

Burning of Oil Spills

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ABSTRACT

This study is directed at understanding the oil spill combustion process and the smoke generated from the burning. Measurements of 1.2 m diameter Murban crude oil pool fires show an initial steady energy release rate of 840 kW/m² which increases to 1860 kW/m² during the vigorous burning associated with boiling of the water sublayer. During the burning of the crude oil pools approximately 10 percent of the crude oil was converted to smoke with a high elemental carbon content in excess of 90 percent. Measurements of polycyclic aromatic hydrocarbon (PAH) components found in the original oil, showed that soot produced in the burning process carried a different distribution of PAH compounds, but that the total concentration of these compounds was equal to that found in the original crude oil.

1. INTRODUCTION

In 1985, the Center for Fire Research (CFR) at the U.S. National Institute of Standards and Technology (NIST) began studies of oil spill combustion. The long range goal of the research program is to provide measurements and means to make quantitative predictions of the fraction of oil in a spill that can be consumed by an in-situ combustion process, the characteristics of the residual oil, and the characteristics of the combustion product flow from the burning oil. It is hoped that this information may be cast into a form that is usable by local officials and oil spill response professionals as part of the decision making process in the event of an oil spill.

Previous results from experiments in which crude oil was burned in a 0.6 m diameter oil pool fires included measurements of burning rate, thermal radiation emission, smoke production and the chemical composition of both the oil and the burn residue (Evans, et al., 1986).

This effort is the first in a two year program to quantify the thermal properties and burning characteristics of the crude oil, the physical and chemical properties of the smoke generated in the combustion process, and the expected dispersal of the soot through the atmosphere and deposition downwind of the oil fires. This report summarizes results from some of the main research thrusts all of which are incomplete at this time.

2. POOL BURNING CHARACTERISTICS

Crude oil burn tests were conducted in the CFR large-scale test building. Details of the experimental apparatus for 0.6 m diameter pool fires with gas analysis and soot sampling are recorded in a previous report (Evans, et al., 1986). Larger test burns were conducted in a new 1.2 m diameter pan

installed under a calorimeter hood. Instrumentation for the larger burns provided for the measurement of flame temperature; oil and water temperature; energy release rate; radiation feedback from the flames to the liquid surface; and radiation from the flames to the surrounding. The energy release rate of the fires burned under this hood are determined using the oxygen consumption calorimeter technique.

The burning characteristics of three types of crude oil were investigated in the large calorimeter -- Alberta Sweet, La Rosa and Murban. These oils differ in composition, notably in the percent of the heavier wax plus asphaltene fractions, with Alberta Sweet crude being the lowest and La Rosa crude being the highest.

The burning characteristics of the three crude oils were measured in burns under the large calorimeter hood. The use of a 1.2 m diameter pan permitted controlled burning experiments to be conducted under conditions representative of the radiation-dominated, turbulent flow regime of larger pool fires. Each oil was studied at four initial layer thicknesses -- 2 mm, 5 mm, 10 mm, and 25 mm. The energy release rate for the Murban crude exhibited an approach to steady-state for the 10 mm and 25 mm layer thicknesses prior to reaching a peak value during the vigorous burning period. The quasi-steady-state energy release rate for the Murban crude was approximately 0.95 MW (840 kW/m²), actually decreasing noticeably prior to the rapid increase in burning corresponding to a peak level of 2.1 MW (1860 kW/m²) just before burnout. The decrease in energy release rate during the steady burning phase (100 to 500) seconds appears to be associated with the changing composition of the crude oil towards the heavier fractions. The corresponding values of steady-state and peak energy release rates for the Alberta Sweet crude were 1.15 MW (1000 kW/m²) and 2.7 MW (2400 kW/m²). These values are significantly greater than the area specific energy release rate for Alberta Sweet crude (720 kW/m²) measured in the smaller 0.6 m diameter pan fire used for soot measurements. The peak energy release rate for the La Rosa crude was approximately 50% greater than for the Murban crude.

The oil residue remaining following burnout varied with the type of oil and the layer thickness. With one exception, more oil remained from the thickest (25 mm) layer of each oil and slightly more residue remained with the La Rosa crude than with the other oils. The measured residue for all tests ranged from 0.6 kg to 1.2 kg corresponding to a layer depth of approximately 0.6 mm to 1.2 mm.

3. SMOKE AND GAS EMISSIONS

The chemical characterization of the smoke produced by burning crude oil is important data for total evaluation of the effects of oil spill combustion. Measurements in this study included the organic versus elemental carbon in the smoke, the quantity of selected polynuclear aromatic (PAH) compounds in the smoke, and the amount of CO₂, CO, NO, and NO_x emitted. Much of the analysis effort was concentrated on the PAH analysis. These PAH compounds are of environmental concern, because some have been reported to be

carcinogenic to animals (Boyland, 1981). The results of the PAH analysis are compared with the PAH content of the original crude oil.

