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EFFECTS OF WEATHERING ON THE FLAMMABILITY OF OILS

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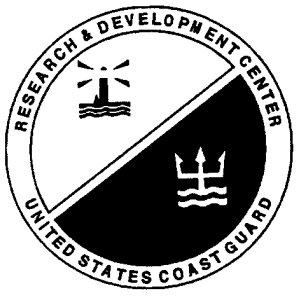

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16. Abstract (MAXIMUM 200 WORDS)

Many crude oils and fuel oils are flammable and pose a significant fire hazard if not handled properly. When an oil is accidentally spilled and exposed to the environment, the flammability characteristics of the oil can change significantly as it evaporates. A numerical weathering model that simulates the weathering and consequent changes in flammability was developed. The time required for a representative group of flammable oils to weather to a non-flammable state under various spill conditions was estimated. The effects of the level of mixing caused by environmental factors were closely examined.

Results of simulations indicate that flammable crude oils weather very slowly when there are no natural mixing mechanisms at work. In these cases weathering times are very sensitive to the thickness of the oil. In contrast, if there are effective mechanisms for mixing the oil, it weathers much more quickly and the weathering time is less sensitive to thickness.

Simulations indicate that flammable fuel oils are less likely to become non-flammable during weathering. Weathered gasoline remains flammable until it is almost completely evaporated.

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EXECUTIVE SUMMARY

When a common petroleum product spills in the marine environment, it begins to evaporate and a flammable atmosphere can form over the spill. U.S. Coast Guard (USCG) Vessel Response Plans (33 CFR 155) require responding vessels to be on site at a spill within two hours after detection and that booms are deployed within one hour. While this rapid response time is needed to minimize the spread of the spill, there is an inherent danger of explosion and fire due to the natural volatility and flammability of the spilled oil and petroleum products. This effort focused on developing a weathering tool which would benefit the Coast Guard by providing the technical foundation and guidance in these situations, and could be used to support a rule-making project for oil spill response vessels, ensuring the safety of response personnel.

Exposure to the marine environment can result in rapid changes to the oil's composition and, consequently, the oil's flammability. An oil slick will remain flammable until it weathers and loses its volatile components. Evaporation is the dominant weathering process responsible for changes in composition during the first few days following a spill. This study employed numerical modeling to examine how the evaporation and flammability characteristics of some representative flammable oils change after a spill in a confined area, such as a boomed area in a harbor. The model results predict how much time must pass from the time of an oil spill until the oil slick is no longer flammable.

The flash point of an oil is the temperature at which there is sufficient airborne concentration of the oil to be ignited by a spark or other ignition source. Flash points are commonly used to assess flammability hazards associated with oils that are transported. The Code of Federal Regulations uses flash points as the basis for grading liquids that are transported. Grade D and E liquids have flash points greater than 26.7°C (80°F) and are not considered flammable (U.S. Coast Guard, 1997). The flash point alone is not adequate to describe the flammability hazard associated with an oil in the environment, since the effects of wind and oil thickness can reduce the flammability hazard for oils while on the water. However, flash points are useful indicators of the dangers inherent in

handling oils recovered from a spill. If the flash point of an oil is below the ambient temperature, the vapors in a vessel containing the oil may form a fuel-air mixture that can be ignited by a spark or other ignition source.

The numerical model developed for this study was specially constructed for oil slicks confined by booms and in fairly calm waters (i.e., in a harbor.) This model was used to simulate oil evaporation and flash point changes for cases where sufficient mixing from wind and sea occurs to keep the oil homogeneous (well-mixed oils), and for cases where there was no mixing and the conditions are calm. These represent the extremes of mixing that possibly occur in a spill and bound the operational conditions. The time required for some representative flammable oils to weather to Grade D, flash point reaching or exceeding 26.7°C (80°F), were computed for various conditions of mixing, temperature, and slick thickness. The weathering of five flammable crude oils and gasoline were modeled. It was not necessary to model diesel fuel since it is not a flammable liquid in an unweathered state. The weathering times were generally very sensitive to the thickness and to the level of mixing.

All five stratified crude oils thicker than one centimeter, except Avalon at 30°C, were predicted to take over 100 hours to weather to Grade D. In contrast, the same five crude oils under well-mixed conditions weathered to Grade D in less than three hours. This study indicated that flammable crude oils in thick slicks under calm conditions lose their volatile components very slowly and remain flammable for days following a spill. Crude oils that spread thin in open-water spills, or those effectively mixed by wave action, lose their volatile components in a matter of hours.

