

**Laboratory Testing to Determine  
*In Situ* Burning Parameters  
for Six Additional U.S. OCS Crude Oils**

**Prepared for the**

**United States Department of the Interior  
Minerals Management Service  
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## EXECUTIVE SUMMARY

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The Minerals Management Service (MMS) continued a laboratory test program, started in 1997, to determine the following parameters with respect to the *in situ* burning of six additional U.S. Outer Continental Shelf (OCS) crude oils:

- The evaporation behavior under different environmental conditions
- The limits to ignition using gelled gasoline igniters imposed by evaporation and emulsification
- The ability of commercially-available emulsion breakers and alternative fuel igniters to extend the window-of-opportunity for ignition of stable emulsions
- The effects of wave action on the combustion of emulsion slicks
- The likelihood of the residues sinking after efficient burns of thick slicks of the crude oils

Before oil spill response plans are developed or approved, it is important to understand the physical behavior of the spilled oil and how it changes over time. The *Catalog of Crude Oil and Oil Products Properties*, jointly funded by MMS and Environment Canada, contains the physical and chemical data of over 380 different types of oils, including some information on dispersibility. This research project is intended to provide additional data that should be considered when developing oil spill response plans. For these six OCS crude oils, we now have the information required to make an informed decision regarding the *window of opportunity* for various response options and can coordinate a multi-approach response involving burning, dispersing and skimming.

A summary of the results of the tests is presented on the following page.



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- D.C. Brieland of Chevron Pipeline, who provided the South Pass Crude Oil
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# 1. INTRODUCTION

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*In situ* burning offers the potential to quickly and efficiently remove large quantities of oil, and can be an effective countermeasure during a spill cleanup. Unfortunately, spills at sea are subject to evaporation and emulsification, which can quickly lead to a spilled oil becoming unignitable and end the possibility of a successful *in situ* burn.

Recently, research has focused on extending the window-of-opportunity for *in situ* burning by developing more powerful igniters, and investigating the use of chemical surfactants that break water-in-oil emulsions (SL Ross 1995, Guénette et al. 1994). Bech et al. (1993) concluded that the burning process for water-in-oil emulsions is much more complex than for water-free oil.

Success at breaking and burning depends on oil-specific factors (Strøm-Kristiansen et al. 1995) and cannot necessarily be predicted based on an oil's physical properties. These findings were supported by the results of the previous MMS *in situ* burning study: in some cases oils from the same geographic area, with similar physical properties, behaved quite differently with regards to *in situ* burning (SL Ross 1998).

In light of this dependency on oil properties, it is vital that specific oils be tested to determine the suitability of *in situ* burning as a response for each. Data for each oil must be collected on the effects of oil evaporation and emulsion formation on ignitability, burn rate and oil removal efficiency, and the potential for emulsion breakers to extend the window-of-opportunity. Burn tests should be conducted with each selected oil in a range of conditions and with a variety of commercial chemical surfactant products.

Another concern that must be addressed is the fate of the residue from a successful *in situ* burn, specifically whether it would be buoyant. Recent experiences that involved accidental burning on the sea of large volumes of heavy crude oils during actual spills (Moller 1992, Turbini et al. 1993) and recent large-scale experiments involving thick slicks of moderately heavy oil (Buist et al. 1995) have shown that some burn residues may sink. Clearly, the propensity of the burn residue of an oil to sink should be determined prior to implementing an *in situ* burn.

The most likely source of oil spills in the Gulf of Mexico is not oil spilled from a single geologic field, such as would be the case during a blowout, but commingled oil from several different fields from a pipeline. Once developed, oil produced from one well is transported to a central facility, where it is often mixed (commingled) with other oils produced from other geologic reservoirs of similar properties. The oil is then either stored offshore until transferred to a tanker, or piped to shore through large pipeline systems. The physical and chemical properties of the oils in these systems may vary slightly, but is controlled by the shore terminal chemist; different pipeline systems carry oils of different chemistry.

The Gulf of Mexico and Pacific Regional offices of the Minerals Management Services selected six U.S. Outer Continental Shelf (OCS) crude oils and subjected them to a laboratory test program. Several of the oils selected are commingled pipeline oils. These oils are identified by the pipeline system number and the terminal receiving the commingled oil. Crude oils

representative of a specific geologic reservoir are identified by the API well numbers and lease area and block where the surface facility is located. The date of collection is also recorded. The oils selected by the Gulf of Mexico region were:

- Pipeline System Number 26 – Gibson, LA Terminal commingled crude oil (commonly called Light Louisiana Sweet crude oil)
- Pipeline System Number MP 225 – Main Pass 69 Terminal commingled crude oil
- Pompano commingled crude oil
- South Pass 49 crude oil
- West Delta 143 commingled crude oil

The oil selected by the Pacific Region was:

- Point Arguello crude oil

The objective of the laboratory test program was to determine the following parameters related to *in situ* burning:

- The evaporation behavior under different environmental conditions
- The limits to ignition using gelled gasoline igniters imposed by evaporation and emulsification
- The ability of commercially-available oil spill emulsion breakers and alternative fuel igniters to extend the window-of-opportunity for ignition of stable emulsions
- The effects of wave action on the combustion of emulsion slicks
- The likelihood of the residues sinking after efficient burns of thick slicks of the crude oils

The laboratory test procedures are described in Section 2 and the results are presented in Sections 3 through 8.

## 2. TEST PROCEDURES

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This section describes the test procedures that were used to evaluate the *in situ* burning related characteristics of the six oils.

### 2.1 EVAPORATION

Evaporation is one of the most significant processes that affects an oil when it is spilled. Evaporation removes the volatile, light hydrocarbons from the crude oil and leaves behind the heavier fractions. From the perspective of *in situ* burning, this results in the oil becoming progressively more difficult to ignite. Although high degrees of evaporation alone will not usually preclude the use of burning, it can when combined with other factors, such as high sea states, high wind or emulsification. To assess the effect of evaporation on the ignition and burning characteristics the oils, each was artificially evaporated under controlled conditions.

#### 2.1.1 WIND TUNNEL

A wind tunnel was used to determine the evaporative characteristics of each oil, and to prepare weathered samples for physical property analysis.

Three 900-mL samples of each oil were withdrawn from the containers they were shipped in. One of these was reserved, while the remaining two were poured into shallow metal trays and placed in a wind tunnel operating at a wind speed of approximately 3 m/s (6.7 mph), and an air temperature of approximately 24°C (75°F). The initial thickness of oil in the trays was 2 cm. One sample was removed from the tunnel after two days, and the second after two weeks. The fresh oil and the weathered samples were analyzed for selected physical properties according to the procedures in Table 2-1.

**Table 2-1:** Test procedures for oil analysis

Property	Test Temperature(s)	Equipment	Procedure
Density	15 and 30°C	Anton Paar Densitometer	ASTM D4052-91
Viscosity	15 and 30°C	Brookfield Viscometer	ASTM D2983-87

Density and viscosity are both important properties that affect the behavior of an oil when it is spilled. Knowing these properties at several degrees of evaporation and temperatures allows one to interpolate values for intermediate conditions. Density is particularly important and is used in several subsequent calculations.

While in the wind tunnel, the mass of oil remaining in the trays was measured and recorded regularly – hourly during the initial, rapid evaporation phase, reducing to daily after the two-day sample was removed. The elapsed time at each measurement, the initial thickness of oil in the tray, and the wind tunnel conditions were used to determine the evaporative exposure (Mackay et al.1983), according to:



$$q = \frac{Kt}{x_o} \quad (1)$$

Where:  $q$  is evaporative exposure  
 $K$  is the mass transfer coefficient (m/s)  
 $t$  is elapsed time (s)  
 $x_o$  is initial slick thickness (m)

Evaporative exposure provides a means of correlating the rate of evaporation of an oil under the conditions in the wind tunnel (i.e., slick thickness and wind speed) to other environmental conditions at a spill site. The mass transfer coefficient,  $K$  in the wind tunnel was determined by calibrating the wind tunnel with a tray of pure toluene during use. For a spill situation, the mass transfer coefficient can be estimated from:

$$K = 0.0025U^{0.78} \quad (2)$$

Where:  $U$  is wind speed [m/s]

For spills at sea, it is notoriously difficult to obtain a slick thickness. As such, an average initial thickness, defined as the volume spilled divided by the area of the slick, is substituted for  $x_o$  in equation 2.

