SMOKE REDUCTION FROM POOL FIRES USING FERROCENE AND DERIVATIVES

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INTRODUCTION

In previous publications (Mitchell, 1990, 1991 a,b) it has been reported that the compound ferrocene (dicyclopentadienyl iron) is very effective in reducing smoke emissions from crude oil fires. It is believed, therefore, that the use of such additives will be beneficial in making the In-Situ combustion of oil spills more environmentally acceptable. A number of other applications involving large pool fires can also benefit from the use of smoke reducing chemicals. This paper will describe some recent studies that have been made to investigate the efficacy of ferrocene derivatives in reducing smoke emissions from crude oil and a number of other hydrocarbon fuels.

FERROCENE DERIVATIVES

A series of acyl and alkyl substituted ferrocene derivatives have been synthesized in the laboratories of ESSO Resources and at the University of Western Ontario and laboratory scale burn tests have been performed to determine their relative smoke reducing efficiencies. In these tests, a 10 ml of oil/additive mixture is burned in a crucible and the smoke, arising from the combustion, is drawn through a fibreglass filter by means of a vacuum pump. The soot, collected on the filter and on the filter holder is scraped off and its volume measured[1]. The tests are usually repeated three times to yield a consistent average soot volume.

A list of the compounds studied is given in Table I and figure 1 is bargraph showing the relative smoke yields from using these compounds, at a concentration of 2% by weight, in Norman Wells Crude Oil. Figure 2 shows a similar bargraph for the same additives used at 0.2% concentration.

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[1]Because of the small soot masses collected and the high temperatures that the filter is subjected to, it has been found that measuring the soot volume gives results that are much more consistent that soot mass measurements.

Environment Canada. Arctic and Marine Oilspill Program Technical Seminar, 15th. June 10-12, 1992, Edmonton, Canada, Environment Canada, Ottawa, Ontario, 681-687 pp, 1992.

#	Additive	Formula	FW	m.p.	b.p.
1	Ferrocene	(C5H5)2Fe	186	174	249
2	Butyl	(C4H9)(C5H4)Fe(C5H5)	242	L	183
4	Pentyl	(C5H11)(C5H4)Fe(C5H5)	256	L	90
5	Butyryl	(C3H7CO)(C5H4)Fe(C5H5)	256	L	144
6	Valeroyl	(C4H9CO)(C5H4)Fe(C5H5)	270		92
7	Iso-Valeroyl	(C4H9CO)(C5H4)FE(C5H5)	270		150
8	Dimethyl	(CH3)2Fe(C5H4)2	216		
9	Trimethyl Acetyl	(CH3)3Fe(C5H4)(C5H3)	230		
10	Hexanoyl	(C5H11CO)(C5H4)Fe(C5H5)	284	L	161
11	Heptanoyl	(C6H13CO)(C5H4)Fe(C5H5)	298	L	84
12	Octanoyl	(C7H15CO)(C5H4)Fe(C5H5)	312		
13	Oct/Dioctanoyl	[10%](C7H15CO)2(C5H4)2Fe	325	L	
14	Decanoyl	(C9H19CO)(C5H4)Fe(C5H5)	340		203
15	Lauroyl	(C11H23CO)(C5H4)Fe(C5H5)	368	36	
16	Myristoyl	(C13H27CO)(C5H4)Fe(C5H5)	396		
17	Palmitoyl	(C15H31CO)(C5H4)Fe(C5H5)	424	59	
18	Stearoyl	(C17H35CO)(C5H4)Fe(C5H5)	452		

It can be seen that as the molecular weight increases, the effectiveness of a given additive decreases when added at a fixed weight concentration. Since iron, however, is the active smoke reducing agent, increasing the molecular weight means that, for a given additive, the percentage of iron is reduced. Normalizing the smoke yields to the percentage of iron used shows that the variation between the additives is much less and indeed for the 0.2% case, the efficiency per iron atom is constant.

Also shown in figures 1 and 2 is the soot yield normalized to the molecular weight of ferrocene. It can be seen that the heavier derivatives are much less effective on a per weight basis than ferrocene. The multiply substituted compounds, however, appear to be more effective than ferrocene.

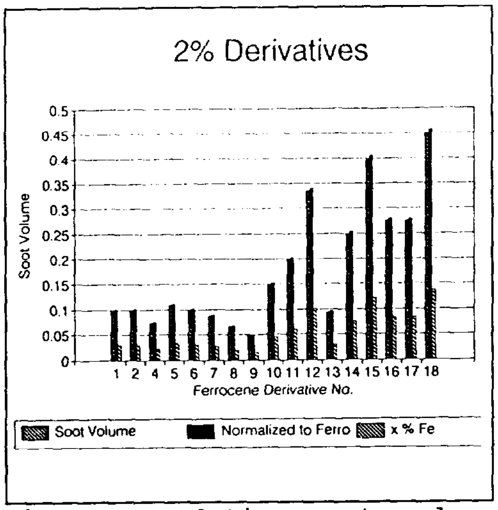

Figure 1. Relative soot volume for the additives listed in Table I, used at 2% concentration.

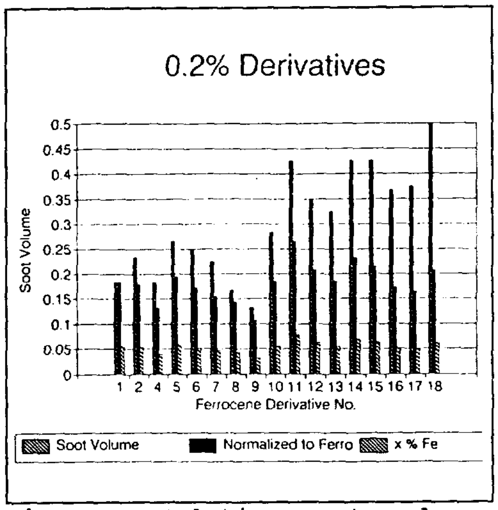

Figure 2. Relative soot volumes for the additives listed in Table I used at 0.2% concentration.