For gasoline, this study predicted that even after most of the gasoline evaporates, it remains a flammable mixture. Given the uncertainties in the models and the variability of gasolines, it seems prudent to treat all weathered gasolines as flammable liquids. The results of the information obtained in this study will be used to write standards for classifying oil spill response vessels that work in flammable atmospheres during various types of fuel or oil spills. This information indicates how long various crude oils, diesel

and gasoline are flammable or explosive after the spill, and therefore, how much precaution must be taken in vessel design to preclude explosions, ignition or fire when the vessel is exposed to vapors.

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SYMBOLS

A	=	surface area of the spill (m^2);
Bi	=	mass Biot number;
C	=	molar concentration (moles m^{-3});
$\overline{C}$	=	spatially averaged molar concentration (moles m^{-3});
D	=	diffusivity (m^2 s);
F_{evap}	=	fraction of oil evaporated;
i	=	used as subscript specifies component;
K_m	=	vapor-phase mass transfer coefficient (m s^{-1});
$k_{\eta,E}$	=	viscosity multiplier for evaporation;
$k_{\eta,T}$	=	viscosity multiplier for temperature (K);
k_1, k_2, k_3	=	coefficients for weathering time formula;
L	=	initial thickness of slick (mm);
MW	=	molecular weight (kg $mole^{-1}$);
N	=	molar flux (mole m^{-2} s^{-1});
P	=	vapor pressure (Pa);
P_∞	=	background partial pressure (Pa);
R	=	gas constant (3.144 J $mole^{-1}$ K^{-1});
Sc	=	Schmidt number;
T_{air}	=	air temperature (K);
T_{oil}	=	oil temperature (K);
t_w	=	time required for oil to weather to Grade D (h);
U	=	wind speed (m s^{-1});
U^M	=	molar average velocity (m s^{-1});
V	=	volume (m^3);
$\overline{V}$	=	molar volume (m^3 $mole^{-1}$);
X	=	diameter of oil spill (m);
z	=	vertical position;
χ	=	mole fraction.
γ	=	dimensionless concentration;
η	=	dynamic viscosity (Pa s);
η°	=	dynamic viscosity of fresh oil (Pa s);
λ	=	eigenvalue;
τ	=	dimensionless time variable.

1.0 INTRODUCTION

The U.S. Coast Guard (USCG) plays a central role in managing the emergency response to, and mitigation of, marine oil spills. Many of the crude oils and refined products involved in spills are flammable and pose a serious fire hazard if suitable precautions in handling and storage are not used. The USCG classifies oils according to their flammability characteristics, and establishes guidelines and regulations for response vessels with regard to their suitability for handling petroleum products (USCG, 1997).

Fuel oils and crude oils are the most common petroleum products spilled in the marine environment. In storage and transport their composition and flammability properties can be readily characterized to ensure compatibility with the vessels used to transport them; however, following a spill an oil's composition and flammability characteristics can change rapidly. Highly flammable oils can lose their volatile components and become less hazardous after being exposed to the environment. This "stabilization" with regard to flammability can happen quickly in spills where there are no confining structures to limit the spread of the oil; once the oil spreads to submillimeter thicknesses, the weathering processes that stabilize the oil are fast. However, spills that occur in harbors or other areas where the oil is kept from freely spreading may weather much more slowly.

Though the weathering processes for oils involved in open-water spills has been studied extensively, very little work has been devoted to understanding the weathering and consequent evolution of the flammability characteristics of confined thick oil spills. This study was designed to examine how the flammability characteristics of volatile crude oils and some select fuel oils evolve with time following spills in confined areas. This information may be used as part of the technical basis for setting design and operation standards for oil spill response vessels involved in recovering flammable oils.

No attempt was made to simulate the weathering of all transported flammable oils, rather a small representative sample of oils were chosen for case studies. The behavior of these oils can

provide some insight into how other flammable oils will behave, and has implications for precautions that should be taken when handling oils.

2.0 BACKGROUND

Alkanes are the dominant constituents of crude oils (Speight, 1980). The chemical model of combustion of alkanes provides a useful way to conceptualize how oils burn. Alkanes are molecules containing carbon and hydrogen atoms linked by single bonds only. The combustion reaction of an alkane molecule containing **n** carbon atoms consumes a number of oxygen molecules defined by the stoichiometric ratio and yields carbon dioxide and water:

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O. \qquad (1)$$

Generally, this reaction can only occur in the gas phase, since the reactants must mix at the molecular level. The ability of a liquid petroleum oil to ignite and sustain a combustion depends on the ratio of fuel to oxygen in the air; this depends on how much of the fuel can vaporize and the confinement of the vapors. The vapor concentration must meet or exceed the "lean limit of flammability" (LLF) to be ignited (Kanury, 1995).