The evaporation was converted from mass evaporated to volume fraction according to:

$$Fv = \frac{m_{initial} / \mathbf{r}_{initial} - m_{final} / \mathbf{r}_{final}}{m_{initial} / \mathbf{r}_{initial}} \quad (3)$$

Where:  $m$  is mass of oil in tray (g)  
 $\mathbf{r}$  is density of oil (g/cm<sup>3</sup>)

A plot of volume fraction evaporated versus evaporative exposure was prepared for each oil using the data from the wind tunnel. Also included in the plot is the evaporation predicted by the Mackay equation under the conditions in the wind tunnel. The equation is given below the plot, and is of the form:

$$Fv = \frac{\ln \left[ 1 + \frac{C_1}{T} q \exp \left( C_2 - \frac{C_3}{T} \right) \right]}{\frac{C_1}{T}} \quad (4)$$

Where:  $Fv$  is volume fraction evaporated  
 $C_1, C_2$  and  $C_3$  are oil-specific constants  
 $T$  is environmental temperature (K)

The constants  $C_1, C_2$  and  $C_3$  were calculated from the wind tunnel evaporation data, and from an ASTM distillation curve of each fresh crude oil. The slope and intercept of the distillation curve are used as a measure of the oil's volatility, which allows evaporation rates at temperatures other than that in the wind tunnel to be predicted.

Equations 1, 2 and 4 can be used to estimate oil evaporation under various spill conditions of temperature, elapsed time and wind speed. As an example of how they can be used, the

evaporative exposure data from the wind tunnel was converted to elapsed time using equations 1 and 2, for the hypothetical situation of a 2-mm thick slick in a 2.5 m/s wind at 24°C. The secondary (upper) x-axis was scaled to display this information. The Mackay curve on the plot applies to only 24°C. If other temperatures are encountered, other curves can be generated using equation 4.

### 2.1.2 SPARGING

Larger quantities of evaporated oil were needed for use in the subsequent burn tests than could be efficiently produced in the wind tunnel. These were prepared by bubbling (also called sparging) compressed air through heated oil in 20-L buckets until the desired amounts had been evaporated.

Weathered samples at two degrees of evaporation were produced. Two degrees of evaporation provided three samples for testing (fresh and two weathered), which allows interpolation for behavior at intermediate conditions. The degrees of evaporation were chosen to give a range of weathering that would be encountered at real spills within achievable response times.

## 2.2 EMULSIFICATION

A key problem that remains with the use of *in situ* burning is the potential for the oil to form a stable water-in-oil (W/O) emulsion. The presence of as little as 25% emulsified water in a slick will usually prevent ignition and burning of the oil. Even if the W/O emulsion is less than fully stable and thus burnable, the presence of water in the oil significantly increases the heat required to ignite it.

### 2.2.1 EMULSION FORMATION-TENDENCY AND STABILITY

The tendency of the oils to form an emulsion and the stability of the resulting emulsion were determined using the rotating flask technique (Zagorski and Mackay, 1982). The test was conducted on both the fresh and weathered samples, at a temperature of 20°C.

The results of the test were used to determine two indicators: the emulsion formation-tendency index, and the emulsion stability index. Both indicators can have three values (see Table 2-2).

**Table 2-2:** Possible results of swirling flask test

Formation-Tendency Index	Emulsion Stability Index
Unlikely to form emulsion	Emulsion very unstable
Moderate tendency to form emulsion	Emulsion moderately stable
High tendency to form emulsion	Emulsion very stable

## **2.2.2 EMULSION BREAKER EFFECTIVENESS**

Chemical surfactants are available that lower the oil-water interfacial tension and promote the coalescence of water droplets in a W/O emulsion. This ideally causes the emulsion to separate. They are commonly used in the crude oil production and refining processes. Their effectiveness is oil-specific and dependent on the properties of the oil.

The effectiveness of three emulsion breaking chemicals (also known as demulsifiers) were tested on 50 % water emulsions made with the weathered crude oil samples:

- Alcopol 0 70% PG (Alcopol)
- Breaxit OEB-9 (Breaxit)
- Vytac-DM (Vytac)

Two dosage ratios of demulsifier to emulsion were used, 1 to 500 and 1 to 5000. The procedure used is detailed in Hokstad et al. (1993) and also involves rotating flasks containing emulsion samples, but in this case with added demulsifiers. In order that the emulsion samples be as homogenous and consistent as possible, they were made by recirculating 3.5 % salt water and oil through a small gear pump. The gear pump technique generally produces emulsions that are more stable than those that form naturally from wave action. The results of the emulsion breaker effectiveness test can therefore be considered as conservative.

The effectiveness of each demulsifier was characterized by the achieved percent dehydration, which is the reduction in the amount of water in the emulsion expressed as a percentage of the initial water content. The percent dehydration was determined immediately (i.e., two minutes after adding the demulsifier) and after a twenty-four hour settling period.

## **2.3 BURN TESTS**

### **2.3.1 BASELINE BURNS**

The limits to ignition imposed by evaporation and emulsion formation were determined by conducting a series of baseline burns. These tests also measured the steady-state burning characteristics of water-free and emulsified slicks of the fresh and weathered crude oils. Beginning with the fresh oil, the water content of the emulsion to be tested was increased stepwise (from 25 to 33, 50 and finally 60% water). This process was then repeated with the weathered oil samples.

The burns were conducted in a wave tank measuring 11 x 1.2 x 1.2 m (L x W x H) that was filled with water to a depth of 85 cm (see Figure 2-1). The air and water temperatures were maintained as close to 20°C as possible. The oil or emulsion was contained in a floating, 40-cm diameter steel ring. For each test, 2.5 L of emulsion was used, which resulted in a 2-cm thick slick.

Emulsions were prepared just prior to each test by recirculating the appropriate volumes of crude oil and water through a small gear pump. The gear pump imparted considerable mixing energy and produced very stable emulsions; even emulsions created using weathered oils with low to moderate stability indices (as measured in the rotating flask apparatus) were usually very stable.

Therefore, the limits to ignition reported can be considered conservative estimates. The common system used for igniting crude oil slicks is the Heli-torch, which uses gelled gasoline for fuel. To simulate this source of ignition, 70 to 100 g of gelled gasoline was used to ignite the baseline burns. Two ignition attempts were made before an emulsion was considered unignitable.

**Figure 2-1:** SL Ross Indoor Wind/Wave Tank



The parameters measured for the baseline burns included:

- initial mass of the oil or emulsion;
- mass of the burn residue;
- air and water temperatures;
- ignition time (time from ignition of gelled gasoline to complete ignition of slick surface); and,
- duration of burn.

The efficiency and rate of each burn were calculated using equations (5) and (6), respectively. Burn efficiency is defined as the ratio of the mass of oil burned to the initial oil mass. Burn rate is defined as the rate of decrease in the equivalent oil thickness of the slick over the period of the burn. For emulsion burns, the residue was assumed to be water free for calculating burn efficiency and burn rate.

$$\text{Burn Efficiency (\%)} = \frac{m_{\text{oil,initial}} - m_{\text{residue}}}{m_{\text{oil,initial}}} \times 100\% \quad (5)$$

Where:  $m_{\text{oil,initial}}$  is the initial mass of oil (g)  
 $m_{\text{residue}}$  is the mass of the residue (g)

$$\text{Burn Rate} = \frac{m_{\text{oil,initial}} - m_{\text{residue}}}{\rho_{\text{oil}} A_{\text{ring}} (t_{\text{extinction}} - t_{\text{ignition}})} \quad (6)$$

Where:

- $\rho_{\text{oil}}$  is the density of the oil at the time of ignition ( $\text{g}/\text{mm}^3$ )
- $A_{\text{ring}}$  is the surface area of the ring ( $\text{mm}^2$ )
- $t_{\text{extinction}}$  is the time from application of the igniter to extinction of flames (min)
- $t_{\text{ignition}}$  is the time from application of the igniter to complete ignition (min)

For a 40-cm diameter burn, the burn rate would be expected to be in the 1 mm/min range for crude oils (Buist et al. 1994). Oils that burn at 1 mm/min at this small scale would be expected to burn at 3.5 mm/min in large (greater than 5-m diameter) fires.

