

**Laboratory Studies of the Physical
Properties of In-Situ Burn Residues**

by

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Abstract

This study investigated the physical properties of residue from in-situ burns of oil. It involved burning small slicks of oil on water, collecting samples of the residue after natural extinction of the fire, then measuring the properties of the residues. The residue properties were compared to the original oil's properties.

Eight oils were selected for the project. These were:

- i) *Alaska North Slope crude*
- ii) *Alberta Sweet Mixed Blend crude*
- iii) *Arabian Heavy crude*
- iv) *Arabian Light crude*
- v) *Bonny Light crude*
- vi) *Iranian Heavy crude*
- vii) *Mayan crude*
- viii) *automotive diesel*

Test burns were conducted using samples of all eight oils when fresh and unweathered. In addition, two of the crude oils (Mayan and Arabian Light) were artificially weathered to investigate the effect of evaporation on burn residue properties.

Burn experiments were carried out in the laboratory on salt water at room temperature (15°C). Three thicknesses of oil were burned: 5, 10 and 15 cm. The physical properties of the residue measured were: density (at two temperatures); and, (for samples with pour points below 45°C) water content; pour point; and, viscosity (at two temperatures). All unburned oils and residues were also chemically analyzed to provide the total fraction of saturates, aromatics, resins and asphaltenes in the samples; however, at the time of writing these data were not yet available.

Preliminary results show that the residues from thick slicks of heavier crudes may sink in salt water. Efforts were made to correlate burn residue density with initial oil properties and burn parameters.

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Introduction

Research on the use of in-situ burning as a marine oil spill countermeasure over the past 25 years has resulted in a rapidly growing acceptance of the technique as an option for spill cleanup. In-situ burning has evolved from its beginnings as a tool for spill response in remote ice-covered waters to a technology that can be used in open water conditions almost anywhere to remove large volumes of oil contained in fire-resistant booms.

One area of concern with the use of in-situ burning has been the fate, properties and potential impacts of the residue remaining after a burn has extinguished. A key aspect has been whether the residue would sink. Studies of residues from melt-pool-type burns (Energetex 1977 and 1980, Dickins and Buist 1981, Evans et al. 1986, Smith and Diaz 1987, Guenette et al. 1994) showed that, although the residue from these types of burns was more dense and much more viscous than the original oil, it would not likely sink, even in fresh water. Recent spill experiences that involved accidental burning on the sea of large volumes of heavy crude oils (the *Haven* and the *Honam Jade* - Moller 1992, Turbini et al. 1993) and recent large-scale experiments involving thick slicks of moderately heavy crude oil contained in fire boom (Buist et al. 1995) have shown that burn residues can indeed sink. The objective of the present study was to examine experimentally the factors that govern the physical and chemical properties of burn residue. This paper focuses on the physical properties of the residue, in particular its density.

Theory

Figure 1 illustrates the major heat and mass transfer processes that occur during the in-situ burning of an oil slick on water. The key process is radiative heat transfer from the flame back to the surface of the slick. This heat is partially used by vaporizing the liquid hydrocarbons which then rise to mix with air above the slick and oxidize, or burn; the remainder transfers through the slick to the underlying water. Once ignited, a burning thick oil slick reaches a quasi-steady-state in which the vaporization rate sustains the necessary heat transfer back to the slick surface.

Extensive tests by Wakamiya et al. (1982) showed that the process by which the oil vaporizes is not a batch distillation (where the lightest, most volatile, components are boiled off from the entire slick first followed by progressively heavier, less volatile components), but is similar to an Equilibrium Flash Vaporization (EFV) in which vapor of essentially constant composition over time is produced by a feed of oil of essentially constant composition. Three observations lend credence to the EFV theory of in-situ combustion: (1) the surface temperatures of burning oil slicks remain relatively constant in the 200 to 300°C range during steady state burning (Wakamiya et al. 1982, Evans et al. 1988, Guenette et al. 1994), if burning were a distillation the surface temperature of the slick would steadily increase; (2) a steep temperature profile exists in the burning slick (Wakamiya et al. 1982, Guenette et al. 1994), indicating a poorly-mixed oil layer, as required for EFV; and, (3) the presence of light ends in the oil residue remaining after a burn (i.e., Energetex 1977, Dome 1981, Wakamiya et al. 1982) which would not be present if in-situ burning was a distillation process. It is believed that EFV occurs during in-situ burning because the hot flames and the insulating characteristics of the oil combine to create high temperatures in a thin surface layer of the slick known as the "hot zone". This promotes near-complete vaporization of the surface of the oil slick with minimal mixing and heat transfer to the underlying oil and/or water layers.