In all tests in this series, Alberta Sweet crude oil was burned in a 0.6 m diameter pool. Approximately 9 liters of crude oil were burned in each test, which corresponded to a fuel depth of about 30 mm. The sample burning time was found to be about fifteen minutes. Smoke samples were collected on filters heated to match the stack temperature, about 100°C, using a heated transfer line ("H" series tests). The smoke sample was collected during the time of visually steady burning. Smoke samples were also collected and diluted before collection on filters with air cooled to about 10°C to simulate the cooling that would naturally occur in a rising smoke plume ("C" series tests). In all tests two samples (sample 1 before sample 2) were collected on the filters before the rapid burning period.

The results of the smoke emission measurements are contained in Table 1. The smoke yield, ϵ , which is defined as the mass of smoke aerosol generated per mass of fuel consumed, is found to have a value of about 0.10. This is similar to the value found in previous test with Prudhoe Bay crude oil (Evans, et al., 1986). The value of ϵ increases in going from sample 1 to sample 2 indicating that the smoke emission increases as the fuel presumably distills leaving the sootier component for the later stage of burning.

The smoke collected in tests C-5 and C-7 was first diluted and thus cooled by the stack sampling probe. The mass flow of ice cooled dilution air is approximately twice the mass flow of the air sampled from the stack. The manifold temperature just prior to the filter is observed to be within two °C of the ambient temperature. The value of ϵ obtained under these conditions is 15% to 20% less than the value obtained for the heated, undiluted sample. Normally, one would expect an increase in ϵ with dilution by cool air resulting from the condensation of organic vapors. The PAH analysis discussed below clearly shows that the higher vapor pressure PAH's are greatly enriched in the diluted sample compared to the high temperature sample. The observed decrease in these tests may be the result of smoke deposition by thermophoresis in the entrance portion of the diluter and by turbulent flow in the mixing region of the diluter.

The emission of CO, CO₂, NO, and NO_x was monitored during selected tests. The concentrations of CO and CO₂ were measured by standard gas analysis instrumentation based on nondispersive infrared spectroscopy. The CO₂ accounts for over 95% of the gaseous products measured as indicated in Table 2. The other principal product of combustion, H₂O, was not measured. The volume fraction of CO, NO, and NO_x relative to CO₂ were found to be about 0.038, 1.5x10⁻⁴, and 4x10⁻⁴, respectively. The concentrations of NO and NO_x were just above the detection threshold.

Smoke aerosol produced by flaming combustion is composed of a graphitic or so called elemental carbon fraction and an organic carbon fraction. Smoke samples were collected on quartz fiber filters and sent to a contract laboratory for thermal-optical analysis for organic/elemental carbon (Johnson, et al., 1981). The elemental carbon content of the smoke was found to be over 90%.

Eight smoke samples weighing 10 mg to 15 mg each were deposited on teflon filters and were analyzed for 15 polynuclear aromatic hydrocarbons (PAH's) using combined liquid and gas chromatographic techniques at both NIST and Environment Canada.

It is known that the crude oil fuels themselves have a PAH component. Overall, for the compounds measured, the total PAH fraction of the smoke and the original oil burned are nearly equal. It is also of interest to compare the amount of selected PAHs per gram of fuel versus the amounts of PAHs collected in the smoke per gram of fuel consumed. As seen in Table 3, the relative concentration of the individual PAHs compounds is different in the fuel compared to the smoke. For example, the concentration of phenanthrene plus anthracene in the fuel (296 $\mu\text{g/g}$) is about 2 times greater than for the smoke (133 $\mu\text{g/g}$ fuel burned), while the concentration of benzo[a]pyrene (BaP) is a factor of three lower for the fuel (5 $\mu\text{g/g}$) compared to the smoke (18 $\mu\text{g/g}$). This indicates that the combustion process itself is generating specific PAHs and that the PAH content of the fuel will not represent the distribution of PAHs emitted. There is about a four-fold enrichment of the four-six ring PAHs in the smoke compared to the crude oil.

BaP has been used as a surrogate for the overall carcinogenic effect of PAHs. The higher BaP concentration in the smoke relative to the fuel is of environmental concern; however, two key issues must be addressed before a full assessment of PAH emission can be made. The effect of burning rate on PAH emission should be analyzed. Smoke was not collected during the very rapid burning stage near the end of a test, but this burning phase may be dominant in a large fire with a thin oil layer. An analysis of the vapor phase PAHs should be made to complete the present analysis that has concentrated on condensed phase products.

4. SUMMARY

An experimental facility was completed to examine the burning conditions of crude oil in a 1.2 m diameter pool fire configuration. This facility permitted controlled burning experiments to be conducted under conditions representative of the radiation-dominated, turbulent flow regime of larger pool fires that might occur on the open ocean or in pools confined by broken ice. Tests with three different crude oils, Alberta Sweet, La Rosa, and Murban were conducted using initial oil depths of 2 mm, 4 mm, 10 mm and 25 mm floated on a deep water layer.