### 2.3.2 EMULSION BREAKER BURNS

Emulsion breaker burn tests were conducted on emulsions that could not be ignited with gelled gas in the baseline burn tests. The objective was to determine if the addition of emulsion breaker would allow the ignition of the slicks, and what affect it would have on the burning characteristics of the oils. The most effective chemical, as determined from the emulsion breaker effectiveness test (see Section 2.2.2) was used.

Emulsion breaker was added to the slick at a dosage ratio of 1:500 (i.e., 5 mL of emulsion breaker). The emulsion breaker was mixed into the slick with a glass stirring rod for two minutes. After mixing, the emulsion was allowed to sit for thirty minutes. After the settling period, gelled gasoline was used to try to ignite the slick. If the gelled gasoline could not ignite the slick, another attempt was made using a 2-mm thick layer of fresh oil as a primer. The 2-mm layer of fresh oil represents the maximum strength of igniter that could reasonably be applied to large area of a real spill. If an oil could not be ignited with the fresh oil layer it was deemed unignitable.

The same parameters were measured for the emulsion breaker burns as for the baseline burns.

### 2.3.3 BURNS IN WAVES

Burn tests in waves were conducted to determine how waves affected the burn characteristics of each of the oils. A 40-cm diameter, floating containment ring was used for these tests. The waves were produced by paddle-board wave generator, located at one end of the tank. Two wave settings were used for the tests: low and high (see Table 2-3).

If the oil was amenable to the use of emulsion breakers with burning (see Section 2.3.2), further emulsion breaker burns were conducted in waves. These were performed with no pre-mixing of the breaker into the slick; the mixing was supplied by the wave action alone.

The same parameters were measured for the burns in waves as for the baseline burns.

**Table 2-3: Wave Properties**

<b>Property</b>	<b>Low Setting</b>	<b>High Setting</b>
Wave Length (m)	3.3	2.0
Wave Period (s)	2.0	1.3
Wave Height (cm)	9 to 11	14 to 15
Wave Steepness	0.03	0.07
Energy (J/m <sup>2</sup> )	123	184

### **2.3.4 RESIDUE BURNS**

Burns were conducted with 5- and sometimes 10-cm thick slicks of the fresh crude oils, and the residues collected.

The residue densities were measured by immersing a piece of the residue in a series of aqueous solutions. Twenty-one solutions of different densities were prepared, covering a range from 0.900 to 1.100 g/cm<sup>3</sup> in increments of 0.01 g/cm<sup>3</sup>. The solutions with densities less than water were made using methanol and water; the baths with densities greater than water were prepared with sodium chloride and water. Each residue sample was first placed in the lowest density solution (i.e., 0.900 g/cm<sup>3</sup>). If the residue floated in this solution, it meant that the density of the residue was less than 0.900 g/cm<sup>3</sup>, and was noted as such in the results. If the residue sank in this solution, it meant that the density of the residue was greater than 0.900 g/cm<sup>3</sup>. These samples were then placed in solutions of higher densities until one was found in which they floated.



### 3. LIGHT LOUISIANA SWEET

Light Louisiana Sweet crude oil is a blend of oils from 60 to 75 platforms in the Central Processing Area of the Gulf of Mexico. It is carried on Pipeline System number 26, operated by Equilon Pipeline Co. pipeline, and was sampled on September 16, 1998, from the Central Gulf Gathering system going into Gibson Terminal (Gibson, LA) after block 28.

#### 3.1 EVAPORATION

The evaporation of Light Louisiana Sweet crude oil is shown in Figure 3-1. The circles represent the data from the wind tunnel, while the solid line shows the evaporation predicted by the Mackay model (see below) at 24°C. The primary x-axis shows evaporative exposure; the secondary (upper) x-axis is scaled to show the elapsed time equivalent to evaporative exposure for the case of a 2-mm thick slick in a 2.5 m/s wind (see equations 1 and 2 in section 2.1.1).

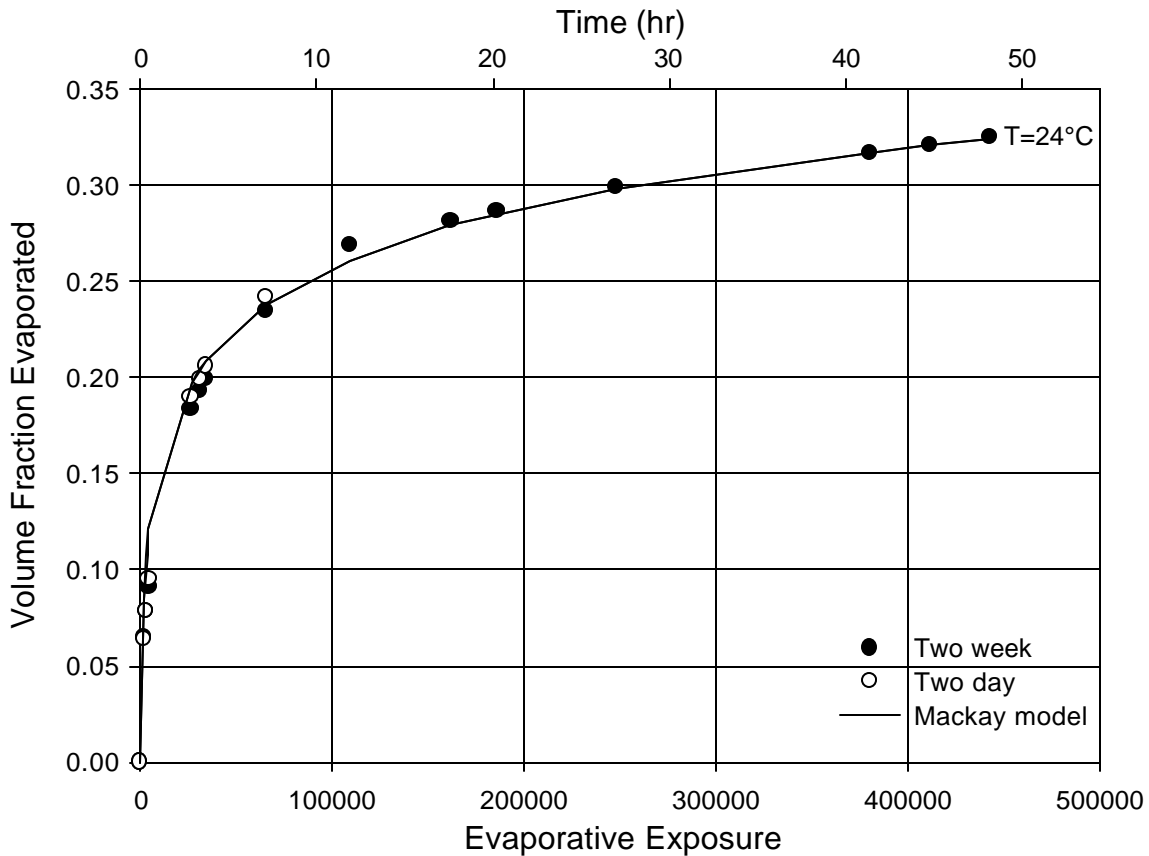


Figure 3-1: Evaporation of Light Louisiana Sweet crude oil



The Mackay evaporation model for Light Louisiana Sweet crude oil is:

$$F_v = \frac{\ln \left[ 1 + \frac{6591.7}{T} q \exp \left( 16 - \frac{7409.8}{T} \right) \right]}{\frac{6591.7}{T}}$$

Where:  $F_v$  is volume fraction evaporated  
 $q$  is evaporative exposure  
 $T$  is environmental temperature (K)

The large-scale weathering produced two evaporated samples of Light Louisiana Sweet Crude Oil. The degrees of evaporation and selected physical properties are given in Table 3-1.