At any given temperature the vapor-phase concentration cannot exceed the saturation concentration, which is the maximum concentration allowed thermodynamically. Generally, the saturation concentration of a volatile liquid decreases sharply as the temperature decreases. So even in cases where the vapors are confined, such as a closed-cup flash point tester, the fluid will not burn if the temperature is so low that the saturation concentration falls below the LLF. (There are some exceptions to this rule, notably when the liquid is in the form of an aerosol.) One way to ensure that a liquid does not burn accidentally is to guarantee the temperature is low enough to keep the saturation concentration below the LLF.

LLFs for many chemicals have been measured and compiled (Kanury, 1995). For small hydrocarbons, the LLF is reached when the molar ratio of fuel to air is about 1:100. For these

chemicals the problem of determining whether a chemical can burn in a confined environment can be reduced to determining the saturation concentration. A more common method for evaluating whether a liquid poses a flammability hazard bypasses the examination of the LLF and saturation concentration, and relies on a direct observation of combustion. Flash point devices are designed to detect the temperature at which there is a possibility that the airborne concentration of fuel is sufficient to sustain a flame. Since flash points are defined by a measurement protocol, they can vary significantly from method to method. A closed-cup flash point is approximately the temperature at which the saturation concentration equals the LLF (Kanury, 1995).

Flash point measurements for chemical mixtures, such as crude oils, can be problematic. As an oil is heated in a flash point device some of the volatile chemicals can be vaporized and lost; by the time the flash point is reached the composition of the sample may have changed significantly. In addition, if there is no mechanism for stirring the sample, the surface of the sample, which determines the concentration in the vapor phase, may be depleted of volatiles and no longer be representative of the bulk composition. Despite the inherent difficulties in measuring flash points, they are indicators of whether an oil stored in a closed tank poses a threat of combustion or explosion, and are used in Federal regulations as the basis for characterizing crudes and fuel oils. Grade D oils have a flash point greater than 26.7°C (80°F) (USCG, 1997).

There have been many efforts to predict flash points from composition or other properties of a sample. The estimation methods for flash points of pure substances and mixtures fall into two categories: those based on boiling point; and those based on composition. The former correlate flash point with the boiling point and have been proposed for pure substances (Li & Moore, 1977; Patil, 1988; Sayanarayana & Kakati, 1991), and for petroleum distillates (Factory Mutual Engineering Corporation, 1967). Compositional methods are based on the concentrations and properties of the individual constituents and have been used for petroleum mixtures, commonly middle distillates (Wickey & Chittenden, 1963; Lenoir, 1975; Butler et al., 1956). The key constituents for oils with low flash points are the low molecular weight compounds, those compounds generally contain fewer than nine carbon atoms.

It should be noted that flash points are less useful in assessing the flammability hazard associated with oils that are not contained in closed vessels. For unconfined spills the effects of wind and thickness can be as important as the flash point in assessing the flammability hazard associated with the spill. For oils with flash points below the ambient temperature, the presence of wind can disperse the vapors and prevent ignition (Murad et al., 1970). Furthermore, when a slick spreads to a thickness on the order of 0.5 millimeter, as would be expected in unconfined spills, even oils with very low flash points do not pose a flammability hazard (Stensaas, 1992).

After oil is released into a marine environment it immediately starts to change. Evaporation is the dominant process affecting the composition of the floating oil during the first week of a spill (Fingas, 1995) The low molecular weight (lighter) compounds are more volatile and evaporate more quickly than the heavier compounds. With progressive evaporation the oil composition changes and, as a result, its physical properties can change dramatically. Any attempt to estimate the time-evolution of flash point depends critically on the ability to predict the evaporation.

