

SOOT REDUCTION CHEMICALS FOR IN-SITU BURNING

Michael E. Moir and Stéphanie Charbonneau
Imperial Oil Resources Division
3535 Research Road N.W.
Calgary, Alberta T2L 2K8, Canada

J. Brian A. Mitchell
University of Western Ontario
Department of Physics
London, Ontario N6A 3K7, Canada

ABSTRACT: A soot reduction additive for use in the in-situ burning of oil spills has been developed. The additive is in the form of a liquid concentrate that can be sprayed on a spill. The soot producing tendency of hydrocarbons decreases in the order: aromatics, branched paraffins, cycloalkanes, normal paraffins. Similarly, the soot reduction ability of ferrocene and derivatives decreases in the order: aromatics, cycloalkanes, branched paraffins, normal paraffins. A method of predicting soot reduction is inferred from model studies and confirmation obtained from experiments on known hydrocarbon mixtures.

In-situ burning, with high removal rates and high efficiencies, is an attractive addition to the suite of oil spill response tools.¹ In-situ burning has not gained wide acceptance, in part due to concern over potential environmental and health hazards associated with soot and hydrocarbon emissions. Soot reduction chemicals added to a spill is one way of overcoming these problems.

Ferrocene, an organometallic compound first synthesized in the early 1950s² has long been recognized as a combustion enhancer and smoke reducing agent. The patent literature is rich in applications ranging from rocket propellant¹⁰ to diesel fuel.^{4,8} Esso in Europe adds ferrocene to home heating oil to help reduce particulate emissions. However, addition of ferrocene to reduce soot from pool fires is a relatively recent innovation.⁵ Unfortunately, ferrocene is a solid at room temperature and dissolves slowly in hydrocarbons, reaching a maximum concentration of 4 percent by weight (wt%). These properties make application of ferrocene to an oil spill impractical. This paper describes an alternative chemical in the final stages of development at Imperial Oil.

Experimental

Work on the soot reducing ability of ferrocene derivatives has been reported earlier.⁷ In this study, a wide range of additives were synthesized in the laboratory at Imperial Oil to optimize the choice of a chemical for oil spill use. All of these mixtures can be applied to oil spills in liquid form and dissolve on contact with the oil. To test the additives, small samples of oil containing the additives were burned in a shallow crucible (Figure 1). The soot was collected by drawing the combustion products through a glass fiber filter with a weak vacuum. The soot was weighed, extracted with solvent, and analyzed by gas chromatography-mass spectrometry. Only the soot reduction results are reported here. Data relating to emission of volatile and polynuclear

aromatic hydrocarbons adsorbed on the filter will be published elsewhere.

Results and discussion

Figure 2 shows the soot reduction achieved when Norman Wells crude oil is burned with the new additive RMS-9757. To compare different additives, concentrations are reported in "ferrocene equivalents." The maximum soot reduction achieved is similar to that reported previously,⁷ but this study reports a reduction of the mass rather than the volume of particulates. Reduction values seem low only because of the dominant contribution of iron oxide to the total particulate mass. Maximum soot reduction is achieved at about 2 wt% ferrocene equivalent, but the most economical treatment rate is about 0.5 wt%.

Thirty-six unique mixtures of ferrocene derivatives were prepared and tested using Norman Wells crude oil at an equivalent ferrocene concentration of 0.25 wt%. A summary of the results is presented in Figure 3. There is a clear but only modest effect of composition of the additive on soot reduction. Tuning the composition of the additive can yield a 10 to 20 percent improvement in soot reduction. Quite surprisingly, when the same experiment was performed on kerosene, soot reduction was substantially reduced (Figure 3). Similarly, for one additive mixture, soot reduction for burning kerosene was less than that for crude oil at all concentrations (Figure 4). The importance of the composition of the hydrocarbon has been pointed out before,^{6,7} and a model compound study was carried out to explore this phenomenon.

