

# LABORATORY STUDIES OF THE PROPERTIES OF IN-SITU BURN RESIDUES

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**ABSTRACT:** This study investigated the physical and chemical properties of the residue from in-situ burns of thick oil slicks. It involved burning small-diameter slicks of oil on water and analyzing the properties of the residues. The objective of the work was to identify the burn conditions that might produce residues that sink.

Eight oils were selected for the project: (1) Alaska North Slope crude; (2) Alberta Sweet Mixed Blend crude; (3) Arabian Heavy crude; (4) Arabian Light crude; (5) Bonny Light crude; (6) Iranian Heavy crude; (7) Mayan crude; and (8) automotive diesel. Burn tests were conducted on all eight oils when fresh and on two of the oils when weathered. Experiments involved burning slicks of three thicknesses (5, 10, and 15 cm) on saltwater at room temperature (15°C). Residue density, water content, pour point, and viscosity were measured. Samples of parent oils and burn residues were fractionated into three boiling point ranges, and each was analyzed to quantify total saturates, aromatics, resins, and asphaltenes.

The results showed that the residues from burns of thicker slicks of heavier crudes and weathered crudes may sink in fresh water or saltwater once they cool to ambient temperatures, whereas burn residues of lighter oils may not sink. Burn residues of all crudes were more dense than their parent oils and were solid or semisolid. Residue density was related to the density of the parent oil, the state of weathering, and slick thickness.

Chemical analysis showed that the burn residues were composed almost exclusively of the higher boiling point (HBP) fraction; virtually all of the lower boiling point fraction and almost all of the middle boiling point fraction had been removed. Most, but not all, of the HBP fraction, which included all of the asphaltenes and resins, was preserved in the burn residue. The in-situ burning process appears to be neither a pure equilibrium flash vaporization nor a pure batch distillation, but rather a process lying somewhere between the two ideals.

The results of the burns of automotive diesel contrasted strongly with those of crude oils. Diesel burns were far more efficient than those of crude oils, leaving only a few millimeters of residue regardless of the thickness of the original slick. The chemical composition of the residue and its properties were changed only slightly from those of the parent oil.

burning has been the fate, properties, and potential impacts of the residue that remains after a burn has extinguished. One key question has been whether the residue would sink. Studies of residues from experimental burns (Energetex, 1977, 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 sink, even in fresh water. On the other hand, 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, in particular its density. Eight oils were selected for the project. These were representative of (1) oils shipped by sea in North American waters; (2) oils that have been involved in tank ship fires that resulted in the residue sinking; or (3) oils that were used in recent in-situ burning field research studies.

## Methods

The experimental methods employed here are described in detail elsewhere (Buist *et al.*, 1995a, 1995b; Trudel *et al.*, 1995). Only a summary is presented here. The eight oils selected for the project were (1) Alaska North Slope (ANS) crude; (2) Alberta Sweet Mixed Blend (ASMB) crude; (3) Arabian Heavy crude; (4) Arabian Light crude; (5) Bonny Light crude; (6) Iranian Heavy crude; (7) Mayan crude; and (8) automotive diesel. Two of these, Arabian Light and Mayan, were artificially weathered by air sparging to two degrees of evaporation. The physical properties of the oils are given in Table 1.

The burns were conducted in a water-filled circular steel pan. Measured amounts of the test oils were contained within a 40-cm-diameter, 20-cm-high metal ring in the center of the pan. The initial oil height was adjusted 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. Samples of the fresh and weathered oils were tested for their density, dynamic viscosity, oil/seawater and oil/air interfacial tensions, pour point, flashpoint, and water content.