Many oil evaporation models have been proposed during the last 30 years (Fingas, 1995). The model proposed by Mackay and Matsugu (1973) has provided the foundation of most of the subsequent models. Their model incorporated many of the fundamental tenets of the evaporation theory described by Dalton in 1802 (Brutsaert, 1982). Mackay and Matsugu recognized that since oil is a multi-component mixture, the evaporation rate could be limited by diffusion within the liquid phase or by diffusion in the vapor phase above the pool. However, their model incorporated a vapor-phase diffusion mechanism only and effectively assumed that the liquid phase remains homogenous. This so-called "well-mixed" condition has been used in most oil spill evaporation models to date. The model described the evaporative flux as a simple function of a vapor-phase mass transfer coefficient, K_m, which characterizes the diffusion in the vapor phase, and the difference between the vapor pressure of the oil (P) and the natural background partial pressure of the oil (P_∞),

$$\frac{1}{A}\cdot\frac{dN}{dt} = -\frac{K_m(P - P_\infty)}{R\cdot T_{air}}. \qquad (2)$$

The natural background pressure of the oil is usually considered negligible.

The application of this model has largely followed two general approaches. So-called pseudo-component models approximate the oil as an ideal mixture of a relatively small number of components. Commonly, a volume flux is used to describe the evaporation of the i^{th} component,

$$\frac{1}{A}\cdot\frac{dV_i}{dt} = -\frac{K_{m,i}\cdot\overline{V}_i\cdot\chi_i\cdot P_i}{R\cdot T_{air}}. \qquad (3)$$

The total evaporative flux is set equal to the sum of the fluxes of the individual components. Payne and coworkers (Payne et al., 1984) created a pseudo-component model that has been used by the National Oceanic and Atmospheric Administration (NOAA) and the U.S. Mineral Management Service. Payne also proposed mechanisms that could account for the mechanical mixing of oils for open-water spills, providing some justification for imposing a well-mixed condition. Jones (1997) developed a simplified version of a pseudo-component model that will be incorporated into the next version of ADIOS, a comprehensive oil weathering model developed by NOAA (Lehr et al., 1997).

Stiver and Mackay (1984) proposed a different approach that has been widely used and is referred to as the Analytical Model. The oil is treated as a single substance with a vapor pressure that varies with the fraction evaporated. In this approach only one equation needs to be solved and it can usually be solved analytically,

Recently, a conceptually different approach based on small-scale laboratory measurements has been proposed by Fingas (1996). In a break with the fundamentals proposed in earlier models, Fingas proposed that the evaporation of oil is not limited by diffusion processes in the vapor phase and can be described by equations that are a function of temperature and time alone. He developed a series of evaporation prediction equations for specific oils based on laboratory measurements.

Thibodeaux used a two-resistance mass-transfer model that accounts for diffusion in both the liquid and gas phases to model the loss of volatile chemicals from thick waste oil ponds (Thibodeaux & Carver, 1997). The method employed an overall mass transfer coefficient constructed from the mass transfer coefficients in the individual phases. Such methods are commonly used in modeling chemical manufacturing processes but are generally not used for marine oil spills.

3.0 MODEL DEVELOPMENT

A numerical model was developed and used to simulate the change in flash point of an oil following a marine spill. Specifically, the model was designed to find the time required for the flash point to reach or exceed 26.7 °C (80 °F). Once the flash point is above this temperature, the liquid is no longer defined as a "flammable liquid" under Coast Guard regulations (USCG, 1997). The model was intended to capture the dominant effects of weathering on oils spilled in protected and confined areas, such as boomed areas in harbors. Accidental spills of this type might occur during fueling, transfer of crude oil cargo, or a collision in a harbor. In such cases, the compositional changes of the oil over the first week can be attributed almost entirely to evaporation. This model did not include effects from many of the weathering processes that can be significant in open water spills where the oil can be subjected to high winds and breaking waves.

As noted above, the evaporation of an oil involves two diffusive processes: the diffusive migration of constituent chemicals through the liquid phase to the surface of the oil where they quickly migrate to the air directly over the surface; and the gas-phase diffusion of the chemicals away from the surface. The latter is dominated by the turbulent mixing caused by the wind. For this study a pseudo-component evaporation model was developed that includes the effects of the both liquid-phase and gas-phase diffusion. This model was used to predict the changes in composition of some representative oils as they weather. An established correlation (Butler et al., 1956) was used to determine the flash point from composition.

The pseudo-component evaporation model developed for this study treats the oil as a mixture of a relatively few distinct constituents. Since crude oils can contain thousands of distinct chemical compounds, this approach groups a large number of compounds as a single component with a distinct set of physical properties. The construction of the pseudo-components follows the form of the data collected using distillation methods. Oil is commonly characterized through a conventional distillation procedure such as the ASTM D86 method or gas chromatographic methods that simulate a conventional distillation (ASTM, 1995). As the oil undergoes a fractional distillation, the volume and boiling point of the distillate are measured.

