger Electron Spectroscopy, (AES), and X-ray Photoelectron Spectroscopy analyses were also performed on the soot samples arising from the ferrocene/oil and iron stearate/oil soot burns. During the Auger analysis, ion beam sputtering was used to remove outer layers of the samples and spectra were taken at different depths. This revealed that indeed, the iron resides in the interior of the soot particles, as expected from the model in which the iron oxide particles behave as nucleation centres, (see figure 4) and that much of the iron is in the oxide form. Again these tests showed that the soot produced from the iron stearate/oil combustion was iron deficient.

#### A METHOD OF INTRODUCING FERROCENE INTO AN OIL SPILL.

For the present it would appear that ferrocene is the most effective soot inhibiting additive that could be used for oil spill combustion. It therefore is important to find an appropriate method for introducing it into the spill. A search for good solvents for ferrocene found that toluene could be used to produce a concentrated solution. When added directly to oil and subsequently burned, however, it produced copious amounts of black smoke.

The ability of toluene to bring ferrocene into solution is however useful as demonstrated in the following test. The solution was absorbed in vermiculite and allowed to dry. The ferrocene soaked vermiculite was then added to the oil, upon which it floated, and after an hour or so, sufficient ferrocene was found to have dissolved in the oil to inhibit smoke emissions to the level experienced in premixed ferrocene/oil burns. It should be noted however that the best results were obtained when the vermiculite was removed prior to combustion. When the vermiculite was allowed to remain, combustion of the ferrocene itself produced considerable amounts of iron oxide particles.

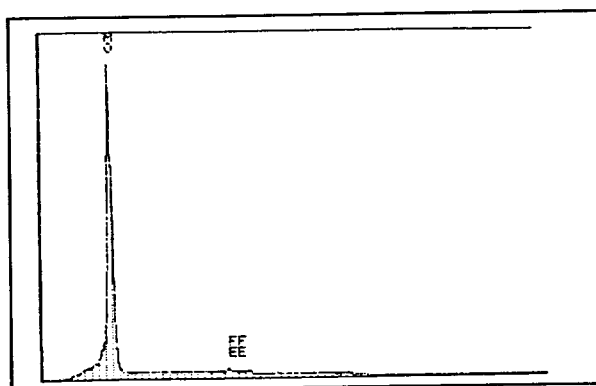


Figure 3a. EDX spectrum of soot collected from combustion of Norman Wells Oil/ferrocene mixture. Note the iron peak.

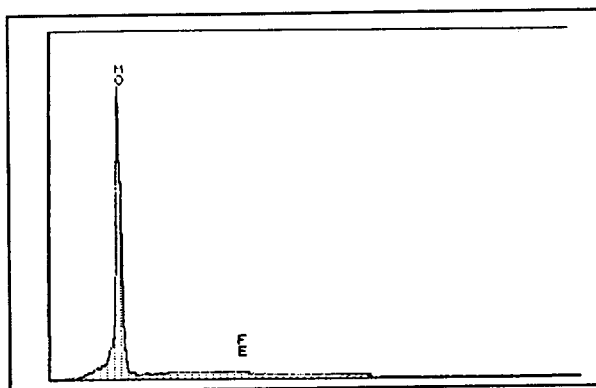


Figure 3b. EDX spectrum of soot collected from combustion of Norman Wells Oil/iron stearate mixture. Note the absence of iron peak.



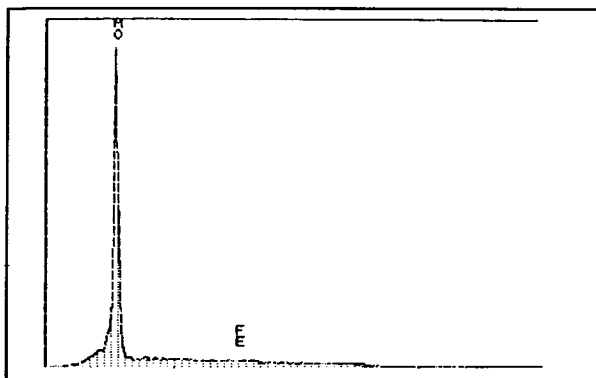


Figure 3c. EDX spectrum of soot collected from combustion of Norman Wells Oil/iron 2-ethyl hexanoate mixture. Note the absence of the iron peak.