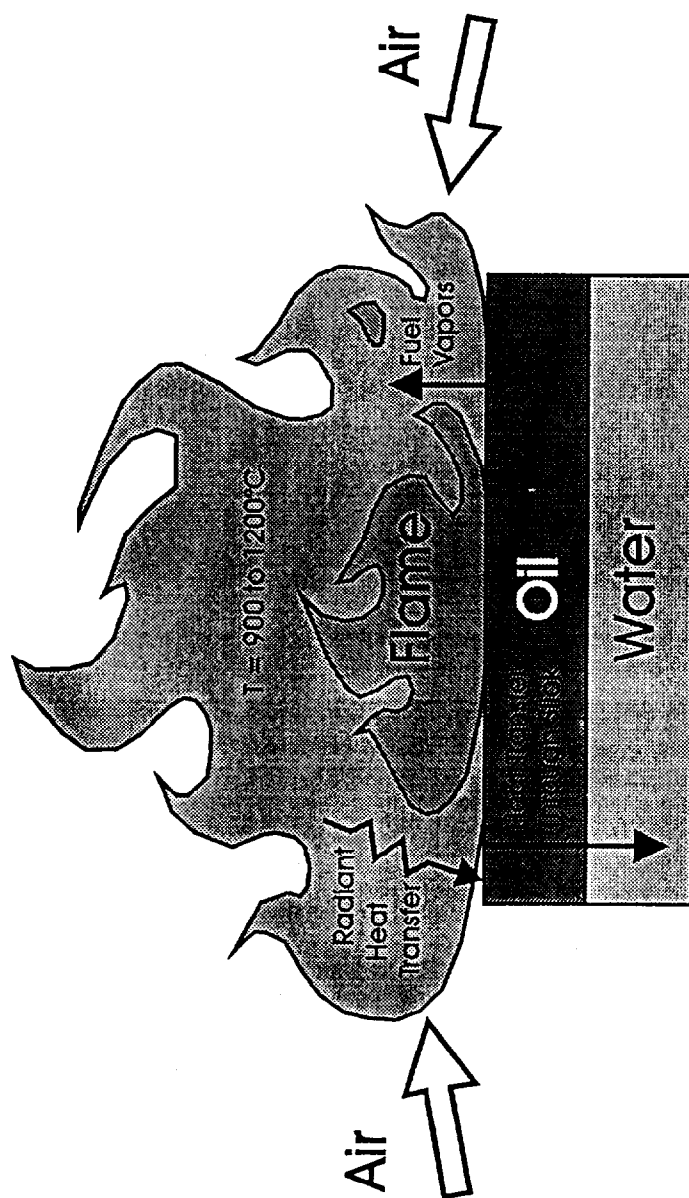


Figure 1 Key heat and mass transfer processes in in-situ burning

It is clear that the vaporization process occurring during in-situ burning of crude oils is not a perfect EFV. It is well known that the burn residue, while still containing some light ends, differs markedly from the original crude. The residue's increased density and altered rheology strongly indicate that there is a progressive concentration of the very high molecular weight compounds in the remaining slick as in-situ burning proceeds. It is this concentration of heavy ends in the residue over time that may explain why residues from burns of relatively thin crude oil slicks (2 cm or less) do not sink while residues from burns of thick slicks of the same crude do sink. The concept of an imperfect EFV may also explain why burn residues of heavier crudes (which have greater initial concentrations of high molecular weight compounds) sink more readily than those of lighter crudes.

Methods

Test Oils

Eight oils, listed below, were selected for the project. These were representative of oils shipped by sea in North American waters, ones that have been involved in tankship fires that resulted in the residue sinking, or were used in recent in-situ burning field research studies.

- i) Alaska North Slope (ANS) crude
- ii) Alberta Sweet Mixed Blend (ASMB) crude
- iii) Arabian Heavy crude
- iv) Arabian Light crude
- v) Bonny Light crude
- vi) Iranian Heavy crude
- vii) Mayan crude
- viii) automotive diesel

Two of these, Arabian Light and Mayan, were artificially weathered to two degrees of evaporation by bubbling air through them. The end points of the artificial evaporation were selected to approximate oil topped to 150°C and 250°C, after Durell et al. 1994. The physical properties of these oils are given in Tables 1 and 2.

Burn Experiments

The burns were conducted in a water-filled circular steel pan measuring 1.2 m in diameter and 32 cm in height (Figure 2). Measured amounts of the test oils were contained in the center of the pan in a 40 cm diameter, 20 cm high metal ring supported by three legs. The initial oil height was adjusted, by altering the water level, to be 1 cm below the lip of the ring. Three slick thicknesses were burned for each fresh oil: 5 cm, 10 cm and 15 cm. These were much greater than has been used in other tests in order to simulate the slick thickness in fire-resistant booms under tow. Only 5 cm thicknesses of the artificially evaporated oils were burned. The burn tests were conducted at room temperature on 35 ppt salt water. A perforated ring of copper tubing connected to a constant-head supply tank was used to gently flush the bottom of the contained slick with cool salt water. This was done in order to better simulate slick conditions in a towed boom at sea. The purpose was to reduce or eliminate the vigorous burn phase (Evans et al. 1988 and 1992) that is often observed during smaller scale and static tests, but not during larger scale tests at sea (Fingas et al. 1995). A fume hood suspended 1.5 m above the test ring and connected to a fan (200

Table 1 - Physical Properties of Test Oils

Oil Type	Interfacial Tension (mN/m)		Density (g/cm ³)		Pour Pt. (°C)	Flash Pt. (°C)	Water Content (% w/wt)
	oil/water	oil/air	@15 °C	@40 °C			
ANS	17.6	32.7	0.880	0.873	<-9	<7	0.080
Arab. Hwy.	28.6	32.5	0.886	0.875	<-9	45	0.103
Arab. Lt.	17	31.6	0.870	0.880	<-12	<7	0.430
20% Arab Lt.	16.6	32.5	0.908	0.899	-3	<9	0.093
31% Arab Lt.	14.8	35.8	0.926	0.912	3	9	0.104
ASMB	11.4	32.2	0.851	0.844	<-9	<10	0.336
Bonny Lt.	15	32.1	0.852	0.842	3	<6	0.080
Diesel	12.7	30.1	0.823	0.819	<-9	44	0.114
Iranian Hwy.	20.8	31.3	0.871	0.862	<-9	<8	0.169
Mayan	23.1	34.8	0.930	0.925	<-9	<6	0.301
12% Mayan	16.6	33.9	0.952	0.942	-6	<6	0.088
22% Mayan	N/M		0.975	0.958	9	30	0.144