The model developed for this study uses the same methodology for constructing pseudo-components as that which will be used in the next version of ADIOS (Jones, 1997) Each volume fraction collected between consecutive temperature measurements was considered a component. The boiling points of the components were equated to the average of the bounding temperature measurements. The vapor pressures of the components at ambient temperature were derived from their boiling points using Antoine's equation (Lyman et al., 1990). The molecular weights and molar volumes of the components were based on boiling point correlations for a series of alkanes from butane to eicosane.

The oil was assumed to be a slick of uniform thickness floating on water, and confined to an area that is not changing in time. Transport was limited to the direction normal to the surface of the water. Each pseudo-component within the oil was governed by the advection-diffusion equation in one dimension:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (U^M \cdot C_i)}{\partial z}. \qquad (4)$$

The second term on the right hand side was neglected since advection was insignificant in this study. The flux at the oil-water interface was assumed to be insignificant. This interface was used to define the zero of the z axis, so the flux at z=0 was set to zero,

$$\frac{\partial C_i}{\partial z}(0,t) = 0. \qquad (5)$$

At the oil-air interface the diffusive flux in the oil was matched to the evaporative flux. The expression for the evaporative flux is consistent with the work of Mackay & Matsugu (1973), Payne et al. (1984), and Jones (1997) and is given by the right hand side of the following equation:

$$D_i \frac{\partial C_i}{\partial z}(L,t) = -\frac{K_{m,i} \cdot P_i}{R \cdot T_{air}} \left[\frac{C_i(L,t)}{\sum_j C_j(L,t)} \right]. \qquad (6)$$

Since the evaporative flux depends on the sum of the concentrations at the surface, the diffusion-advection equations for the individual pseudo-components were coupled through the boundary condition at the oil-air interface.

The value of the gas-phase mass transfer coefficient was based on the work of Mackay and Matsugu (Mackay & Matsugu, 1973),

$$K_{m,i} = 0.0048 \cdot U^{7/9} \cdot X^{-1/9} \cdot Sc_i^{-2/3}. \qquad (7)$$

The value used for the liquid-phase diffusivity, D_i, depended upon the specific implementation of the model. In cases where the molecular diffusivity was used, it was based on an estimation method of Wilke and Chang (Hines & Maddox, 1985)

$$D_i = \frac{5.864 \cdot 10^{-17} MW_i^{1/2} T_{oil}}{\overline{V}_i^{0.6} \eta}. \qquad (8)$$

Since the viscosity of the oil is very sensitive to the temperature, the molecular diffusivity is also strongly dependent on the temperature. The Andrade correlation (Reid et al., 1977) was used to determine the viscosity of the oil at the ambient temperature:

$$\ln\left(\frac{\eta_2}{\eta_1}\right) = k_{\eta,T}\left(\frac{1}{T_{oil,2}} - \frac{1}{T_{oil,1}}\right). \qquad (9)$$

The reference viscosity and the proportionality constant, $k_{\eta,T}$, were based on measured values compiled by the Emergencies Science Division of Environment Canada (Jokuty et al., 1996).

The viscosity can increase by orders of magnitude as an oil evaporates. Consequently, the molecular diffusivity can decrease significantly with increasing evaporation. This relationship between viscosity and fraction of oil evaporated was described by a exponential function (Mackay et al., 1983):

$$\eta = \eta^{o} e^{k_{\eta,E} F_{evap}}. \tag{10}$$

The proportionality constant, $k_{\eta,E}$, was based on measured values compiled by Environment Canada (Jokuty et al., 1996).

The evaporation model provided the basis for estimating the composition of the oil as a function of time. A correlation derived for middle distillate petroleum products (Butler et al., 1956) was used to predict the flash point in the oil based on composition. The vapor pressures of the components, P_i, are functions of temperature. The flash point is the temperature at which the following equality holds, and was solved implicitly:

$$\frac{\sum_i \left[\left(\frac{1}{L} \int_0^L C_i(z,t_w)dz \right) \cdot MW_i \cdot P_i \right]}{\sum_i \left(\frac{1}{L} \int_0^L C_i(z,t_w)dz \right)} = 104.7. \tag{11}$$

Determining the composition and flash point of an oil as it evaporates involved solving the coupled set of advection-diffusion equations with time-dependent diffusivity and auxiliary conditions, one for each pseudo-component. A backward-time, centered-space finite difference formulation (Hoffman, 1992) of the coupled diffusion-advection equations was implemented and solved on a personal computer. At the end of each time step, a spatially averaged liquid-phase

diffusivity and the total molar concentration at the oil-air interface were computed for use in the subsequent time step. See Appendix A for details.