**Table 3-1: Properties of Light Louisiana Sweet crude oil**

Evaporation (by volume)	Fresh	28%	35%
Time at Sea (hr)	0	20	55
API Gravity (°)	38	32	30
Density @ 24°C (kg/m <sup>3</sup> )	835	867	874
Viscosity @ 24°C (cP)	6	41	66

### 3.2 EMULSIFICATION

**Table 3-2: Results of rotating flask test**

Evaporation (by volume)	Fresh	28%	35%
Formation-Tendency	Low	Low	High
Stability	Low	Low	Low

Light Louisiana Sweet crude oil only forms an emulsion when it is highly weathered; even then, the emulsions are unstable.

**Table 3-3: Dehydration achieved by emulsion breakers**

Emulsion Breaker	Dosage Ratio	28% Evaporated		35% Evaporated	
		Immediate	24 hr	Immediate	24 hr
Breaxit	1:500	93	93	100	100
	1:5000	83	88	100	100
Alcopol	1:500	100	100	100	100
	1:5000	93	98	100	100
Vytac	1:500	78	83	98	98
	1:5000	63	88	83	83

The most effective demulsifier was Alcopol, followed closely by Breaxit and Vytac. All breakers were reasonably effective, even at low dosage ratios, owing to the naturally low stability of emulsions of Light Louisiana Sweet crude oil.

### 3.3 BURN TESTS

**Table 3-4:** Results of baseline burns

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	0	0	1.0	89
	25	Emulsion unstable		
28	25	166	0.9	82
	33	130	0.8	81
	50	76	1.4	87
	60	152	1.6	84
35	25	210	1.0	80
	33	154	1.0	81
	50	235	1.4	88
	60	78	1.4	86

The fresh oil would not form a stable emulsion and was, therefore, not tested. The weathered oils were ignitable at all water contents with only gelled gas. No burns were conducted with emulsion breakers since they were not needed with Light Louisiana Sweet emulsions.

**Table 3-5:** Results of burns in waves

Evaporation (% vol.)	Water Content (% vol.)	Wave	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)	Ignition Source
28	50	Low	69	1.0	93	Gas
		High	55	1.1	98	Gas
28	60	Low	49	1.1	89	Gas
		High	74	1.4	94	Gas
35	50	Low	99	0.7	78	Gas
		High	73	1.5	89	Gas

The waves did not have a significant effect on the behavior of Light Louisiana Sweet crude oil.

**Table 3-6:** Results of residue burns

Initial Thickness (mm)	Burn Rate (mm/min)	Efficiency (%)	Residue Density (kg/m <sup>3</sup> )
50	1.07	92	< 950

There was not enough Light Louisiana Sweet crude oil left to perform the 100-mm residue burn. It appears unlikely that residue of a Light Louisiana Sweet crude oil burn would sink.

### 3.4 CONCLUSIONS

Light Louisiana Sweet crude oil is an excellent candidate for *in situ* burning. It ignites easily even when heavily weathered, and does not form stable emulsions.



## 4. MAIN PASS 69 CRUDE OIL

Main Pass crude oil was sampled on October 6, 1998, from the Shell pipeline terminal, located 30 miles south of Venice, LA in the Gulf of Mexico. The terminal is located on the 60-mile pipeline between Main Pass 225 and Main Pass 69 (segment no. 11015) and carries oil from the VK 826 processing facility.

### 4.1 EVAPORATION

The evaporation of Main Pass crude oil is shown in Figure 4-1. The circles represent the data from the wind tunnel, while the solid line shows the evaporation predicted by the Mackay model (see below) at 24°C. The primary x-axis shows evaporative exposure; the secondary (upper) x-axis is scaled to show the elapsed time equivalent to evaporative exposure for the case of a 2-mm thick slick in a 2.5 m/s wind (see equations 1 and 2 in section 2.1.1).

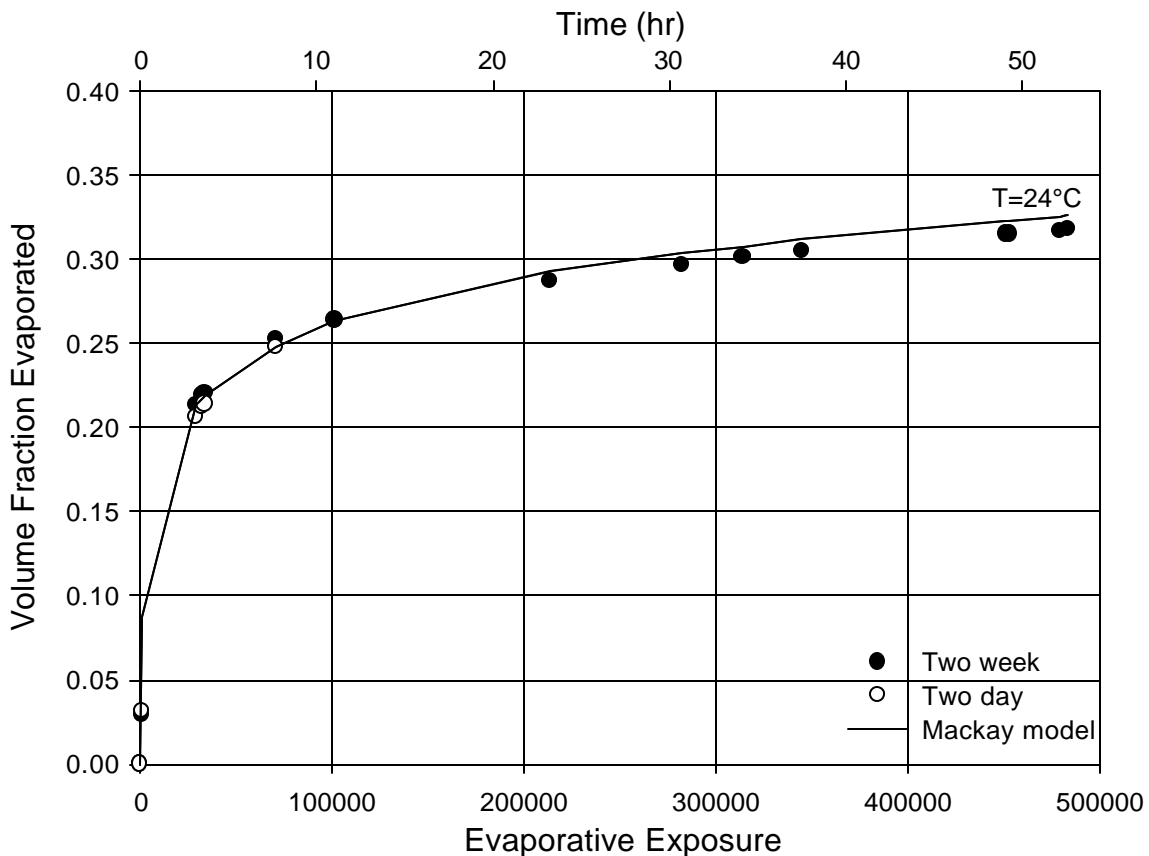


Figure 4-1: Evaporation of Main Pass crude oil

The Mackay evaporation model for Main Pass crude oil is:

$$F_v = \frac{\ln \left[ 1 + \frac{7375}{T} q \exp \left( 12.6 - \frac{6171}{T} \right) \right]}{\frac{7375}{T}}$$

Where:  $F_v$  is volume fraction evaporated  
 $q$  is evaporative exposure  
 $T$  is environmental temperature (K)

The large-scale weathering produced two evaporated samples of Main Pass Crude Oil. The degrees of evaporation and selected physical properties are given in Table 4-1.

**Table 4-1:** Properties of Main Pass crude oil

Evaporation (by volume)	Fresh	27%	31%
Time at Sea (hr)	0	13	37
API Gravity (°)	35	28	27
Density @ 24°C (kg/m <sup>3</sup> )	850	889	895
Viscosity @ 24°C (cP)	6	64	88

## 4.2 EMULSIFICATION

**Table 4-2:** Results of rotating flask test

Evaporation (by volume)	Fresh	27%	31%
Formation-Tendency	Low	High	High
Stability	Low	High	High

Main Pass crude oil readily forms stable emulsions after it has been weathered. The fresh oil did not form an emulsion.