Pure hydrocarbons were selected to represent the broad classes of compounds found in crude oil. Nonane, iso-octane, cyclohexane, and toluene were selected to represent normal paraffins, branched paraffins, cycloalkanes, and aromatics, respectively. As shown in Figure 5, the soot producing tendency of hydrocarbons decreases in the order aromatic >> branched paraffins > cycloalkanes >> normal paraffins—where > means greater than and >> means much greater than—confirming the earlier observations.⁷ More surprising was the range of effectiveness of the soot reduction additive. Indeed, the soot reduction ability of ferrocene and derivatives shows a similar trend: aromatics >> cycloalkanes > branched paraffins > normal paraffins. The trends explain why, with a higher aromatic content and a lower branched paraffin content, soot from burning Norman Wells crude oil can be reduced more effectively than that from kerosene. The effect of hydrocarbon type leads to a possible means of estimating the effectiveness of soot reduction for hydrocarbon mixtures knowing only their

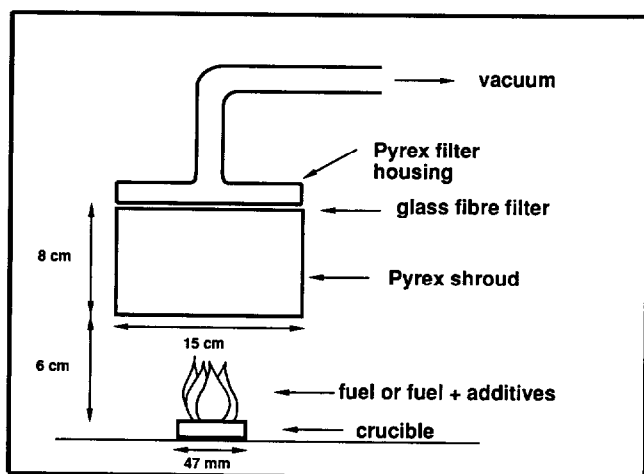


Figure 1. Apparatus for collecting soot from a small scale laboratory hydrocarbon pool fire

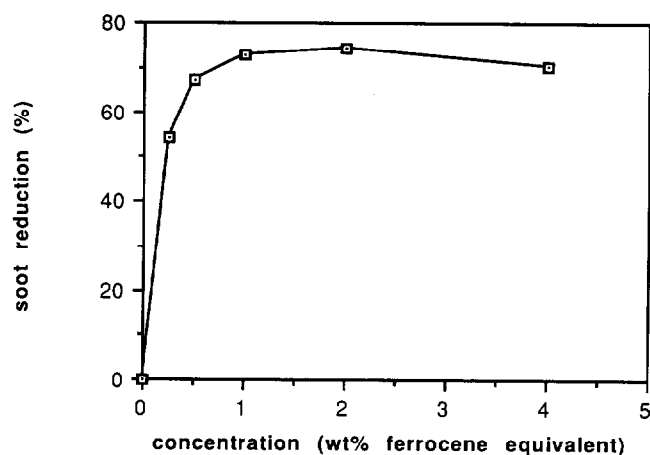


Figure 2. Soot reduction observed when Norman Wells crude oil containing RMS-9757 is burned in the apparatus shown in Figure 1

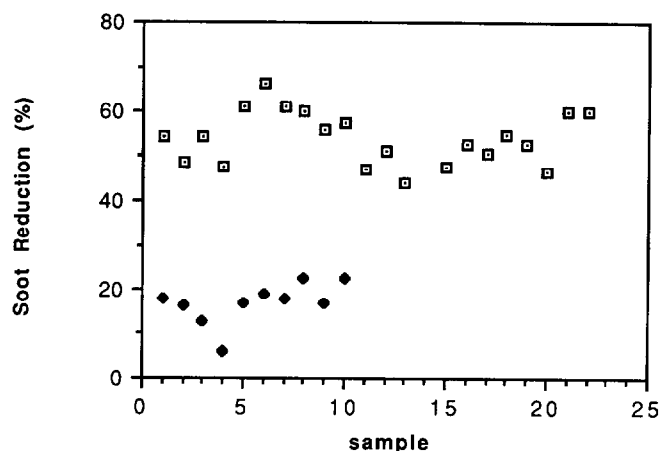


Figure 3. Soot reduction observed when mixtures of ferrocene derivatives are added to Norman Wells crude oil and to kerosene—In this experiment, a concentration of 0.25 wt% ferrocene equivalent is used. (□ = NW crude oil; ♦ = kerosene)