Table 2 - Rheology of Test Oils

Oil Sample	Viscosity (mPas) @15°C	Shear Rate (s ⁻¹)	Viscosity (mPas) @40°C	Shear Rate (s ⁻¹)
ANS	21.2	3.7	10.5	7.3
	21.5	7.3	10.6	14.7
	22.0	14.7	11.6	36.7
Arab. Hvy	56.0	1.8	25.0	3.7
	56.0	3.7	23.0	7.3
	54.8	7.3	24.9	14.7
Arab. Lt.	19.0	3.7	9.5	7.3
	17.5	7.3	8.8	14.7
	18.0	14.7	8.8	36.7
			9.2	73.4
20% Arab. Lt.	90.0	1.3	25.0	2.6
	87.5	2.6	24.0	6.6
	89.0	6.6	25.0	13.2
	90.0	13.2		
31% Arab. Lt.	324.0	0.3	60.0	1.3
	330.0	0.7	60.0	2.6
	340.0	1.3	56.0	6.6
	347.5	2.6	55.5	13.2
ASMB	10.2	7.3	5.4	14.7
	10.5	14.7	5.0	36.7
	9.9	36.7	5.1	73.4
	9.8	73.4		
Bonny Lt.	21.5	3.7	3.5	14.7
	19.0	7.3	3.4	36.7
	16.5	14.7	3.6	73.4
	13.9	36.7		
Diesel	2.8	14.7	2.2	36.7
	2.5	36.7	2.1	73.4
	2.5	73.4		
Iranian Hvy.	18.2	3.7	11.0	7.3
	17.5	7.3	11.8	14.7
	17.3	14.7	12.3	36.7
Mayan	230.0	0.7	55.5	2.6
	225.0	1.3	53.2	6.6
	237.5	2.6	44.9	13.2
12% Mayan	2500.0	2.5	270.0	0.7
	2300.0	6.3	269.0	1.3
	2250.0	12.5	275.0	2.6
	1820.0	0.066		
	1560.0	0.132		
	1688.0	0.3		
	1768.0	0.7		
22% Mayan	32000.0	0.3	1700.0	0.1
	34000.0	0.6	1750.0	0.1
	35000.0	1.3	1700.0	0.3
	35750.0	2.5	1870.0	0.7

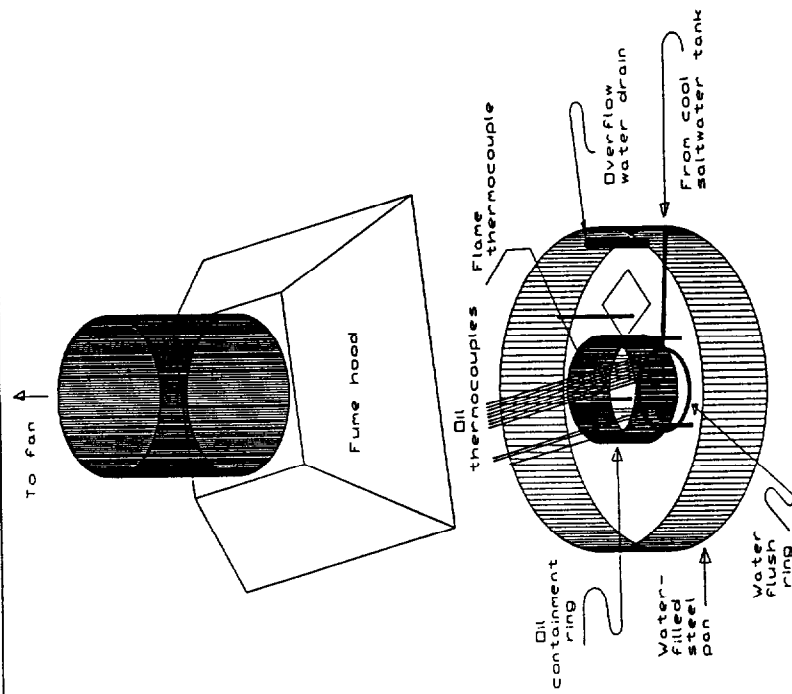


Figure 2 - Burn ring schematic

m³/min) via 60 cm diameter flexible aluminum ducting was used to exhaust the smoke generated by the burns.

Temperatures were measured at eleven locations throughout the slick layer and in the water below the slick. Flame temperatures were also recorded. The thermocouples (Type K) were connected to an A/D board, through a multiplexer to a computer. An adjustable rack was used so that eight of the thermocouples could be moved vertically and positioned at the same initial depth intervals below the oil surface for the different slick thicknesses. All burns were videotaped for archival purposes. After each burn the residue was collected and weighed, to permit the burn efficiency to be calculated, and samples taken for analyses.

Physical Property Analyses

Fresh oil samples were subjected to the following determinations:

- density at 15°C and 40°C using an Anton Parr Model DMA 35 digital densitometer and following ASTM D4052 procedures;
- dynamic viscosity at 15°C and 40°C at three shear rates using a Brookfield Model LV viscometer and following ASTM D2983 procedures;
- oil/seawater and oil/air interfacial tensions at room temperature using a Central Scientific Company DuNuoy Ring Apparatus following ASTM D971 procedures;
- pour point using the Kohler Pour Point Chamber and following ASTM D97 procedures;
- flash point using the Cleveland Open Cup apparatus following ASTM D93 procedures; and
- water content using an Orion Model AF8 Karl Fischer titrator following procedures developed by Environment Canada.

Burn residue samples were divided into two groups: those that were fluid at 45°C and those that were not. Residue samples that were fluid were analyzed to determine: density at 15°C and 40°C; viscosity at 15°C and 40°C, pour point and water content using the procedures described above for the fresh oil samples.