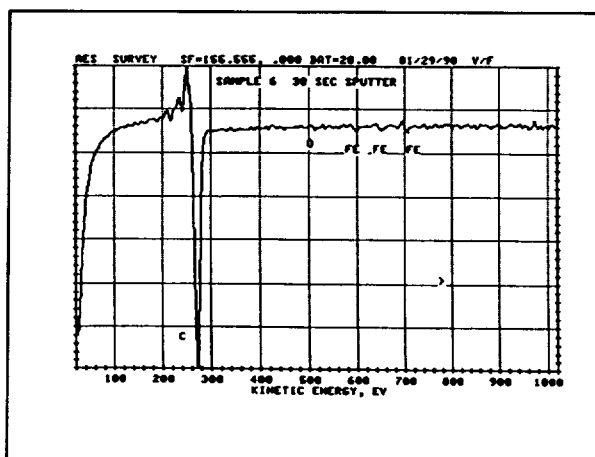


Figure 4a. Auger spectrum of soot collected from combustion of Norman Wells Oil/ferrocene mixture. 30 seconds sputter time, iron peaks very small.

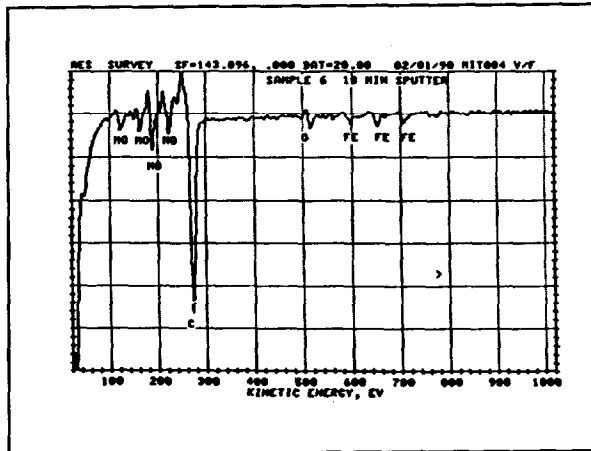


Figure 4b. Auger spectrum from same sample as shown in 4a, after 18 minutes of sputtering, (corresponding to a depth of 0.5 microns into sample). Note the three iron peaks.

## CONCLUSIONS.

These findings are very exciting for they offer the promise of being able to burn crude oil spills with greatly reduced smoke emissions. Clearly there is room for improvement in the method of introducing ferrocene into the spill and work is progressing in this direction. It is intended that mesoscale tests will commence in the near future and that these will include realistic oil on water burns.

## ACKNOWLEDGEMENTS.

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## REFERENCES.

1. Brown, H.M. and Goodman, R.H. "In Situ Burning of Oil in Ice Leads," Proceedings of the Ninth AMOP Technical Seminar, June 10-12, 1986, Edmonton, Alberta, Canada, Environment Canada, Ottawa, K1A 0H3, 1986.
2. Howard, J.B. and Kausch, W.J. Soot Control by Fuel Additives. Prog. Energy and Combust. Sci. 6, 263, 1980.
3. Mitchell, J.B.A. and Miller, J.M. Studies of the Effects of Metallic and Gaseous Additives in the Control of Soot Formation in Diffusion Flames. Combustion and Flame 75, 45, 1989.
4. Ritrievi, K.E., Longwell, J.P. and Sarofim, A.F. The Effects of Ferrocene Addition on Soot Particle Inception and Growth in Premixed ethylene Flames. Combustion and Flame, 70, 17, 1987.
5. Evans, D. et al. Burning, Smoke Production and Smoke Dispersion from Oil Spill Combustion. NIST Report, 1989.