EFFECTIVENESS OF FERROCENE FOR OTHER FUELS

During the course of this project, series of burn tests were performed at London Municipal Airport in which ferrocene was premixed with JETB fuel at varying concentrations. Although the volume of fuel used in these fires was moderate (102 gallons/fire), their areal extent was large since the fuel was poured directly onto the ground. The estimated fire dimensions were about 50' in diameter. It was found that the soot yields from these fires was larger than expected even when the additive was used in a concentration of 2%. This unexpected result prompted a series of laboratory scale burn tests in which several different fuels were burned, with and without ferrocene addition. Again soot yields were measured using the technique described above. The results are quite surprising and are shown in figure 3.

Particularly noticeable is the very large soot yield from the gasoline fuel. Even using ferrocene, the smoke yield exceeds that for untreated Norman Wells crude oil!

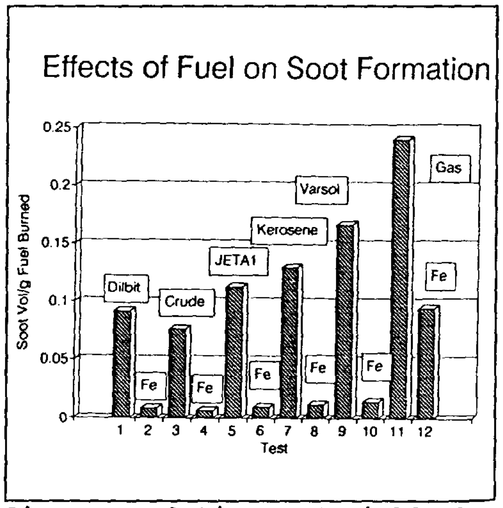

Figure 3 Relative soot yields for various fuels with and without ferrocene addition.

Work is continuing to find an additive that will be more effective than ferrocene in reducing smoke yields for light fuels such as gasoline or JETB. A series of intermediate-size test burns is scheduled to be performed at the National Fire Laboratory in Ottawa in which this additive will be tested and the emissions arising from the combustion of such light-fuel/additive mixtures will be analyzed.

MESO-SCALE TESTING OF SMOKE REDUCTION FROM DILBIT COMBUSTION

As mentioned in earlier reports, ferrocene, while being very effective in reducing smoke emissions from crude oil fires, is not suitable for use in oil spills for it is a solid compound which is more dense than water. In addition it is not very soluble in oil. The information gathered from this research program has allowed us to develop a new additive which is in liquid form and which can be sprayed directly onto the oil surface. This additive, designated RMS 9757 may be scheduled for production by ESSO Chemicals Ltd.

A test of this additive was performed at the Calgary Fire Training Centre in March. Dilbit was used as the fuel and this was floated on top of water in an 8' x 8' burn pan. Figures 5 and 6 show the fires from untreated and treated Dilbit and it can be seen that a dramatic reduction in smoke yield was found in the latter case. This was very encouraging for it was the first trial of an additive directly sprayed onto the fuel.

ON OCEAN TESTING

An In-Situ Burn Test has been planned for the Beaufort Sea of the coast of Northern Alaska for August, 1992. This is sponsored by the US Coast Guard and co-ordinated by Alaska Clean Seas. We have been asked to participate in this test and plan to perform a burn test in which the additive RMS 9757 will be sprayed onto 100 bbls of North Slope Crude Oil contained inside a 3M Fire Boom, prior to combustion. Air sampling equipment mounted on surface vessels and on an aircraft belonging to the University of Washington will be used to analyze the emissions arising from this burn test.

REFERENCES

1. Mitchell, J.B.A. and Janssen E. *The Use of Additives for Smoke Reduction from Burning Pool Fires* in *Proceedings of the Fourteenth Arctic and Marine Oil Spill Program Technical Seminar,* Vancouver, p. 391, 1991.
2. J.B.A. Mitchell *Smoke Reduction from Burning Crude Oil Using Ferrocene and its Derivatives* Combustion and Flame **86**, 179, 1991.
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ACKNOWLEDGEMENTS

The authors would like to thank ESSO Resources Canada Ltd. for the generous financial support for this project and Dave Larson of ESSO Chemicals Ltd. for help in arranging the meso-scale tests at Calgary and London. Special thanks are due to John Lee, Fire Chief at London Airport and to the Calgary Fire Department for providing the facilities and assistance in performing these tests. Paul Morgan and Frank Van Dam performed some of the chemical syntheses and Richard Barber assisted with the laboratory scale burn tests. Their efforts are gratefully acknowledged.

Figure 4. Burn test using untreated Dilbit on water. (8' x 8' Burn Pan).

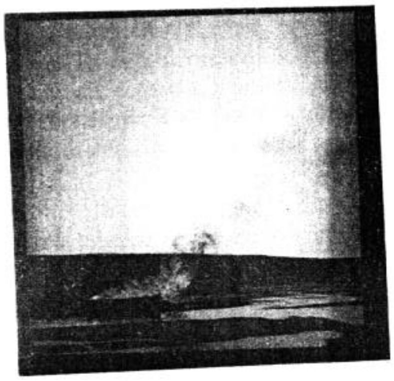

Figure 5. Burn test using treated Dilbit on water.