All fresh crude oils, weathered crude oils, and burn residues were chemically characterized using common methods to provide (1) the

Research on the use of in-situ burning as a marine oil spill countermeasure has resulted in a rapidly growing acceptance of the technique as an option for spill cleanup. However, one area of concern with in-situ

Table 1. Physical properties of fresh (unburned) oils

	Oil density (g/cm <sup>3</sup> C)		Interfacial tension (mN/m)		Pour point (°C)	Flashpoint (°C)	Water content (% wt/wt)
	@ 15°C	@ 40°C	Oil/water	Oil/air			
Diesel	0.823	0.819	12.7	30.1	< -9	44	0.114
ASMB	0.851	0.844	11.4	32.2	< -9	< 10	0.336
Bonny Light	0.852	0.842	15	32.1	3	< 6	0.080
Arabian Light	0.870	0.860	17	31.6	< -12	< 7	0.430
Arabian Light, 20%	0.908	0.899	16.6	32.5	-3	< 9	0.093
Arabian Light, 31%	0.926	0.912	14.8	35.8	3	9	0.104
Iranian Heavy	0.871	0.862	20.8	31.3	< -9	< 8	0.169
ANS	0.880	0.873	17.6	32.7	< -9	< 7	0.080
Arabian Heavy	0.886	0.875	28.6	32.5	< -9	45	0.103
Mayan	0.930	0.925	23.1	34.8	< -9	< 6	0.301
Mayan, 12%	0.952	0.942	16.6	33.9	-6	< 6	0.088
Mayan, 22%	0.975	0.958	No data	No data	9	30	0.144

composition of each in terms of the proportion of constituents in each of the boiling ranges as follows: initial boiling point (IBP) to 204°C, 204°C to 538°C, and greater than 538°C; and (2) chemical composition in terms of total saturates, total aromatics, total resins, and total asphaltenes in each boiling point range.

## Results and discussion

**Physical properties of the burn residues.** Table 2 lists the oil and residue masses and burn efficiencies calculated for the test burns. The highest efficiency was consistently achieved with the diesel burns, the residue from which was equivalent to a slick less than 1 mm thick for all three initial thicknesses. Burns of all other oils resulted in residue amounts equivalent to thicknesses greater than 2 mm. These results are consistent with those of earlier studies (Buist *et al.*, 1994). The least efficient burns involved Mayan crude and Arabian Heavy crude, the oils with the highest densities. Weathering of the oils appeared to decrease burn efficiency slightly, an effect that has been noted before (Bech *et al.*, 1992). This trend in the data 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 relatively early in the test, about 25 minutes after ignition. Examination of the temperature readings in the slick indicated that abnormal convective heat transfer was occurring. The viscosity data in Table 1 indicate that the Bonny Light has an unusu-

ally 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 from the other crudes.

Table 3 shows the densities of the burn residues at 15°C and 40°C. Samples with values denoted as >1.100 at 15°C (>1.086 at 40°C) exceeded test range. In general, densities of the burn residues increased with those of the parent oils for the 5-cm-thick slicks, but this relationship is far less clear for the 15-cm-thick slicks. It is worthy of note that none of the residues sank until the burn had extinguished and the residue had cooled. 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 semisolid not unlike cold roofing tar.

**Residue density increase.** Figure 1 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 (1.000 g/cm<sup>3</sup>) and normal seawater (1.025 g/cm<sup>3</sup>). It is clear that efficient burning of thick slicks significantly increases 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.

The results of the present study are consistent with those of Buist *et al.* (1995a), who reported that residue from a test burn of a

Table 2. Summary of burn efficiency data

Oil type	5-cm-thick slick			10-cm-thick slick			15-cm-thick slick		
	Oil mass (kg)		Burn efficiency (mass %)	Oil mass (kg)		Burn efficiency (mass %)	Oil mass (kg)		Burn efficiency (mass %)
	Initial	Final		Initial	Final		Initial	Final	
Diesel	5.35	0.07	98.6	10.70	0.07	99.3	16.05	0.05	99.7
ASMB	5.76	0.66	88.5	11.25	0.30	97.3	16.31	0.59	96.4
Bonny Light	5.54	0.53	90.4	11.08	0.52	95.3	16.61	( <sup>1</sup> )	( <sup>1</sup> )
Arabian Light	5.44	0.35	93.5	11.00	0.21	98.1	15.95	1.98	87.6
Arabian Light, 20%	5.99	0.96	84.0						
Arabian Light, 31%	6.12	0.48	92.2						
Iranian Heavy	5.51	0.34	93.8						
ANS	5.72	0.86	84.9	9.68	0.96	91.6	16.68	1.51	90.9
Arabian Heavy	3.65	0.91	75.2	10.97	1.95	82.3	16.94	3.00	90.9
Mayan	6.05	1.51	75.1	11.55	2.97	74.3	17.41	5.04	71.1
Mayan, 12 %	6.40	1.78	72.2						
Mayan, 22 %	6.20	1.84	70.3						