**Table 4-3:** Dehydration achieved by emulsion breakers

Emulsion Breaker	Dosage Ratio	27% Evaporated		31% Evaporated	
		Immediate	24 hr	Immediate	24 hr
Brexit	1:500	93	98	88	88
	1:5000	0	5	15	15
Alcopol	1:500	93	100	88	93
	1:5000	39	83	5	5
Vytac	1:500	0	0	0	0
	1:5000	0	0	0	0

The most effective demulsifiers were Alcopol and Brexit. Vytac was not effective. The breakers were only effective at the 1:500 dosage ratio. Alcopol was used in the emulsion breaker burns.

### 4.3 BURN TESTS

**Table 4-4:** Results of baseline burns

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	0	5	1.8	95
	25	26	1.1	83
	33	46	1.2	85
	50	50	1.1	83
	60	85	1.2	73
27	25	Did not ignite		

The fresh oil was ignitable at all degrees of emulsification with only gelled gas. Emulsions made with Main Pass crude oil at higher degrees of weathering were unignitable with gelled gas.

**Table 4-5:** Results of burns with Alcopol

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
27	25	64	0.7	77
	33	163	0.7	75
	50	Did not ignite		
31	25	20	0.7	76
	33	118	0.7	73
	50	213	0.7	69
	60	341	0.8	71

The fact that the 50% and 60% water emulsions of the 31% evaporated Main Pass were successfully ignited indicates that the same emulsions of the 27% evaporated oil could probably have been ignited on a second or third attempt. The Alcopol greatly extended the limits to ignition imposed by emulsification for both degrees of weathering. This is very promising: even highly weathered and emulsified Main Pass crude can be burned.

**Table 4-6:** Results of burns in waves

Evaporation (% vol.)	Water Content (% vol.)	Wave	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)	Ignition Source
27	33	Low	62	0.7	77	Gas +
		High	72	1.1	79	Alcopol
31	0	Low	45	1	94	Gas
		High	62	1.3	89	Gas
31	33	Low				Gas +
		High	170	1.3	87	Alcopol

There was not enough weathered oil left to do the low wave burn at 33% water. The wave burns with Alcopol were done without pre-mixing the breaker into the slick; the wave action alone was enough to mix the breaker and allow the ignition of the oil.

There was not enough oil left to perform residue burns with Main Pass crude oil.

#### **4.4 CONCLUSIONS**

Main Pass crude oil is a good candidate for *in situ* burning. Emulsion breakers and/or a strong ignition source may be needed if the oil is highly weathered and emulsified.

## 5. POINT ARGUELLO CRUDE OIL

The crude oil was sampled on October 9, 1998, from platform Hermosa in the Point Arguello unit in the Pacific OCS region. Crude oil from the platform is transported to shore in the PAPCO pipeline, owned by the Point Arguello Pipeline Company to the Gaviota plant.

### 5.1 EVAPORATION

The evaporation of Point Arguello crude oil is shown in Figure 5-1. The circles represent the data from the wind tunnel, while the solid line shows the evaporation predicted by the Mackay model (see below) at 24°C. The primary x-axis shows evaporative exposure; the secondary (upper) x-axis is scaled to show the elapsed time equivalent to evaporative exposure for the case of a 2-mm thick slick in a 2.5 m/s wind (see equations 1 and 2 in section 2.1.1).

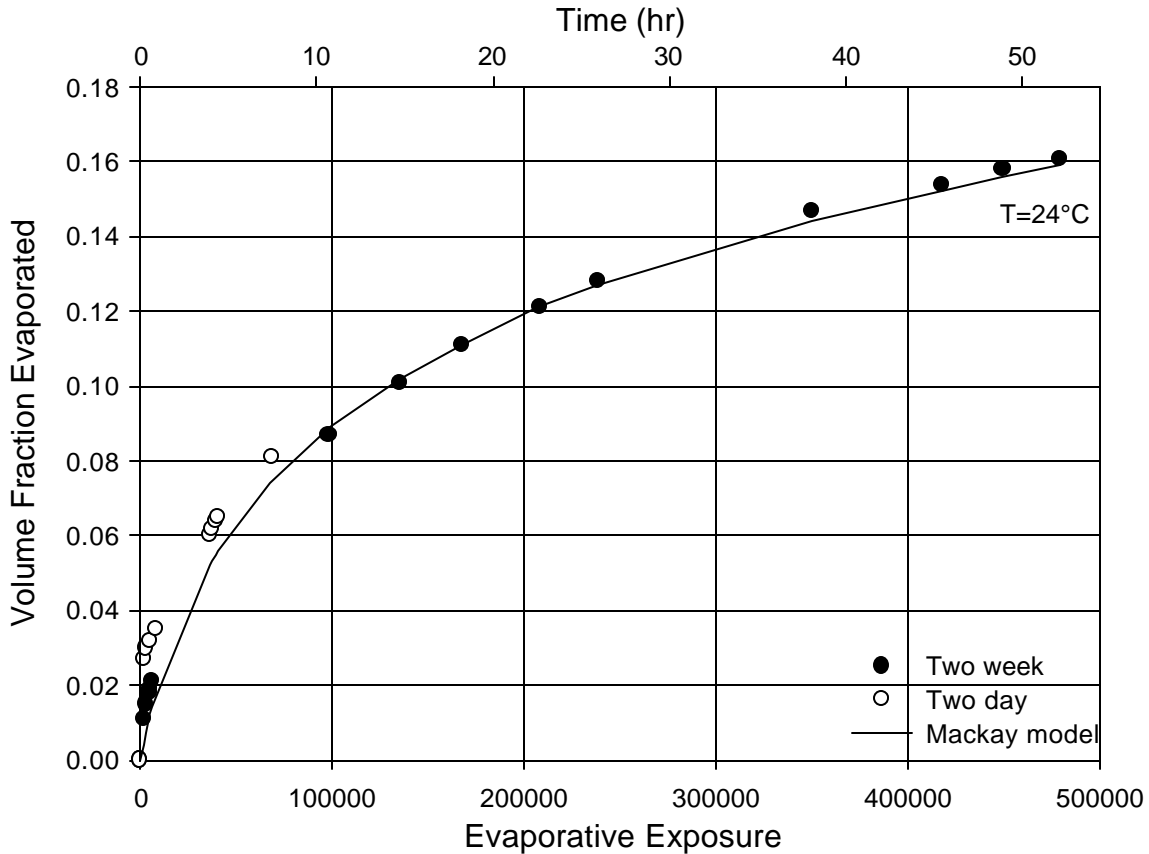


Figure 5-1: Evaporation of Point Arguello crude oil



The Mackay evaporation model for Point Arguello crude oil is:

$$F_v = \frac{\ln \left[ 1 + \frac{6130.6}{T} \theta \exp \left( 1 - \frac{398.6}{T} \right) \right]}{6130.6}$$

Where: Fv is volume fraction evaporated  
 $\theta$  is evaporative exposure  
 T is environmental temperature (K)

The large-scale weathering produced two evaporated samples of Point Arguello crude oil. The degrees of evaporation and selected physical properties are given in Table 5-1.

**Table 5-1:** Properties of Point Arguello crude oil

Evaporation (by volume)	Fresh	7%	16%
Time at Sea (hr)	0	8	52
API Gravity (°)	21	19	16
Density @ 24°C (kg/m <sup>3</sup> )	926	942	960
Viscosity @ 24°C (cP)	604	2485	12,374

## 5.2 EMULSIFICATION

**Table 5-2:** Results of rotating flask test

Evaporation (by volume)	Fresh	7%	16%
Formation-Tendency	High	High	High
Stability	High	High	High

Point Arguello crude oil readily forms stable emulsions at all degrees of evaporation.

**Table 5-3:** Dehydration (%) achieved by emulsion breakers

Emulsion Breaker	Dosage Ratio	7% Evaporated	
		Immediate	24 hr
Brexit	1:500	0	5
	1:5000	0	0
Alcopol	1:500	9	37
	1:5000	5	5
Vytac	1:500	9	37
	1:5000	0	5

The 16% evaporated crude oil was too viscous to form an emulsion with the equipment used, and was not subjected to the emulsion breaker test. None of the breakers worked very well, especially at the lower dosage rate. Alcopol was used in the subsequent emulsion breaker burns.

### 5.3 BURN TESTS

**Table 5-4:** Results of Baseline Burns

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	0	37	0.9	75
	25	Did not ignite		
7	0	48	0.8	68
16	0	48	1.1	76

Point Arguello crude was unignitable with gelled gas once it had become emulsified.