For those residue samples that were not fluid at 45°C, only their density was measured at 15°C and 40°C. This was accomplished by immersing a sample of the residue in a series of aqueous solutions. Twenty one solution baths were prepared to cover the density range 0.900 to 1.100 g/cm³ in increments of 0.01 g/cm³. The baths with densities less than water were made using methanol/water solutions; the baths with densities greater than water were prepared using sodium chloride/water solutions. Each residue sample was first placed in a pure water bath; depending on whether the sample sank or floated it was placed in solutions of progressively higher or lower density until one was found in which it floated or sank, respectively. At this point the density of the previous bath and the one in which the sample floated or sank was confirmed using the digital densitometer. The density of the residue sample was then assigned the value of the average of the density of

the solution in the two baths. For the determination at 40°C both the residue sample and the aqueous solutions were maintained in a constant temperature bath.

Results and Discussion

Table 3 lists the oil and residue masses for each burn, as well as the overall length of time each burn lasted (from ignition to extinction). The 5 cm crude burns generally lasted 50 minutes; the 10 cm crude burns averaged 95 minutes; and, the 15 cm burns lasted 120 to 150 minutes. The exception was the 15 cm burn of Bonny Light which boiled over the lip of the ring 25 minutes after ignition. Of the crude oils, the ASMB consistently had the shortest burns. The diesel burned faster than the crudes, which is to be expected at this scale of burn (Buist et al. 1994).

Table 4 lists the burn efficiencies calculated for the test burns. The highest efficiency was consistently achieved with the diesel burns, which resulted in an amount of residue equivalent to less than 1 mm for all three initial thicknesses. All other burns resulted in residue amounts equivalent to thicknesses greater than 2 mm. These results are consistent with the results of earlier studies (Buist et al. 1994). The least efficient burns involved Mayan crude, the oil with the highest density; the second least efficient burns involved Arab Heavy crude, the oil with the second highest density. Weathering of the oil appeared to decrease burn efficiency slightly, an effect that has been noted before (Bech et al. 1992). This trend in the data in Table 4 is far from certain.

The burn with a 15 cm slick of Bonny Light crude was unique in that the oil boiled out of the burn ring about 25 minutes after ignition. Examination of the temperature readings in the slick indicate that the upper 5 cm of the slick was at a constant temperature of 200°C after about 10 minutes, indicating that abnormal convective heat transfer was occurring. The viscosity data in Table 2 indicates that the Bonny Light has an unusually steep decline in viscosity with increasing temperature which may explain the anomalous onset of convection. At this time it is not clear why the Bonny Light behaved differently than the other crudes.

Table 5 lists the densities of the burn residues. Samples with values denoted as > 1.100 at 15°C (> 1.086 at 40°C) sank in the most dense solution bath. Table 6 gives the densities and water contents of the residues from the burns that produced a liquid residue. Table 7 contains the viscosity data for the diesel burn residues. The diesel residue viscosity was greater than that of the diesel fuel, but it was still a liquid. It is worthy of note that none of the test burns experienced residue sinking until the burn had extinguished and the residue had cooled. In other words, at the slick temperatures during combustion (200 to 300°C), the density of the residue was less than that of the underlying water. As the residue cooled its density increased and eventually exceeded that of the water. It should also be noted that, for all but the diesel tests and the failed 15 cm Bonny Light test, as the residue cooled it solidified. The residue from the heavier test oils (Iranian Heavy, Arab Heavy and Mayan) formed a brittle solid; the others (ANS, Arab Light, ASMB and Bonny Light) formed a semi-solid not unlike cold roofing tar. None of these residues softened appreciably at 45°C.

Residue Density Increase

Figure 3 shows the increase in residue density at 15°C with increasing initial oil thickness for the eight fresh oils tested. The horizontal lines show the density of fresh water

Table 3 - Test Burn Data

Oil Type	5 cm Burn			10 cm Burn			15 cm Burn		
	Oil Mass (kg)	Residue	Burn Time (min.)	Oil Mass (kg)	Residue	Burn Time (min.)	Oil Mass (kg)	Residue	Burn Time (min.)
Ans	5.7200	0.8653	57.03	9.6800	0.9590	98.53	16.6798	1.5112	135.77
Arab. Hvy.	3.6492	0.9066	49.13	10.9657	1.9454	92.00	16.9370	3.0000	153.85
Arab. Lt.	5.4436	0.3515	50.67	11.0041	0.2099	102.52	15.9465	1.9795	148.15
20% Arab. Lt.	5.9883	0.9564	66.10						
31% Arab. Lt.	6.1176	0.4780	62.12						
ASMB	5.7553	0.6638	37.67	11.2469	0.3016	83.50	16.3090	0.5847	118.38
Bonny Lt.	5.5380	0.5339	42.05	11.0760	0.5229	93.57	16.6140	BlowUp	
Diesel	5.3495	0.0748	25.65	10.6990	0.0715	49.33	16.0485	0.0548	65.78
Iranian Hvy.	5.5079	0.3428	43.33						
Mayan	6.0450	1.5076	49.97	11.5523	2.9736	94.23	17.4074	5.0367	144.00
12% Mayan	6.3963	1.7764	52.48						
22% Mayan	6.2037	1.8420	54.72						

Table 4 - Test Burn Oil Removal Efficiencies

Oil Type	Burn Efficiency (Mass %)		
	5 cm Burn	10 cm Burn	15 cm Burn
Ans	84.9	91.6	90.9
Arab. Hvy.	75.2	82.3	90.9
Arab. Lt.	93.5	98.1	87.6
20% Arab. Lt.	84.0		
31% Arab. Lt.	92.2		
ASMB	88.5	97.3	96.4
Bonny Lt.	90.4	95.3	*
Diesel	98.6	99.3	99.7
Iranian Hvy.	93.8		
Mayan	75.1	74.3	71.1
12% Mayan	72.2		
22% Mayan	70.3		