1. Early boilover resulted in unreliable data.

Table 3. Densities of oils and burn residues

Oil type	Density at 15°C (g/cm <sup>3</sup> )				Density at 40°C (g/cm <sup>3</sup> )			
	Fresh oil	5-cm burn	10-cm burn	15-cm burn	Fresh oil	5-cm burn	10-cm burn	15-cm burn?
Diesel	0.823	0.879	0.885	0.883	0.819	0.870	0.877	0.875
ASMB	0.851	0.985	1.015	1.055	0.844	0.971	1.011	1.040
Bonny Light	0.852	0.955	0.975	0.873 <sub>1</sub>	0.842	0.971	0.981	0.865 <sub>1</sub>
Arabian Light	0.870	1.035	1.065	1.065	0.860	1.020	1.030	1.069
Arabian Light, 20%	0.908	1.065			0.899	1.050		
Arabian Light, 31%	0.926	1.075			0.912	1.069		
Iranian Heavy	0.871	1.055			0.862	1.030		
ANS	0.880	1.025	1.075	1.045	0.873	1.020	1.068	1.040
Arabian Heavy	0.886	>1.100	>1.100	>1.100	0.875	>1.100	>1.100	>1.100
Mayan	0.930	>1.100	>1.100	>1.100	0.925	>1.100	>1.100	>1.100
Mayan, 12%	0.952	>1.100			0.942	>1.086		
Mayan, 22%	0.975	>1.100			0.958	>1.086		

1. Early boilover resulted in unreliable data.

17.5-cm-thick slick of fresh ANS crude sank in both saltwater and fresh water after it cooled. The data from the burns of ANS in the present study, shown in Figure 1, indicate that the density of the residue from the 10- and 15-cm burns of ANS crude exceeded 1.025 g/cm<sup>3</sup> at 15°C and would therefore also sink in both fresh water and saltwater. The results of the tests with ASMB in the present study are not consistent with those of Fingas *et al.* (1995). They reported that the residue from a burn of ASMB during the NOBE offshore experiment had a density of 0.936 g/cm<sup>3</sup>, far lower than the densities of 0.985 to 1.055 g/cm<sup>3</sup> observed here. This inconsistency may be 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 saltwater. After a spill of some 2000 tons of Arabian Heavy crude from the *M/T Honam Jade*, a cleanup contractor ignited the main slick, which burned for 2 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 seawater.

Figure 2 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. The residue density data at 40°C in Table 3 show that the same trend appears to have occurred for the evaporated Mayan crude.

**Chemical composition of oils and residues.** The residues of all burns contained solid materials (at 163°C) except for those of diesel and Bonny Light crude oils. The amounts of solids present ranged from 0.5% to 34.0% of the total weight of residue. There did not appear to be any apparent correlation between the amount of solid material and any of the experimental parameters. The composition of the solid materials was not determined. They could be (1) very-high-molecular-weight hydrocarbons precipitated out of the oil as a result of the combustion process or (2) ash or soot from the combustion zone that had fallen back into the liquid oil during the burning process.