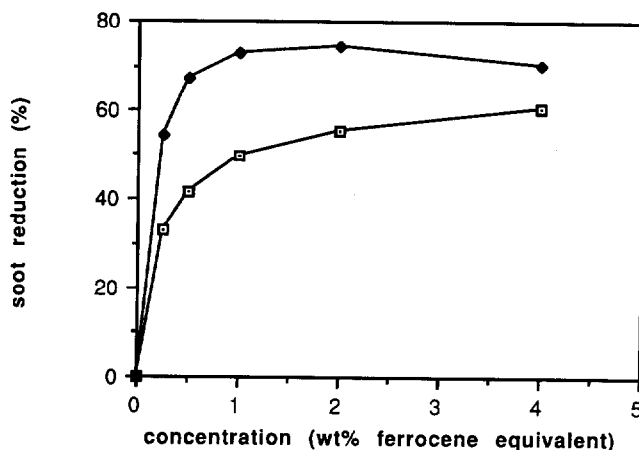


Figure 4. Soot reduction observed when kerosene containing RMS-9757 is burned in the apparatus shown in Figure 1—The higher concentration of branched hydrocarbons in kerosene than in crude oil gives rise to lower soot reduction. (□ = kerosene; ♦ = NW oil)

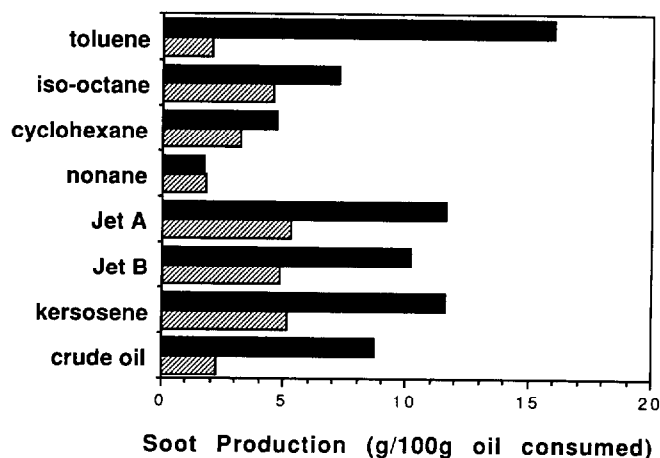


Figure 5. Soot production for a range of hydrocarbon mixtures with and without RMS-9757 at a concentration of 2 wt% ferrocene equivalent—Note the marked effect of hydrocarbon type. (■ = no additive; ▨ = 2 wt% additive)

composition. Soot reduction using RMS-9757 can be estimated from the following equation:

$$\text{Soot reduction} = 1 - \frac{(1.7P + 4.5N + 2A)}{(1.8P + 7.2N + 16A)} \quad (1)$$

Where: P = concentration of normal paraffins (wt%)
N = concentration of branched hydrocarbons (wt%)
A = concentration of aromatic hydrocarbons (wt%)

The validity of equation 1 was tested using known compositions to estimate soot reduction: Norman Wells crude, calculated 64 percent, observed 74 percent; kerosene, calculated 53 percent, observed 56 percent. From such a limited set of model compounds, and considering the oversimplified oil compositional model, the agreement is remarkably good. In any event, hydrocarbon composition should be considered as a major influence on soot yield and soot reduction, along with the influence of fire size.^{2,3} Future research will expand on this concept.

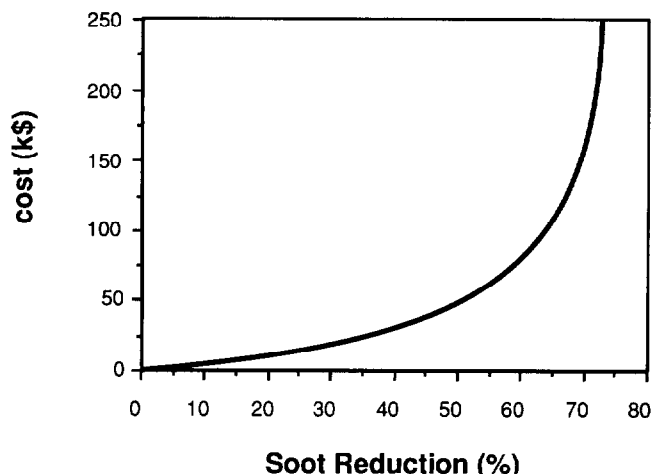


Figure 6. Approximate cost of RMS-9757 as a function of soot reduction for a 10,000 barrel spill of Norman Wells crude oil—Oils containing more branched paraffins will require more soot reducing additive.