4.0 SELECTION OF OILS AND SPILL CONDITIONS

The selection of crude oils for this study was based on measured flash points, the completeness of physical property data, and the perceived quality of the data. Only oils with measured flash points below 26.7 °C (80°F) were considered. The estimation method developed for this study required distillation data and viscosities as a function of temperature and fraction evaporated. The database of oil properties compiled by Environment Canada (Jokuty et al., 1996) is the most extensive source of data of this type, so the search was narrowed to oils from this database.

Data quality was difficult to assess. Since flash points of oils depend critically on the most volatile constituents, oils with closely spaced distillation cuts at the low-temperature end of the range were selected. To eliminate any errors from mixing data from two different samples from the same well, oils with data collected from different labs were eliminated. Only 21 oils in the Environment Canada database satisfied all these conditions, they are listed in Table 1. From this short list, five crude oils were selected for case studies: Arabian Light; West Texas Sour; Point Arguello Light; South Pass Block 67; and Avalon. The data used in this study for these five oils are in Appendix C.

Only data for one unleaded gasoline were available in the Environment Canada database, and no viscosity data were available for that sample. The viscosity was estimated based on measurements of other gasolines in the database.

To reduce the number of simulations only spill parameters that have the largest impacts on weathering times were varied; these include liquid phase diffusivities, temperature, and thickness. Realistic worst-case values were used for other environmental parameters.

During an actual spill, waves and wind may provide enough mechanical agitation to cause some vertical mixing of the oil. The degree of mixing of the oil has a pronounced effect on the effective liquid-phase diffusivities and, consequently, on the weathering times. In cases where waves and wind are effective at keeping the oils completely mixed, weathering is limited by diffusion in the vapor phase; these cases are referred to as "well-mixed" and represent one extreme in the range of possibilities. At the other extreme, oil confined by a boom in calm waters my undergo minimal agitation and chemicals migrate to the surface of the oil through molecular diffusion only. These cases are referred to as "stratified" since concentration gradients can develop in the oil. The extremes of mixing were studied and are reported here.

Table 1. Flash points for crude oils extracted from the Environment Canada database (Jokuty et al., 1996).

Name	API gravity	Measured flash point (°C)	Estimated flash point (°C)
Avalon	36	14	8
ASMB (Petawawa)	35	-9	-19
Arabian Light	32	-20	-20
Carpinteria	23	-15	-36
Empire	34	-9	-3
Hout	32	-18	-45
Iranian Heavy	30	-15	-20
Main Pass Block 37	39	-6	-14
Point Arguello Light	30	-6	-7
Rangely	34	-2	12
Santa Clara	22	-24	-18
Ship Shoal Block 239	26	11	-5
Ship Shoal Block 269	39	-7	-5
South Pass Block 60	36	-4	-19
South Pass Block 67	16	-1	-5
South Pass Block 93	33	-7	-4
South Timbalier Block 130	35	5	-4
Statfjord	38	-12	-17
Terra Nova (1994)	36	-22	-32
Terra Nova (Petawawa)	32	4	-8
West Texas Sour	30	-14	-16

Oil temperatures may be slightly below to well above the water temperature depending on the degree of exposure to sunlight during a spill. Since water temperatures and exposure to sunlight

vary significantly during times and in locations where this study might be applied, a single "worst-case" temperature was not selected. Three temperatures were used to show the effect that temperature variability has on the weathering times.

The thickness of an oil has a large impact on the weathering time. Open-water spills quickly spread to sub-millimeter thicknesses (Belen et al., 1983), but spills confined by booms may be quite thick. Thicknesses up to 10 centimeters were considered in this study.

Other environmental and spill parameters were selected that would most closely represent realistic worst case conditions during a spill in a harbor. Generally, oil weathers more slowly under lower wind speeds, so a wind speed of 1.5 meters per second was selected to be consistent with that used in recent U.S. Environmental Protection Agency regulations governing the reporting of risk management plans for industrial facilities (U.S. Environmental Protection Agency, 1999). Wind speeds have very little effect on the predicted weathering times for stratified oils since the weathering times are limited by diffusion within the liquid oil. Even for well-mixed oils the effects of wind speeds are limited; doubling the wind speed decreased weathering times by about 40 percent.