The composition of the unburned oils and burn residues, in terms of boiling point fractions, is given in Table 4. The data show that none of the residues of any of the crude oil burns, regardless of slick thickness, contained any of the lower boiling point fractions (IBP to 204°C). Since the lower boiling point fraction is a common constituent of all of the

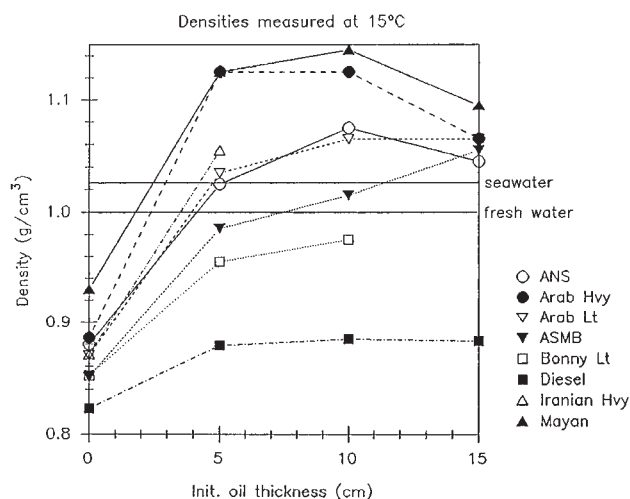


Figure 1. Residue density

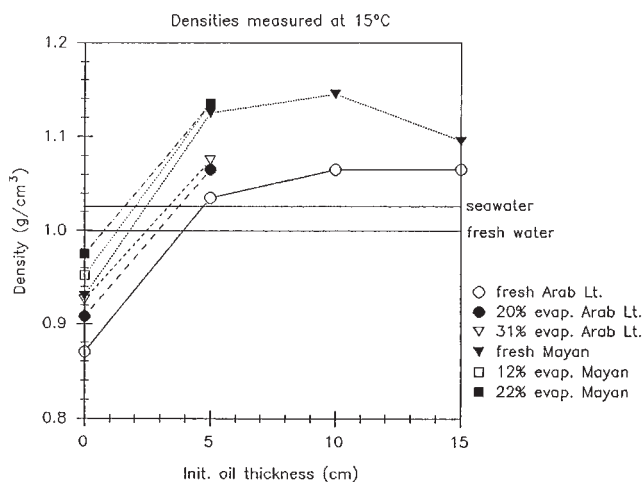


Figure 2. Effect of evaporation on residue density

Table 4. Percent composition of unburned oils and burned residues by boiling point fraction

Oil type	Treatment	Weight of residue	Composition (weight%)		
			IBP to 204°C	204°C to 538°C	>538°C
Diesel	Fresh oil	—	18.3	81.7	0
	5-cm burn	—	1.4	98.6	0
	10-cm burn	—	1.8	98.2	0
	15-cm burn	—	4.4	95.6	0
ASMB <sub>1</sub>	Fresh oil	—	21.8	63.6	14.5
	5-cm burn	—	0	25.7	74.3
	10-cm burn	—	0	7.6	92.4
	15-cm burn	—	0	4.0	95.9
Bonny Light	Fresh oil	—	20.6	71.8	7.6
	5-cm burn	—	0	41.5	58.5
	10-cm burn	—	0	14.7	85.3
	15-cm burn	—	No data	No data	No data
Arabian Light	Fresh oil	—	18.6	55.4	26.1
	5-cm burn	—	0	9.2	90.8
	10-cm burn	—	0	5.3	94.7
	15-cm burn	—	0	6.5	93.5
Iranian Heavy	Fresh oil	—	20.9	52.2	26.9
	5-cm burn	—	0	13.1	86.9
ANS	Fresh Oil	—	17.2	57.2	25.02
	5-cm burn	—	0	9.6	90.4
	10-cm burn	—	0	6.3	93.7
	15-cm burn	—	0	8.7	91.2
Arabian Heavy	Fresh oil	—	15.6	49.9	34.5
	5-cm burn	—	0	9.3	90.7
	10-cm burn	—	0	8.2	91.8
	15-cm burn	—	0	8.7	91.3
Mayan	Fresh oil	—	14.2	45.6	40.2
	5-cm burn	—	0	9.0	91.0
	10-cm burn	—	0	14.1	85.9
	15-cm burn	—	0	13.1	86.9
Arab Light	Fresh oil	—	18.6	55.4	26.1
	5-cm burn	—	0	9.2	90.8
Arab Light (20% evap.)	Unburned oil	—	9.1	61.5	29.5
	5-cm burn	—	0	5.4	94.6
Arab Light (31% evap.)	Unburned oil	—	2.0	64.8	33.2
	5-cm burn	—	0	8.8	91.3
Mayan	Fresh oil	—	14.2	45.6	40.2
	5-cm burn	—	0	9.0	91.0
Mayan (12% evap.)	Unburned oil	—	7.4	49.3	43.3
	5-cm burn	—	0	6.5	93.5
Mayan (22% evap.)	Unburned oil	—	0	50.2	49.8
	5-cm burn	—	0	3.2	96.8