* This sample boiled over and the burn was not complete

Table 5 - Burn Residue Densities

Oil Type	Density at 15 °C (g/cm ³)			Density at 40 °C (g/cm ³)		
	5 cm	10 cm	15 cm	5 cm	10 cm	15 cm
Ans	1.025	1.075	1.045	1.020	1.068	1.040
Arab. Hvy.	>1.100	>1.100	1.065	>1.086	1.084	1.020
Arab. Lt.	1.035	1.065	1.065	1.020	1.030	1.069
20% Arab. Lt.	1.065			1.050		
31% Arab. Lt.	1.075			1.069		
ASMB	0.985	1.015	1.055	0.971	1.011	1.040
Bonny Lt.	0.955	0.975	0.873	0.971	0.981	0.865
Diesel	0.879	0.885	0.883	0.870	0.877	0.875
Iranian Hvy.	1.055			1.030		
Mayan	>1.100	>1.100	1.095	1.084	1.084	1.059
12% Mayan	>1.100			>1.086		
22% Mayan	>1.100			>1.086		

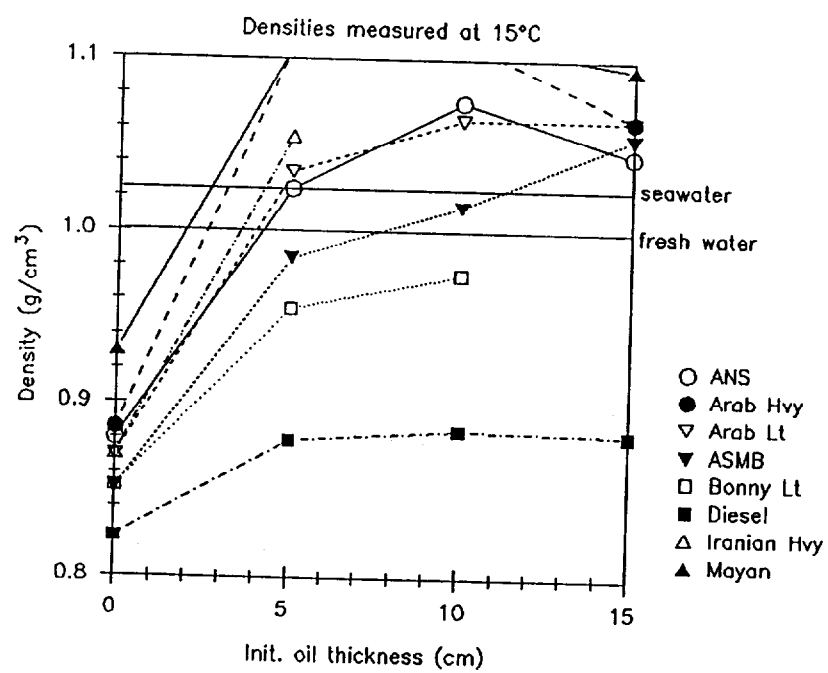
Table 6 - Liquid Burn Residue Properties

Residue	Water Content (% wt/wt)	Pour Point (°C)	Density	
			@15°C (g/cm³)	@ 40°C (g/cm³)
Diesel 5cm	2.859	<-12	0.885	0.870
Diesel 10cm	4.160	<-9	0.879	0.877
Diesel 15cm	7.100	<-9	0.883	0.875
Bonny Lt. 15cm	3.382		0.873	0.865

Table 7 - Burn Residue Viscosity Data

Burn Residue	T = 15°C		T = 40°C	
	Viscosity (mPas)	Shear Rate (s⁻¹)	Viscosity (mPas)	Shear Rate (s⁻¹)
Diesel 5cm	11.5	7.344	9.5	14.688
	12.6	14.688	9.4	36.72
	13.44	36.72	9.25	73.44
Diesel 10cm	28	3.672	20	3.672
	27	7.344	18.5	7.344
	25	14.688	17.25	14.688
			15.35	36.72
Diesel 15cm	21	3.672	14.1	7.344
	21.5	7.344	14	14.688
	21	14.688	12.2	36.72
	19	36.72		

Figure 3 – Residue Density



(1.000 g/cm³) and normal sea water (1.025 g/cm³). It is clear that efficient burning of thick slicks does significantly increase the density of the residue, and may do so to a point where the residue can sink. It is also apparent that heavier crude oils produce residues that are more susceptible to sinking. The density of the residue from the diesel burns does not appear to increase as much as for crude oils and, after an initial increase, appears not to be a strong function of slick thickness.

Buist et al. (1995) reported that the residue from a contained burn of 17.5 cm of fresh ANS crude sank in fresh water as it cooled; the cold burn residue also sank in sea water. The data in Figure 3 indicate that the density of the residue from the 10 and 15 cm burns of ANS crude exceeded 1.025 g/cm³ at 15°C. Fingas et al. (1995) report that the residue from the NOBE offshore burn of ASMB crude had a density of 0.936 g/cm³ and a viscosity of 100,000 mPas. This apparent contradiction of the results presented here for ASMB crude is possibly due to the fact that the NOBE burn involved a continuous feed of fresh oil into the burn pocket of a towed boom, as opposed to a burn of a thick contained slick as simulated by these tests.