For a given thickness, weathering times increased slightly with increasing area. A spill area of 1000 m^2 was chosen as a realistic worst-case. It should be noted that area effects are minimal; for example, doubling the area increased the weathering time less than 7 percent.

5.0 RESULTS AND DISCUSSION

Equation (11) was used with the pseudo-component analysis to predict the flash point of the unweathered crude oils used for this study. Comparisons of measured and predicted flash points for the 21 oils that met the selection criteria are presented in Table 1 and Figure 1. The root-mean-square deviation between the measured and predicted flash points was 11°C.

Some of the difficulties associated with measuring flash points of crude oils are addressed above. The Emergencies Science Division of Environment Canada modified a commercial flash point

instrument to overcome some of these difficulties. Steve Whiticar, one the authors of the database, suggested that the measured flash points are reproducible to within 3°C but gave no estimates of systematic errors. (Whiticar, 1998).

A numerical simulation was used to predict how the average composition and flash points of five representative oils change as they weather. As the oils weathered the lighter components, which contribute to the low initial flash points of these oils, were preferentially lost to evaporation. The times required for the oils to weather to Grade D (flash point > 26.7°C) are presented graphically in figures 2 through 6. An algebraic formula for weathering times as a function of thickness was also developed using a least-squares fit to the numerically generated data:

$$t_w = k_1 e^{\{k_2 \ln L + k_3 (\ln L)^2\}} \tag{12}$$

where the thickness, L, is in millimeters and the weathering time, t_w, is in hours. This formula is valid for weathering greater than one hour and less than 100 hours. The values for the coefficients, k_1, k_2, k_3, depend on the oil, the degree of mixing, and the oil temperature; they are listed in Table 2. In all but one case $k_3 = 0$, and the formula reduces to

$$t_w = k_1 \cdot L^{k_2}. \tag{13}$$

The weathering times for well-mixed oils was linearly related to the thickness ($k_2 = 1$).

Gasoline was modeled using only the well-mixed conditions and the results are presented in Figure 7. The magnitude of the errors associated with the stratified model when applied to gasoline precluded its use. Furthermore, since there is less resistance to vertical circulation in low viscosity fluids like gasoline, a well-mixed model is more reasonable even under a broad range of conditions. A more revealing result is presented in Figure 8 that shows the flash point as a function of the fraction of the gasoline that evaporates. Since gasoline is composed of mostly low flash point chemicals, most of it must evaporate for the flash point to reach 26.7 °C.

Table 2. Coefficients for computing the time required for stratified and well-mixed oils to weather to Grade D.

Name	Temp (°C)	Stratified oils k_1 (h)	k_2	k_3	Well-mixed oils k_1 (h)	k_2
Avalon	0	242.0	2.3736	0	.09408	1.000
	15	1.680	2.3233	0	.04664	1.000
	30	.0472	1.7371	.09203	.02586	1.000
Arabian Light	0	12.30	2.1981	0	.14159	1.000
	15	5.581	2.2477	0	.06943	1.000
	30	2.744	2.3028	0	.03702	1.000
South Pass Block 67	0	18.22	2.0741	0	.24845	1.000
	15	7.865	2.1002	0	.11853	1.000
	30	3.655	2.1298	0	.06174	1.000
West Texas Sour	0	66.25	2.2042	0	.19742	1.000
	15	5.886	2.2465	0	.09545	1.000
	30	1.608	2.2594	0	.05046	1.000
Point Arguello Light	0	41.86	2.3418	0	.15695	1.000
	15	12.71	2.4019	0	.07555	1.000
	30	4.197	2.4824	0	.04001	1.000

Thickness and temperature have large effects of weathering times though the mechanisms and degree of sensitivity to these parameters are different for well-mixed and stratified oils. Weathering times were roughly proportional to thickness for well-mixed oils; for a given mass, thicker oil simply translated into a smaller surface area for evaporation. For stratified oils, the effect of thickness is due to the length of the diffusion path and the weathering times increased approximately with the square of the thickness (e.g. doubling the thickness increased the weathering time by approximately a factor of four).