1. Alberta Sweet Mixed Blend

unburned crude oils, this fraction is clearly completely consumed from the crude oils during burning. All of the burn residues of crude oils did contain some quantity of the middle boiling point fraction. Despite the fact that this fraction made up a major proportion, if not the majority, of the fresh oil, it made up only a small fraction of the residue from most burns. This indicates that this fraction, too, was preferentially consumed during burning. The largest proportion of each residue of most crude oils was made up of heavy ends (the high boiling point fraction). This fraction made up 7% to 40% of the fresh oil, but this increased to 75% to over 90% in the burn residue, indicating selective concentration of these heavy ends in the oil during burning. These results indicate that, in these studies, burning is an imperfect equilibrium flash vaporization.

In order to better understand the composition of the residue and the changes that take place as a result of in-situ burning, Tables 5, 6, and 7 were prepared. Tables 5 and 6 illustrate the changes in amounts of the different boiling point fractions and major chemical groups (saturates, aromatics, resins, and asphaltenes) in the parent oils and residues during the burns of two example oils, ASMB and Arabian Heavy crude oil, respectively. Data are based on 100 grams of oil burned. Data for all eight oils burned are presented in Buist *et al.* (1995b). Table 7 illustrates

the changes in relative abundances of the various fractions of diesel fuel oil and diesel burn residue. In Tables 5 and 6, note the results for the fraction "538°C+." These data show that, although the constituents of this group are diminished in the residues, they are diminished to a far lesser degree than were the lower boiling point fractions. The data from the burns of Alberta Sweet Mixed Blend, given in Table 5, show that the asphaltene fraction was almost completely preserved in the residue after the burns. This preservation of the asphaltene fraction was common in burns of many of the other fresh and weathered crude oils. This lends further credence to the imperfect EFV theory: that the heaviest compounds are concentrated in the residue and not burned. The fact that the burn residues of crude oils are composed largely of asphaltenes, high-boiling-point aromatics, resins, and solid material (at 163°C) accounts for their semisolid rheology at ambient temperatures.

Table 7 presents the results of the chemical analyses of the parent oil and burn residues of diesel fuel. The residues contained no solids and, like the unburned diesel fuel, the residues contained no higher boiling point fraction (538°C+ fraction). Unlike residues from the crude oil burn, residues from diesel burns did contain some volatiles (IBP to 204°C boiling point fraction). Unlike the crude oils, the diesel residues