The properties of the residues from the Iranian Heavy and Arabian Heavy test burns appear to be consistent with the properties of burn residue from actual spills of these oils. Some of the residue from the accidental burning of uncontained thick slicks of Iranian Heavy crude oil beside the stricken tanker *M/T Haven* is reported to have sunk to the bottom (Moller 1992, Turbini et al. 1993). The residue from the 5 cm burn of Iranian Heavy crude in the present study had a density that exceeded that of salt water. After a spill of some 2000 tonnes of Arabian Heavy crude from the *M/T Honam Jade* a cleanup contractor ignited the main slick which burned for two hours; after the burn extinguished the residue sank (Moller 1992). The residue from all three burns of Arab Heavy crude in the present study had densities greater than sea water.

Figure 4 illustrates the effect of evaporation of a crude oil on the density of the burn residue. The density of the residue from 5 cm slicks of Arab Light crude increases with increasing degree of evaporation. Perusal of the residue density data at 40°C in Table 7 indicates that the same trend appears to have occurred for the evaporated Mayan crude.

Preliminary Residue Density Correlation

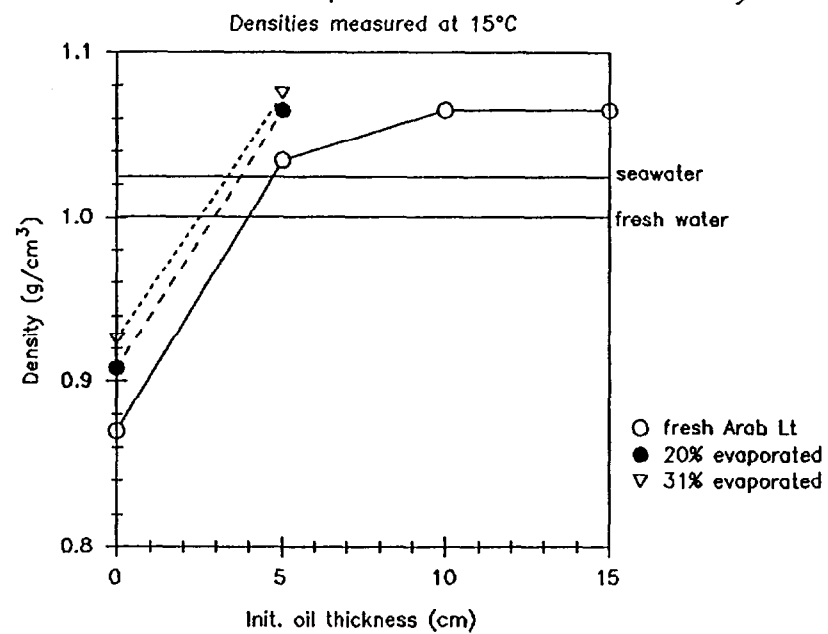
One of the goals of this study was to attempt to correlate burn residue properties with oil- and/or burn-parameters. The preliminary thoughts of the study team are presented here.

If the fuel vaporization process involved with in-situ burning is like an imperfect EFV, then it should be possible to correlate residue density change with initial oil properties and a measure of the degree of concentration of heavy ends that occurs during a given burn. It seems logical that the degree of concentration, for a given oil, should relate to the amount of oil burned and the efficiency of the burn. One expression that incorporates both of these factors is the product of the burn efficiency and the initial thickness or:

$$\rho/\rho_o = f(F_{BV}X_o) \quad (1)$$

where ρ, ρ_o = the residue and initial oil density respectively [g/cm³]
 F_{BV} = volumetric fraction of oil burned
 X_o = initial oil thickness [cm]

Figure 4 – Effect of Evaporation on Residue Density



The term $F_{BV}X_o$ is equivalent to the thickness of oil burned.

The volumetric fraction of oil burned can be calculated from the mass fraction burned (F_{BM}) by:

$$(1 - F_{BV}) = (1 - F_{BM})\rho_o/\rho \quad (2)$$

Figure 5 shows a plot of the ratio of residue density to fresh oil density as a function of $F_{BV}X_o$. This graph uses the densities at 40°C since there are fewer over-range data points at this temperature than at 15°C. It appears that there is a common trend of increasing density ratio with increasing amount of oil burned; however, the data scatter is fairly high. This could be due to inaccuracies in the density measurements, oil-related factors and/or burn-process-related factors. Once the chemical analyses of the residues are complete, the reasons for the differences may become more clear. The possible contribution of the vigorous burn phase to the data scatter is discussed later.

One interesting feature of Figure 5 is that the data for the crude oils are generally grouped around a common trend, while the data for the diesel fuel are distinctly different. This could be due to the fact that diesel, as a refined fuel, has few heavy ends to concentrate, and thus the residue is not significantly different from the original fuel.

The data appears to fit an equation of the form:

$$\rho/\rho_o = 1 + C_1(1 - \exp(-C_2F_{BV}X_o)) \quad (3)$$

where C_1 = a constant, which appears to have a value in the range of 0.2 for crude oils and 0.07 for diesel
 C_2 = another constant [cm^{-1}] which appears to have a value in the range of 0.33 cm^{-1}

This equation has the properties that:

- as either F_{BV} or X_o approaches 0 the density of the residue approaches the density of the initial oil;
- as the power of the exponential increases the density ratio increases, rapidly at first but more slowly as the power increases. This seems reasonable for an imperfect EFV process, each increment of heavy ends added to the remaining slick would result in a progressively smaller increase in the density of the remaining slick;
- the density ratio tends to a maximum value on the order of 1.20 for crudes and 1.07 for diesel (this value may be oil-type controlled).

The fit of equation 3 to the data is illustrated in Figure 6. The results of the chemical analyses may allow additional oil-related factors to be incorporated into Equation 3. Further tests will be required to determine any scaling factors (i.e., burn diameter).