Economics of soot reduction

Oil spill response in general is not an inexpensive undertaking, and application of soot reduction additives is no exception. While the chemicals discussed in this paper are in development and are not yet commercially available, it is estimated that the cost will be in the neighborhood of \$20 per kilogram. Using an application rate of 1 wt%, the cost of soot reduction additive for a 10,000 bbl spill of Norman Wells crude oil would be approximately \$250,000.

The cost of the soot reduction additive will have to be weighed against the environmental or health risks presented by the soot. For example, in a given spill situation it may not be necessary to remove all the soot, a lesser soot reduction may achieve the desired reduction in risk. This point is well illustrated in Figure 6 where it can be seen that for Norman Wells crude oil, additive worth \$250,000 removes only twice as much soot as additive worth \$25,000. The cost of the additive will increase for oils containing more branched paraffins.

Toxicity of ferrocene, its derivatives, and their combustion products

Ferrocene and its alkyl derivatives are considered to be relatively nontoxic. In animal studies, the LD_{50} for ferrocene in mice has been reported as 600 mg/kg while dogs have survived treatment up to 1000 mg/kg for three months. Similarly, ethylferrocene has been found to be nontoxic at doses up to 500 mg/kg. The alkyl derivatives used in this study have not been subjected to rigorous toxicity testing; but there is no reason to expect that the toxicity will be any different than for other

tested alkyl ferrocenes. In any event, toxicity testing will be done as part of the product development process. The only new combustion product found in the soot is particulate iron oxide (rust). Long-term exposure to air contaminated with iron oxide (as in a foundry) is considered to present a respirable dust hazard with no long-term health effects. For in-situ burning, neither the concentration nor time of exposure is sufficient to justify a health concern.

Conclusions

An effective, easily applied soot reduction additive for use in the in-situ burning of oil spills has been developed. While improvements in the additive can be made by adjusting the composition of the mixture, the composition of the hydrocarbon is the most important factor controlling the efficacy of the soot reduction additive. This suggests that the composition of the oil and the degree of smoke reduction required need to be considered as part of an oil spill response plan.

References

1. Allen, A. A., 1988. Comparison of response options for offshore oil spills. *Proceedings of the Eleventh Arctic and Marine Oil Spill Technical Seminar*. Environment Canada, Edmonton, Alberta, pp289-306
2. Evans, D. D., G. W. Mulholland, J. R. Lawson, E. J. Tenneyson, M. F. Fingas, P. A. Tebeau, and J. R. Gould, 1991. Burning of oil spills. *Proceedings of the 1991 International Oil Spill Conference*. American Petroleum Institution, Washington, D.C., pp677-680
3. Evans, D. D., W. D. Walton, H. R. Baum, K. A. Notarianni, J. R. Lawson, H. C. Tang, K. R. Keydel, R. G. Rehm, D. Madrzykowski, R. H. Zile, H. Koseki, E. J. Tenneyson, 1992. In-situ burning of oil spills: Mesoscale experiments. *Proceedings of the Fifteenth Arctic and Marine Oil Spill Program Technical Seminar*. Environment Canada, Edmonton, Alberta, pp593-657
4. Farrar, D. H., 1990. Engine Cleaning Additives for Diesel Fuel. U.S. Patent 4,908,045
5. Mitchell, J. B. A., 1990. The effectiveness of ferrocene in reducing smoke emission from burning crude oil. *Proceedings of the Thirteenth Arctic and Marine Oil Spill Program Technical Seminar*. Environment Canada, Edmonton, Alberta, pp75-85
6. Mitchell, J. B. A., 1991. Smoke reduction from pool fires using ferrocene and derivatives *Combustion and Flame*, v86, p179
7. Mitchell, J. B. A. and M. E. Moir, 1992. Smoke reduction from pool fires using ferrocene and derivatives. *Proceedings of the Fifteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Edmonton, Alberta, pp681-688
8. Syntex, 1977. Improved Combustion Engine Fuel and Processes. British Patent 1,477,806
9. Woodward, R. B., M. Rosenblum, and M. C. Whiting, 1952. *Journal of the American Chemical Society*, v74, p3458
10. Zimmer-Galler, Roswitha, 1973. Burning Rate Catalyst. U.S. Patent 3,755,311