**Table 5-5:** Results of burns with Alcopol

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	25	Did not ignite		

Not surprisingly, and as the emulsion breaker results indicated, Alcopol was unable to extend the limits to ignition.

**Table 5-6:** Results of burns in waves

Evaporation (% vol.)	Water Content (% vol.)	Wave	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)	Ignition Source
0	0	Low	26	2.0	85	Gas
		High	40	2.5	81	Gas
7	0	Low	29	1.2	78	Gas
		High	44	1.7	54	Gas
16	0	Low	61	1.2	76	Gas
		High	Oil sank			Gas

The waves did not have a significant effect on the burning of Pt. Arguello.

**Table 5-7:** Results of residue burns

Slick Thickness (mm)	Burn Rate (mm/min)	Efficiency (%)	Residue Density (kg/m <sup>3</sup> )
50	0.9	72	1065
100	0.8	86	1065

The residues of both thicknesses of burns exceeded that of salt water by a considerable amount. If an *in situ* burn of Point Arguello crude is conducted, care must be taken to collect the residue before it cools and sinks.

### 5.4 CONCLUSIONS

Point Arguello crude oil would not be a good candidate for *in situ* burning owing to the tendency for it to form highly stable emulsions.



## 6. POMPANO CRUDE OIL

The crude oil was sampled on October 23, 1998, from the BP Amoco platform in VK 989 of the Gulf of Mexico. Production from the subsea template in MC 28 flows back to the platform for processing.

### 6.1 EVAPORATION

The evaporation of Pompano crude oil is shown in Figure 6-1. The circles represent the data from the wind tunnel, while the solid line shows the evaporation predicted by the Mackay model (see below) at 24°C. The primary x-axis shows evaporative exposure; the secondary (upper) x-axis is scaled to show the elapsed time equivalent to evaporative exposure for the case of a 2-mm thick slick in a 2.5 m/s wind (see equations 1 and 2 in section 2.1.1).

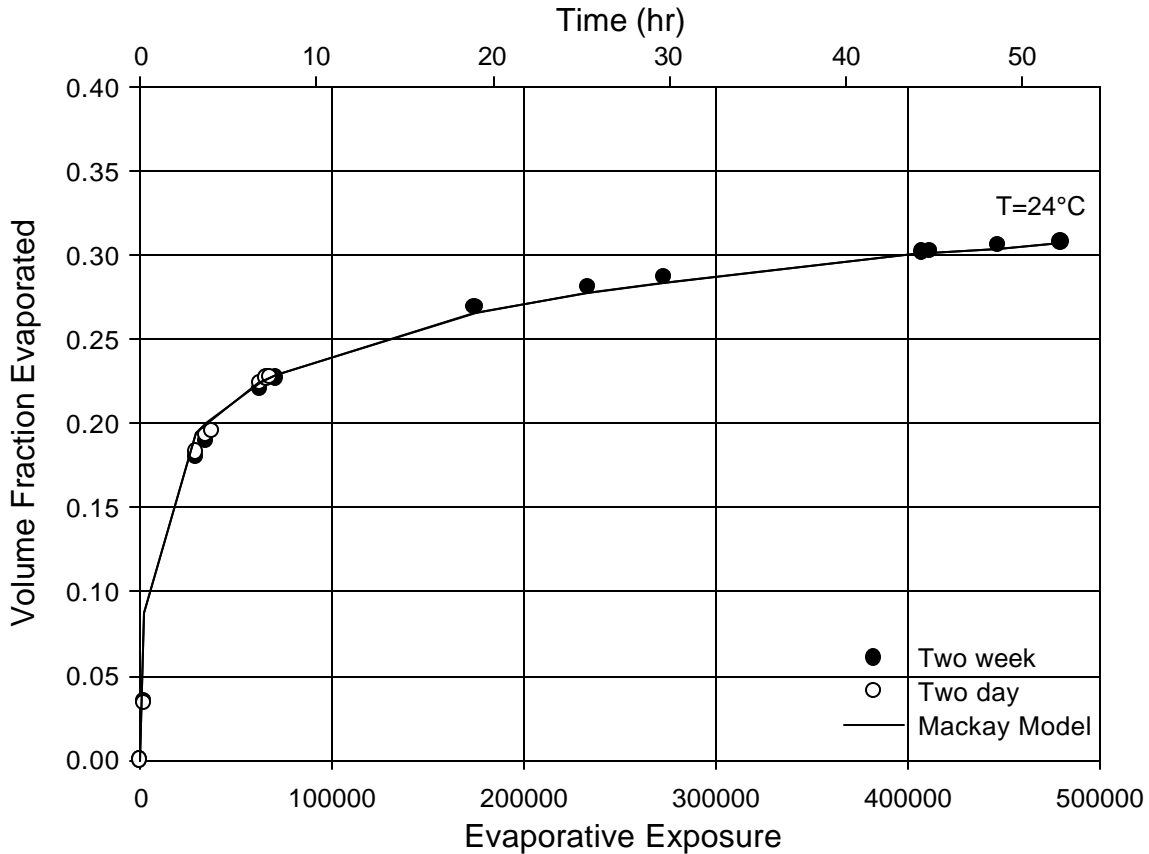


Figure 6-1: Evaporation of Pompano crude oil

The Mackay evaporation model for Pompano crude oil is:

$$F_v = \frac{\ln \left[ 1 + \frac{7281.9}{T} q \exp \left( 8.5 - \frac{5130.2}{T} \right) \right]}{7281.9 T}$$

Where: Fv is volume fraction evaporated  
 θ is evaporative exposure  
 T is environmental temperature (K)

The large-scale weathering produced two evaporated samples of Pompano crude oil. The degrees of evaporation and selected physical properties are given in Table 6-1.

**Table 6-1:** Properties of Pompano crude oil

Evaporation (by volume)	Fresh	24%	30%
Time at Sea (hr)	0	10	44
API Gravity (°)	33	27	25
Density @ 24°C (kg/m <sup>3</sup> )	857	894	903
Viscosity @ 24°C (cP)	13	81	127

## 6.2 EMULSIFICATION

**Table 6-2:** Results of rotating flask test

Evaporation (by volume)	Fresh	24%	30%
Formation-Tendency	Low	High	High
Stability	Low	Moderate	Moderate

Pompano crude oil forms emulsions only after weathering. If allowed to settle, the emulsions will naturally break somewhat, but some emulsion will still remain.

**Table 6-3:** Dehydration achieved by emulsion breakers

Emulsion Breaker	Dosage Ratio	24% Evaporated		30% Evaporated	
		Immediate	24 hr	Immediate	24 hr
Breaxit	1:500	54	49	54	54
	1:5000	10	15	5	15
Alcopol	1:500	73	73	68	68
	1:5000	24	24	24	29
Vytac	1:500	0	0	0	0
	1:5000	0	0	0	0

The most effective demulsifier was Alcopol, followed by Breaxit. Vytac was not effective. The breakers were only truly effective at the higher dosage rate. Alcopol was used in the emulsion breaker burns.

### 6.3 BURN TESTS

**Table 6-4:** Results of Baseline Burns

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	0	0	1.25	86
	25	43	0.8	78
	33	100	0.6	79
	50	100	0.8	73
	60	115	0.4	86
24	25	Did not ignite		
30	25			

The fresh crude oil was easily ignited at all emulsion water contents. The weathered crude was more difficult to ignite owing to the higher emulsion stability.

**Table 6-5:** Results of burns with Alcopol

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
24	25	293	1.0	83
	33	10*	0.5	71
	50	260	0.6	65
	60	310	0.5	74
30	25	297	0.7	70
	33	16*	0.5	68
	50	Did not ignite		

\* 2 mm of fresh crude used as ignition source

The Alcopol considerably extended the limits to ignition of the 24% evaporated Pompano. It also extended the limits for the 30% weathered sample, but the 50% water emulsion was still unignitable.

**Table 6-6:** Results of burns in waves

Evaporation (% vol.)	Water Content (% vol.)	Wave	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)	Ignition Source
24	33	Low	63	0.7	86	Gas +
		High	188	1.0	82	Alcopol
30	33	Low	128	0.8	88	Gas +
		High	158	0.8	76	Alcopol

Wave action was enough to mix the Alcopol into the test slicks and permit ignition. The waves did not have a significant effect on the burn behavior.