Several of the oils appear to produce residues with densities and density ratios that reach a maximum, then decline. Specifically these are Arabian Heavy, ANS and Mayan. It is believed that this may be due to the onset of a long vigorous burn phase during the test with these oils. The 15 cm thick burn of Arab Heavy experienced a 10 minute vigorous

Figure 5 — Correlation of Density Ratio

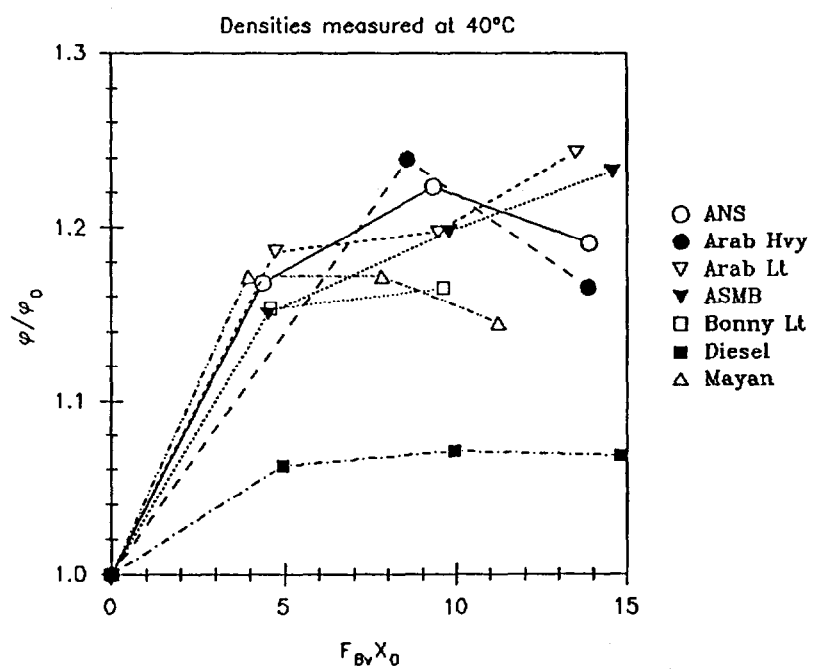
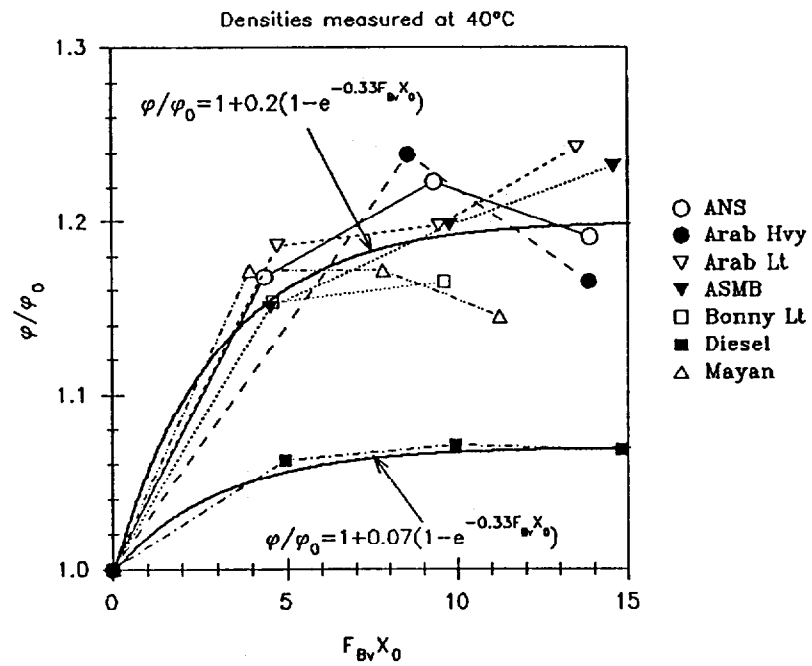


Figure 6 — Comparison of Model with Data



burn phase, as opposed to 3 to 4 minutes for the 5 and 10 cm burns. Likewise the 15 cm ANS burn involved a 5 minute vigorous burn phase in comparison with 1 to 2 minutes for the 5 and 10 cm burns. All three thicknesses of Mayan crude burned involved vigorous burn phases with durations of 6 to 7 minutes. The remainder of the oils had vigorous burn phases that did not increase dramatically with increasing thicknesses and were in the 1 to 3 minute range. The combustion process during the vigorous burn phase is fundamentally different than during steady burning; the vigorous burn phase involves droplets of liquid oil being propelled into the combustion zone above the slick where they vaporize and burn completely. This atomization process would not involve concentration of heavy ends in the remaining slick, but would be a true EFV. This would mean that the early onset of a vigorous burn phase would result in a burn residue with a lower density than would otherwise be expected. It should be noted that the vigorous burn phase is likely an artifact of the test apparatus; this phenomena may not occur at sea.

Guenette et al. (1994) present the following equations for the increase in density for burn residues of Statfjord and ANS crude.

$$\rho = 0.908 + 0.03 F_{BV} [\text{g/cm}^3] \text{ for Statfjord crude} \quad (4)$$

$$\rho = 0.942 + 0.03 F_{BV} [\text{g/cm}^3] \text{ for ANS crude} \quad (5)$$

Although based on a statistical analysis of residue densities from 0.5, 1 and 2 cm thick burns, these correlations do not appear to adequately represent situations beyond these bounds. For example, the density at 15°C of the ANS crude used in their experiments was 0.878 g/cm³ whereas equation 5, with $F_{BV}=0$ would predict a density of 0.942 g/cm³. It is also clear that, for thick slicks of ANS crude, it is possible for the burn residue density to exceed 1.025 g/cm³, whereas the maximum predicted density from equation 5 is 0.972 g/cm³. It is interesting to note that this maximum predicted residue density, divided by their reported fresh oil density gives a ratio of 1.1, which is almost identical to the value predicted by Equation 3 for a 95% efficiency burn of a 2 cm thick slick of crude oil.