**Table 5. Mass balance data for Alberta Sweet Mixed Blend Crude oil**

Based on 100 g of crude oil burned	Crude	5-cm burn	10-cm burn	15-cm burn
Weight of residue (g)		11.5	2.7	3.6
Weight of solid residue (g)		0.07	0.46	1.22
Weight of liquid residue (g)		11.42	2.23	2.37
Weight of IBP–204°C cut (g)	21.87	0.00	0.00	0.00
Weight of 204–538°C cut (g)	63.65	2.93	0.16	0.095
Weight of 538°C+ cut (g)	14.48	8.49	2.06	2.27
	@15°C/@40°C			
Amount of saturates in IBP–204°C (mL)	22.10/22.28	0.00	0.00	0.00
Amount of olefins in IBP–204°C (mL)	0.20/0.20	0.00	0.00	0.00
Amount of aromatics in IBP–204°C (mL)	3.39/3.42	0.00	0.00	0.00
Weight of saturates in 204–538°C (g)	42.56	1.51	0.07	0.04
Weight of aromatics in 204–538°C (g)	19.46	1.30	0.08	0.04
Weight of polar aromatics in 204–538°C (g)	1.61	0.11	0.00	0.00
Weight of saturates in 538°C+ (g)	3.89	1.86	0.23	0.21
Weight of aromatics in 538°C+ (g)	6.83	4.22	0.79	0.81
Weight of resins in 538°C+ (g)	2.13	1.20	0.21	0.20
Weight of asphaltenes in 538°C+ (g)	1.61	1.20	0.82	1.04
Total saturates (g)		3.38	0.31	0.26
Total olefins (g)		0.00	0.00	0.00
Total aromatics (g)		5.52	0.87	0.85
Total polar aromatics (g)		0.11	0.00	0.00
Total resins (g)		1.20	0.21	0.20
Total asphaltenes (g)		1.20	0.82	1.04
Composition of liquid residue				
Saturates (wt %)		29.58	13.94	11.10
Olefins (wt %)		0.00	0.00	0.00
Aromatics (wt %)		48.34	39.25	36.19
Polar aromatics (wt %)		1.02	0.36	0.14
Resins (wt %)		10.51	9.70	8.46
Asphaltenes (wt %)		10.51	36.72	44.08

**Table 6. Mass balance data for Arabian Heavy Crude**

Based on 100 g of crude oil burned	Crude	5-cm burn	10-cm burn	15-cm burn
Weight of residue (g)		24.8	17.7	9.1
Weight of solid residue (g)		2.33	0.08	1.19
Weight of liquid residue (g)		22.46	17.61	7.90
Weight of IBP–204°C cut (g)	15.62	0.00	0.00	0.00
Weight of 204–538°C cut (g)	49.88	2.07	1.44	0.68
Weight of 538°C+ cut (g)	34.50	20.38	16.16	7.21
	@15°C/@40°C			
Amount of saturates in IBP–204°C (mL)	16.53/16.74	0.00	0.00	0.00
Amount of olefins in IBP–204°C (mL)	0.00/0.00	0.00	0.00	0.00
Amount of aromatics in IBP–204°C (mL)	1.09/1.10	0.00	0.00	0.00
Weight of saturates in 204–538°C (g)	28.04	0.75	0.51	0.24
Weight of aromatics in 204–538°C (g)	20.97	1.25	0.87	0.40
Weight of polar aromatics in 204–538°C (g)	0.85	0.06	0.04	0.03
Weight of saturates in 538°C+ (g)	3.78	1.26	1.02	0.60
Weight of aromatics in 538°C+ (g)	18.15	8.12	6.51	3.03
Weight of resins in 538°C+ (g)	3.88	1.66	1.94	0.74
Weight of asphaltenes in 538°C+ (g)	8.67	9.33	6.67	2.83
Total saturates (g)		2.01	1.54	0.85
Total aromatics (g)		9.38	7.39	3.44
Total polar aromatics (g)		0.06	0.04	0.03
Total resins (g)		1.66	1.94	0.74
Total asphaltenes (g)		9.33	6.67	2.83
Composition of liquid residue				
Saturates (wt%)		8.98	8.77	10.81
Aromatics (wt%)		41.76	42.00	43.56
Polar aromatics (wt%)		0.28	0.26	0.40
Resins (wt%)		7.41	11.06	9.38
Asphaltenes (wt%)		41.54	37.88	35.83