Not enough fresh crude was available, so the residue burn was done with 24% evaporated Pompano.

**Table 6-7:** Results of residue burns with 24% evaporated Pompano crude oil

<b>Thickness (mm)</b>	<b>Burn Rate (mm/min)</b>	<b>Efficiency (%)</b>	<b>Residue Density (kg/m<sup>3</sup>)</b>
50	0.8	92	1010

The density of the residue was less than that of salt water. Considering that the weathered sample was used in the burn, which probably makes the results closer to a 65- or 70-mm thick slick of fresh oil, it appears unlikely that residues of Pompano would sink.

## **6.4 CONCLUSIONS**

Pompano crude oil is a good candidate for in situ burning. It may require the use of emulsion breakers if the oil is weathered and emulsified, but it responds well to such treatment.

## 7. SOUTH PASS 49 CRUDE OIL

The crude oil was sampled from Chevron Pipeline Company's South Pass 49 pipeline, which is part of the West Bay system in the Gulf of Mexico. It comprises oil from the following fields: Mississippi Canyon 20, Mississippi Canyon 109, South Pass 49 and South Pass 45. The pipeline starts at the South Pass 49 field and ends at the South Pass 49 onshore facility, near Venice, LA.

### 7.1 EVAPORATION

The evaporation of South Pass 49 crude oil is shown in Figure 7-1. The circles represent the data from the wind tunnel, while the solid line shows the evaporation predicted by the Mackay model (see below) at 24°C. The primary x-axis shows evaporative exposure; the secondary (upper) x-axis is scaled to show the elapsed time equivalent to evaporative exposure for the case of a 2-mm thick slick in a 2.5 m/s wind (see equations 1 and 2 in section 2.1.1).

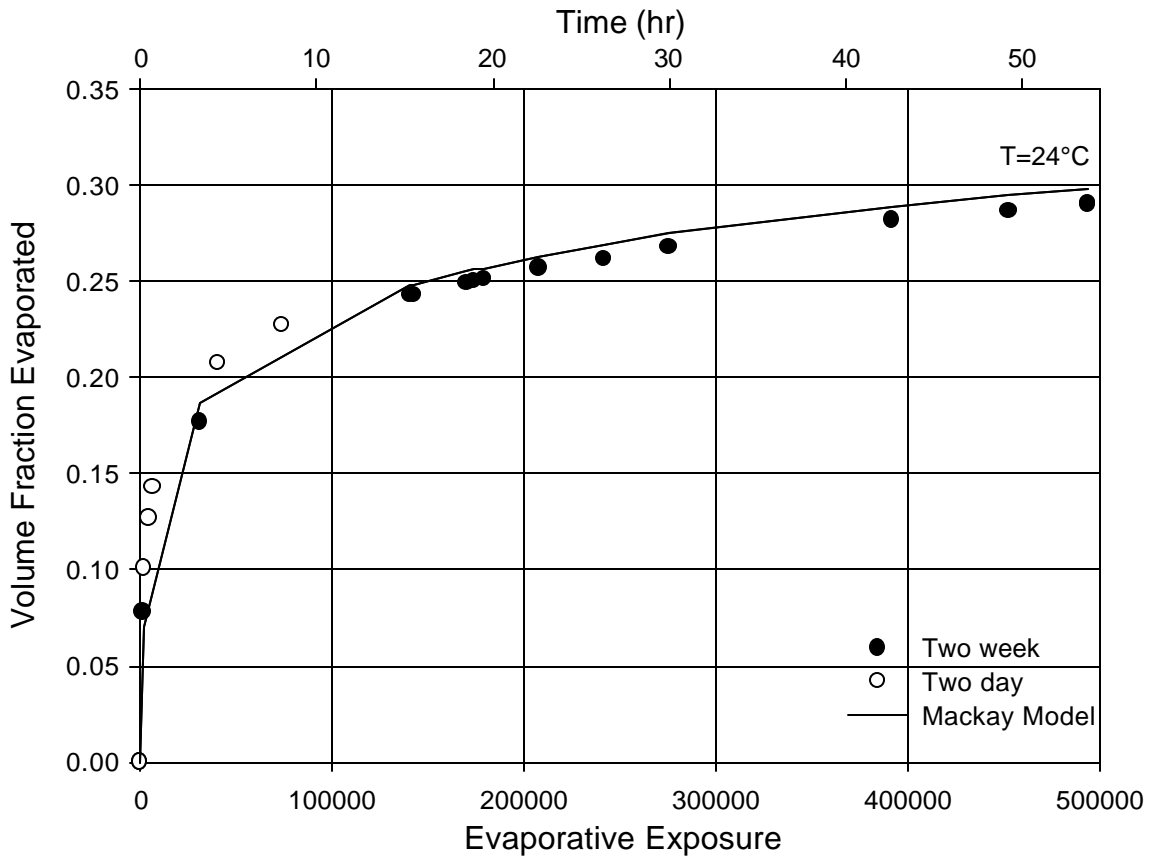


Figure 7-1. Evaporation of South Pass 49 crude oil



The Mackay evaporation model for South Pass 49 crude oil is:

$$F_v = \frac{\ln \left[ 1 + \frac{7371.5}{T} \theta \exp \left( 14 - \frac{6802.4}{T} \right) \right]}{7371.5}$$

Where: Fv is volume fraction evaporated  
 $\theta$  is evaporative exposure  
 T is environmental temperature (K)

The large-scale weathering produced two evaporated samples of South Pass 49 crude oil. The degrees of evaporation and selected physical properties are given in Table 7-1.

**Table 7-1:** Properties of South Pass 49 crude oil

Evaporation (by volume)	Fresh	24%	29%
Time at Sea (hr)	0	15	49
API Gravity (°)	30	24	23
Density @ 24°C (kg/m <sup>3</sup> )	873	910	917
Viscosity @ 24°C (cP)	13	103	154

## 7.2 EMULSIFICATION

**Table 7-2:** Results of rotating flask test

Evaporation (by volume)	Fresh	24%	29%
Formation-Tendency	Low	Moderate	High
Stability	Low	Low	Low

The tendency of South Pass 49 crude oil to form an emulsion increases with evaporation; however, the emulsions will break if allowed to settle.

**Table 7-3:** Dehydration achieved by emulsion breakers

Emulsion Breaker	Dosage Ratio	24% Evaporated		29% Evaporated	
		Immediate	24 hr	Immediate	24 hr
Brexit	1:500	44	83	34	68
	1:5000	0	5	0	5
Alcopol	1:500	73	78	88	88
	1:5000	5	24	0	29
Vytac	1:500	0	49	5	5
	1:5000	0	24	0	0

Brexit and Alcopol were both effective at breaking emulsions of South Pass crude oil. Alcopol was more effective with the higher weathered oil, and worked faster. Vytac was not effective. The breakers were only truly effective at the higher dosage rate.

### 7.3 BURN TESTS

**Table 7-4:** Results of baseline burns

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	0	0	1.5	93
	25	57	0.6	73
	33	83	0.5	75
	50	Did not ignite		
24	25	Did not ignite		

The fresh oil was ignitable up to 33% water. The weathered samples were unignitable once emulsified.

**Table 7-5:** Results of burns with Alcopol

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	50	102	1.0	68
	60	363	0.7	59
24	25	190	0.6	72
	33	Did not ignite		
29	25	40*	0.6	68
	33	Did not ignite		

\* 2 mm fresh crude used as ignition source

The Alcopol helped somewhat with burning South Pass 49 emulsions, but not as much as might be expected given the low emulsion stability exhibited in the rotating flask tests.

**Table 7-6:** Results of burns in waves

Evaporation (% vol.)	Water Content (% vol.)	Wave	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)	Ignition Source
24	25	Low	0	0.8	87	2 mm oil
		High	0	1.0	79	+ Alcopol
29	25	Low	0	0.7	85	2 mm oil
		High	Oil dispersed			+ Alcopol

Wave action alone was not sufficient to mix the breaker into the slicks and allow ignition. The breaker had to be mixed in by hand before the slicks could be burned successfully. The 25% water emulsion of the 29% weathered sample dispersed in the high waves.