Figure 7 shows the density ratios measured at 15°C as a function of $F_{BV}X_o$. The anomalous behavior of the Bonny Light crude is again apparent. It is not clear why this crude behaves differently than the others; the results of the chemical analyses yet to be completed may shed some light on this.

For the other oils plotted on Figure 7, comparison with Figure 6 shows that the use of a density ratio adequately deals with measurement temperature effects; that is to say that the trend in the data and the model prediction (equation 3) do not appear to be a strong function of the temperature at which the two densities are measured.

Figure 8 shows the effect of evaporation of the oil prior to burning on the density ratio. Considering the data scatter in Figure 7, no conclusions can be drawn; however, it appears that increased evaporation may cause a slight reduction in burn density ratio. Again, the results of the chemical analyses may shed further light on this aspect of the study. In the end it may prove to be oil-type related.

Summary

The preliminary results of this study indicate that residues from thick, batch-type in-situ burns of heavier crudes will sink. It is believed that the vaporization of the liquid

Figure 7 — Density Ratio at 15°C

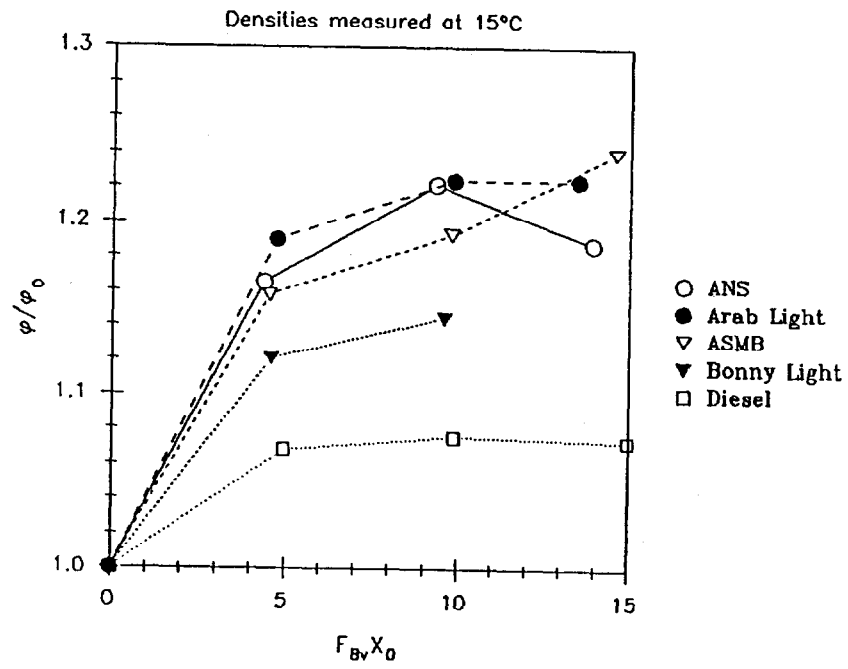
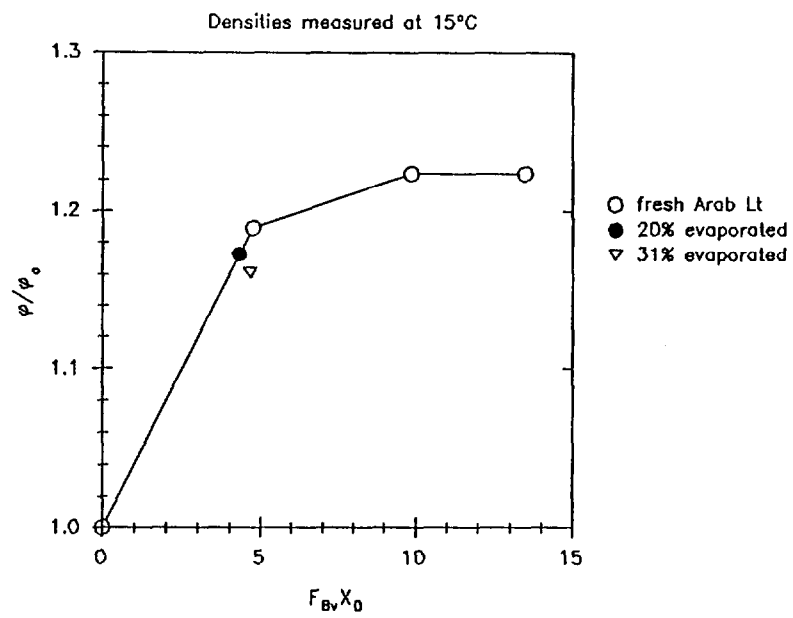


Figure 8 – Effect of Evaporation on Density Ratio



slick beneath the fire is an imperfect Equilibrium Flash Vaporization that concentrates high molecular weight compounds in the remaining slick. This causes a progressive increase in the density of the residue. The ratio of the density of the residue to that of the original oil appears to correlate with the amount of slick burned, represented by the product of the volume fraction burned and the initial slick thickness. A preliminary mathematical model has been proposed to represent the data. The effect of evaporation of the initial oil is to result in a more dense burn residue. It is not certain that evaporation causes a discernable effect on the density ratio.

It also appears that the burn process occurring in a situation where fresh oil is continuously fed into a fire is different than the batch process modelled in this study and results in a less dense residue.

The analysis of the chemistry of the burn residues and its relationship to the original oil is ongoing. It is believed that the results of the chemical analyses will shed further light on the processes causing burn residue property changes.

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