Table 7. Chemical composition data for diesel

	Diesel			
	Crude	5-cm burn	10-cm burn	15-cm burn
Burn Efficiency (%)		98.60	99.30	99.70
Percent Solid (wt%)		0.00	0.00	0.00
Yield by ASTM D-1160 (wt%)				
IBP–204°C	18.30	1.35	1.80	4.38
204–538°C	81.70	98.65	98.20	95.62
538°C+	0.00	0.00	0.00	0.00
<b>Total</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>
Max. distillation temp. (°C)	400+	400+	400+	400+
FIA-ASTM D-1319 (IBP 204°C)				
Saturates (LV %)	81.20			
Olefins (LV %)	0.50			
Aromatics (LV %)	18.30			
<b>Total (LV %)</b>	<b>100.00</b>			
BSG-ASTM D-2549 (204–538°C)				
Saturates (wt%)	70.41	64.09	63.30	62.17
Aromatics (wt%)	29.04	34.70	35.17	36.21
Polar aromatics (wt%)	0.55	1.21	1.53	1.62
<b>Total (wt%)</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>

foamed during the fractional distillation phase of the chemical analysis, thus preventing the separation of the low boiling point fraction from the middle boiling point fraction. Since the residue could not be fractionated, (1) the IBP to 204°C fraction was quantified using a simulated distillation procedure (ASTM D-2887); and (2) the saturate/aromatic content of the residue was determined from the residue as a whole by the BSG-ASTM D2549 procedure. The composition of the residue samples, other than the loss of the small volatile fraction, is very similar to that of the fresh diesel. The complete lack of nonvolatile components in the residue samples explains their low viscosity at ambient temperatures. None of the samples contained solid materials. Since most of the crude residue samples contained solids, it appears that these materials are probably precipitates from the heavy ends of the crude as opposed to ash or salt crystals.

The data provide some insight into the effect of slick thickness on the relationship between the specific gravity of the parent oil and that of the burn residue. In general, increasing slick thickness leads to an increase in residue density. However, for the heavier oils, this relationship between residue density and slick thickness held only for the thinner slicks. In slicks greater than 10 cm in thickness, the residue density declined with increasing slick thickness. In all burns of thicker crude oil slicks, the residues were composed almost totally of the high boiling point fraction, made up to a large extent of asphaltenes. However, the residues from the thinner slicks of the lighter crudes contained much greater proportions of the lighter, middle-boiling-point-range compounds, which would explain the lower densities of these residues. Unfortunately, the present results do little to explain why the specific gravities of residues of heavier oil decrease with increasing slick thickness for the thicker slicks.

The burns conducted using weathered Arabian Light and Mayan crude oils, reported in Buist *et al.* (1995b), showed that densities of burn residues of weathered oils were greater than those of the fresh oils. The chemical analyses of the unburned oils and residues (see Table 1) show that artificial "weathering" selectively depletes the lower boiling point fraction of these oils. As was the case with fresh crudes, burning completely depletes the lower boiling point fraction of weathered oils and greatly diminishes the concentration of the middle boiling point fraction. In general, in the burn residues of "weathered" oils, the middle boiling point fraction is more greatly depleted than in the burn residues of the fresh oil. This is consistent with the greater densities of the burn residues of the "weathered" oils.

**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:

$$\rho/\rho_0 = f(F_{BV}X_0) \quad (1)$$

Where:  $\rho, \rho_0$  = the residue and initial oil density, respectively (g/cm<sup>3</sup>)  
 $F_{BV}$  = volumetric fraction of oil burned  
 $X_0$  = initial oil thickness (cm)

The term  $F_{BV}X_0$  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:

$$(1 - F_{BV}) = (1 - F_{BM}) \rho_0/\rho \quad (2)$$

Figure 3 shows a plot of the ratio of residue density to fresh oil density as a function of  $F_{BV}X_0$ . This graph uses the densities at 40°C since there are fewer over-range data points at this temperature than at 15°C. It