**Table 7-7:** Results of residue burns

Thickness (mm)	Burn Rate (mm/min)	Efficiency (%)	Residue Density (kg/m <sup>3</sup> )
50	0.8	93	980
100	0.8	92	1065

The density of the residue of the 50-mm thick slick was less than that of 35-ppt salt water, while the density of the 100-mm residue exceeded it. This indicates that the residue of efficient burns

may sink if the initial thickness is high enough, but that under most circumstances, the residue will float.

## **7.4 CONCLUSIONS**

South Pass 49 crude oil is a fairly good candidate for *in situ* burning. Alcopol was able to extend the limits to ignition for the emulsified samples. The residue of efficient burns of very thick slicks may sink.

## 8. WEST DELTA 143 CRUDE OIL

The crude oil was sampled in December, 1998, from Equilon Pipeline Company's processing facility West Delta 143 (WD 143), after processing. After WD 143, the oil flows on pipeline segment 10553 to BM 3.

### 8.1 EVAPORATION

The evaporation of West Delta 143 crude oil is shown in Figure 8-1. The circles represent the data from the wind tunnel, while the solid line shows the evaporation predicted by the Mackay model (see below) at 24°C. The primary x-axis shows evaporative exposure; the secondary (upper) x-axis is scaled to show the elapsed time equivalent to evaporative exposure for the case of a 2-mm thick slick in a 2.5 m/s wind (see equations 1 and 2 in section 2.1.1).

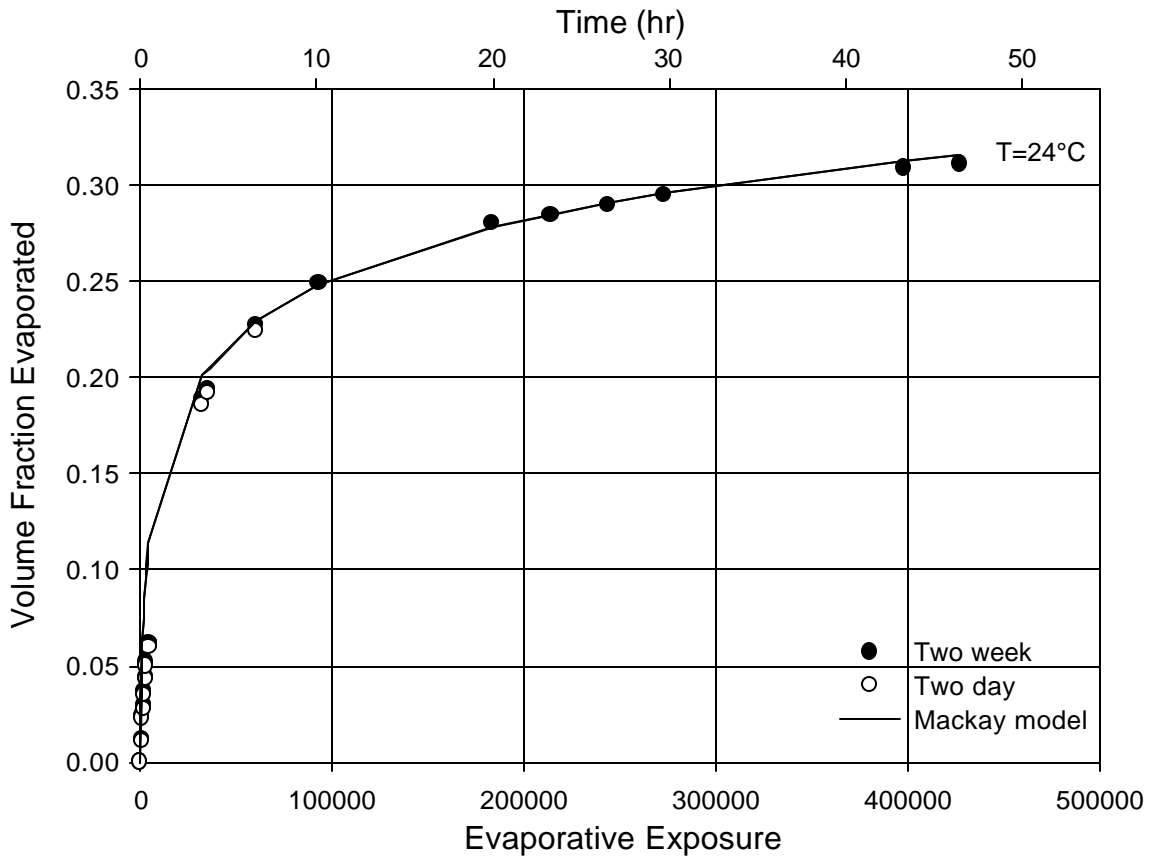


Figure 8-1. Evaporation of West Delta 143 crude oil

The Mackay evaporation model for West Delta 143 crude oil is:

$$F_v = \frac{\ln \left[ 1 + \frac{6643.9}{T} q \exp \left( 4 - \frac{3896.6}{T} \right) \right]}{6643.9 T}$$

Where: Fv is volume fraction evaporated  
 θ is evaporative exposure  
 T is environmental temperature (K)

The large-scale weathering produced two evaporated samples of West Delta 143 crude oil. The degrees of evaporation and selected physical properties are given in Table 8-1.

**Table 8-1: Properties of West Delta 143 crude oil**

Evaporation (by volume)	Fresh	29%	31%
Time at Sea (hr)	0	20	46
API Gravity (°)	30	19	18
Density @ 24°C (kg/m <sup>3</sup> )	878	938	944
Viscosity @ 24°C (cP)	17	491	703

## 8.2 EMULSIFICATION

**Table 8-2: Results of rotating flask test**

Evaporation (by volume)	Fresh	29%	31%
Formation-Tendency	High	High	High
Stability	High	High	High

West Delta 143 crude oil readily forms stable emulsions, even when fresh.

**Table 8-3: Dehydration achieved by emulsion breakers**

Emulsion Breaker	Dosage Ratio	29% Evaporated		31% Evaporated	
		Immediate	24 hr	Immediate	24 hr
Brexit	1:500	5	63	0	44
	1:5000	0	0	0	5
Alcopol	1:500	0	73	0	59
	1:5000	0	0	0	0
Vytac	1:500	0	44	0	10
	1:5000	0	0	0	0

Brexit and Alcopol were both somewhat effective at breaking emulsions of West Delta crude oil, but required some time. Vytac was not effective. The breakers were only effective at the higher dosage rate.

### 8.3 BURN TESTS

**Table 8-4:** Results of baseline burns

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	0	20	0.9	75
	25	Did not ignite		
24	25	Did not ignite		

West Delta 143 was unignitable by gelled gas after it was emulsified.

**Table 8-5:** Results of burns with Alcopol

Evaporation (% vol.)	Water Content (% vol.)	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)
0	25	Did not ignite		

The Alcopol did not help with the ignition of the emulsified West Delta, even using 2mm of fresh crude oil as the igniter. It is possible that more time would help the emulsion breaker to work.

**Table 8-6:** Results of burns in waves

Evaporation (% vol.)	Water Content (% vol.)	Wave	Ignition Time (s)	Burn Rate (mm/min)	Burn Efficiency (%)	Ignition Source
24	0	Low	73	1.0	86	Gas
		High	54	1.0	88	Gas
29	0	Low	64	1.0	90	Gas
		High	53	0.9	73	Gas

The waves did not significantly affect the burning of West Delta 143.

**Table 8-7:** Results of residue burns

Thickness (mm)	Burn Rate (mm/min)	Efficiency (%)	Residue Density (kg/m <sup>3</sup> )
50	0.9	91	1045
100	0.9	94	1065

The density of the residues of the 50- and 100-mm thick slicks exceeded that of seawater. It is likely that residues of efficient burns of thick slicks of West Delta 143 would sink after cooling.

### 8.4 CONCLUSIONS

West Delta 143 crude oil would not be a good candidate for *in situ* burning. It is possible that the oil may burn if it is ignited when fresh and unemulsified. It is also possible that emulsion breakers may extend the ignitability if they are given 1 or 2 hours to work.



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## **APPENDIX 1**

### **BURN TEST RESULTS**