At oil depths of 10 mm and 25 mm each oil exhibited two distinct burning stages. The first was associated with a progressive vaporization of the burning oil layer and the other with more intense, short duration burning in which the oil surface was churned and splattered by boiling water under the thin oil layer. For Murban crude oil, the steady burning resulted in energy release rates of 840 kW/m^2 which increased to 1860 kW/m^2 during the vigorous burning before extinction. Residual oil left on the water surface at the end of natural burning corresponded to a uniform layer depth of 0.6 mm to 1.2 mm.

The burning of Alberta Sweet crude oil results in a high smoke emission with ϵ about 0.10 (10% conversion to smoke). The smoke has a high elemental carbon component in excess of 90% resulting in a highly light absorbing soot. The primary gaseous product of combustion is CO_2 with the CO concentration about a factor of 25 lower than CO_2 . The emission of NO and NO_x are less than one thousandth the concentration of CO_2 .

Independent analyses of the PAH content of the smoke by the National Institute of Standards and Technology and Environment Canada showed the same trends and had good overall agreement for 12 individual PAHs. The PAH content of the smoke was nearly equal to that in the original oil burned. The PAH content of the smoke was enriched in the larger species in comparison with the fuel. The concentration of benzo[a]pyrene, which is often used as a surrogate for the carcinogenic effect of PAH, was found to be three times greater in the crude oil smoke per gram of fuel consumed compared to the crude oil itself. The concentrations of the three ring PAHs were found to be very sensitive to the filter collection temperature. Thus, it is important to use a diluter when sampling the PAHs to simulate the conditions existing in a rising smoke plume.

5. ACKNOWLEDGEMENTS

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TABLE 1. SUMMARY OF SMOKE EMISSION DATA FOR 60 CM DIAMETER ALBERTA SWEET CRUDE OIL POOL FIRES

Property	Test H-1 sample 1	Test H-1 sample 2	Test H-4 sample 1	Test H-4 sample 2	Test H average	Test C-5	Test C-7	Test C average
dQ/dt, kW	217	172	234	191	204	205	203	204
dm/dt, g/s	5.27	4.40	5.63	4.93	5.06	4.98	5.57	5.28
H, kJ/g	37.4	39.8	41.7	38.8	39.4	41.1	36.3	38.7
ϵ_1	0.076	0.119	0.100	0.110	0.101	0.087	0.079	0.083
ϵ_2	0.070	0.110	0.089	0.101	0.093	0.080	0.079	0.080

Legend:

H-1 and H-4 refer to identical crude oil burns in which the filter collection system was heated to about 100 °C. C-5 and C-7 refer to identical crude oil burns in which the smoke is cooled to ambient temperature in a sampling dilution system. dQ/dt - heat release rate of the fuel. dm/dt - burning rate of the fuel. H - heat of combustion. ϵ_1 and ϵ_2 refer to the smoke yield based on a flux method and a carbon balance method, respectively.

TABLE 2. GASEOUS EMISSION FROM ALBERTA SWEET CRUDE OIL

Species	C-6 ppm	C-7 ppm	C-6 fract. ^a	C-7 fract. ^a
CO ₂	4600	4900		
CO	174	187	0.038	0.038
NO	0.7	0.7	1.6x10 ⁻⁴	1.5x10 ⁻⁴
NO _x	2.3	1.7	5.0x10 ⁻⁴	4.0x10 ⁻⁴

^a Volume fraction of gas species relative to CO₂.

TABLE 3. COMPARISON OF PAH CONTENT OF ALBERTA SWEET CRUDE OIL AND SMOKE FROM BURNED OIL

PAH	Crude Oil $\mu\text{g/g}$ ^a	Smoke $\mu\text{g/g}$ ^d
Acenaphthylene	61	
Acenaphthene	N.D.	
Fluorene	188	
Phenanthrene	296 ^c	104
Anthracene		29
Fluoranthene	22	73
Acephenanthrylene		40
Pyrene	21	84
Benzo[ghi]fluoranthene		22
Cyclopenta[cd]pyrene		54
Benz[a]anthracene	N.D.	22
Chrysene/Triphenylene	30	23
Benzo[b,j,k]fluoranthene	N.D.	39
Benzo[e]pyrene	21	12
Benzo[a]pyrene	5	18
Perylene	N.D.	4
Indeno[1,2,3-cd]pyrene	N.D.	19
Benzo[ghi]perylene	N.D.	21
Total Concentration of PAHs	395	448

^a $\mu\text{g PAH/g}$ crude oil. Analysis performed by Environment Canada.

^b $\mu\text{g PAH/g}$ of crude oil burned assuming smoke emission factor, ϵ , of 0.10 and PAH emission data from C-5, #2. Analysis performed by NIST.

^c This number represents the sum of phenanthrene and anthracene.