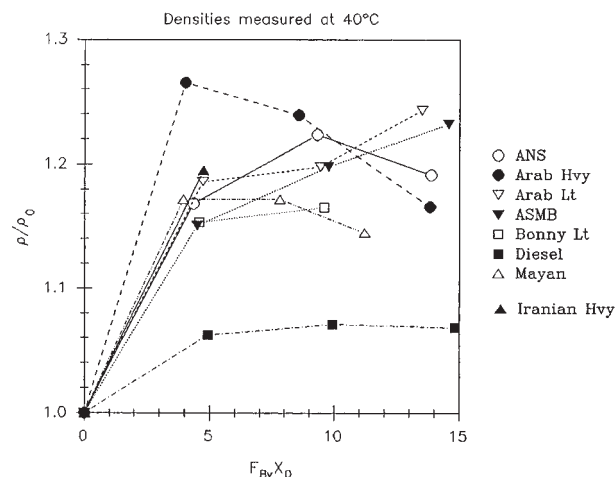


Figure 3. Correlation of residue density



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 3 is that the data for the crude oils are generally grouped around a common trend, whereas 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 appear to fit an equation of the form

$$\rho/\rho_0 = 1 + C_1[1 - \exp(-C_2 F_{BV} X_0)] \quad (3)$$

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 [ $\text{cm}^{-1}$ ], which appears to have a value in the range of  $0.33 \text{ cm}^{-1}$

This equation has the properties that (1) as either  $F_{BV}$  or  $X_0$  approaches 0 the density of the residue approaches the density of the initial oil; and (2) 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. Hence 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 4. 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).

As mentioned in text preceding, several of the oils appear to produce residues with densities and density ratios that reach a maximum and 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 combustion process during the vigorous burn phase is fundamentally different from 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 the 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 phenomenon may not occur at sea.

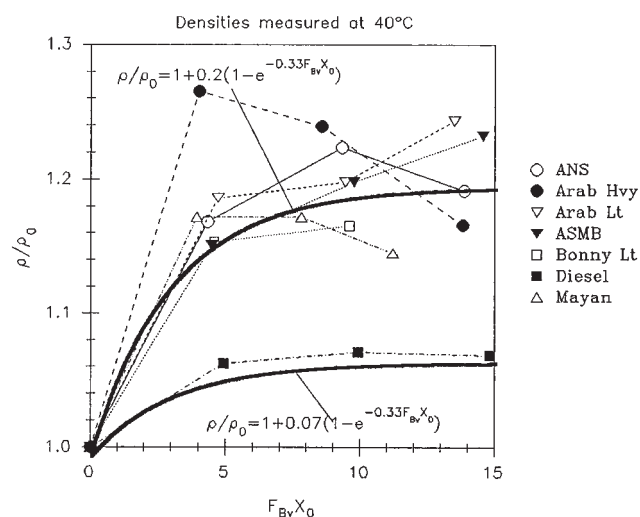


Figure 4. Comparison of model with data

## Summary

The 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 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 denser burn residue. It is not certain that evaporation causes a discernible effect on the density ratio. The process explains the semisolid or near-solid rheology of the residue.

Samples of the residues from most of the crude oil burn tests contained significant amounts of solids (at  $163^\circ\text{C}$ ). The source of this solid material may be precipitation of very heavy ends of the crude as a result of the concentration process occurring during the imperfect equilibrium flash vaporization. The only residue samples that did not contain solids were from the diesel and Bonny Light burns.

None of the burn residues from crude oils contained any volatiles (with boiling points up to  $204^\circ\text{C}$  or approximately  $C_{12}$ ); all contained some portion of the medium volatility compounds (boiling points between  $204^\circ\text{C}$  and  $538^\circ\text{C}$ ). The majority of the residues were composed of nonvolatile compounds with boiling points greater than  $538^\circ\text{C}$ . For most of the crudes, the asphaltenes and high-boiling-point (HBP) aromatics appeared to be preserved and concentrated into the burn residue. Asphaltenes, HBP aromatics, and resins were the main components of most crude burn residue samples, and this, in conjunction with the high solids content of these same residue samples, is believed to be responsible for the semisolid and near-solid rheology of the residues at ambient temperatures, as observed in Buist *et al.* (1995b).

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