Temperature also had large effects on the required weathering times for both the stratified and well-mixed oils. With increasing temperature the vapor pressures of the constituents increased; this boosted the diffusive flux in the gas phase and the weathering time was reduced. For stratified oils the temperature effect was due predominantly to its influence on viscosity . Molecular diffusivity is closely tied to the viscosity of the oil; with increasing temperature,

diffusivity increased, and weathering times decreased. Of the five oils studied, the weathering times for Avalon Crude were the most sensitive to temperature because its viscosity is the most sensitive to temperature.

The differences between oils was largely due to differences in volatile components and viscosity. Viscosities change as an oil weathers so the initial viscosities alone cannot be used to rank the expected weathering times of stratified oils with similar initial flash points. However, there is a general trend in the relationship between viscosity and weathering time.

The differences between the stratified and well-mixed oils are dramatic. Molecular diffusion, which was most often the rate limiting process for stratified oils, was generally much slower for volatile constituents than the gas-phase diffusion which limited the well-mixed rate. Under most circumstances the stratified oils weathered very slowly. In all cases except Avalon at 30 °C, a stratified slick thicker than 1 centimeter required over 100 hours to weather. In actual spills weathering will occur much more quickly if there are natural mechanisms for mixing the oil. For the five crude oils in this study, well-mixed slicks up to a one centimeter thick weathered within three hours even at low ambient temperatures.

6.0 UNCERTAINTY ANALYSIS

Possible sources of error can be conveniently divided into those inherent to the formulation of the model (model errors), those associated with numerical implementation (numerical errors), and those associated with input parameters (parametric errors). Model errors arise from the inaccuracies in the model assumptions or descriptions of the physical processes. The magnitude of model errors are difficult to estimate in the absence of experimental data. Numerical errors can arise when the fundamental equations used to describe the processes are implemented and solved numerically using a computer; for this study these errors were easy to assess and minimize. Parametric errors are best described as the errors in the output of a model caused by errors in the input. In applying the results of this study to any actual spill, the dominant errors in the weathering times are expected from the large uncertainties in the input data.

Uncertainty in the liquid-phase diffusivity of the oil is probably the largest source of uncertainty in the model output. Errors in the diffusivity can arise from the uncertainties in the level of mixing, the temperature of the oil, the viscosity of the oil, and from inherent errors in the correlation used to determine the molecular diffusivity (equation 8). Of these, the level of mixing probably introduces the largest uncertainty. As stated above, it is possible for wind and waves to agitate and cause some vertical mixing of the oil. There is no easy way to assess the effectiveness of this mixing so the results from the two extreme cases are presented: no vertical mixing (stratified oil) and complete mixing (well-mixed oil). Errors in the viscosity of the oil can also have a pronounced effect on results; the rate of diffusion in the liquid phase decreases with increasing viscosity. The correlation itself yields results that are reliable to within about 30 percent (Hines & Maddox, 1985).

Errors in temperature affect the vapor pressure of the components and the viscosity values used to compute molecular diffusivity. Depending on the circumstance of a spill, it can be extremely difficult to estimate the temperature of an oil. On sunny days, solar heating of the oil surface can be dramatic. During an experimental spill in Mobile Alabama, Jones et al. (1992) observed the surface temperature of a six-centimeter oil slick rise 23°C above the water temperature due to solar radiation. On the other hand, spills at night or kept in the shade can be expected to have a lower temperature than the water due to evaporative cooling. These effects are accentuated for very thick stratified slicks. Figures 2 through 6 show results for a range of temperatures so the reader can estimate the possible bounds on the weathering times based on the particular conditions of the spill.

The process of spilling and skimming oil is usually effective at mixing the oil. How long the mixing occurs and how thick the oil is during this process cannot be known and the processes would be difficult to model. It should be noted that the mixing and spreading that occurs during the release and skimming may play a larger part in the weathering of the oil than the many hours spent on the water's surface. This study did not account for these processes.

7.0 CONCLUSIONS

This study was limited to low wind speeds. This limitation was not significant for stratified oils since weathering was relatively insensitive to wind speed. However at higher wind speeds well-mixed oils weathered more quickly; doubling wind speeds reduced weathering times by about 40 percent. In actual spills, uncertainties in temperature, thickness, oil composition and viscosity would be expected to introduce significant ambiguities.

This study indicates that the time required for any of the five crude oils to weather to Grade D depends critically on whether it is stratified or well-mixed. These represent the extremes that bound the conditions expected in an actual spill. There are a variety of possible mechanism for mixing: the process of releasing the oil and the process of skimming are effective at mixing the oil, but may only persist for a few minutes; wave action can cause the slick to alternately be squeezed and stretched; winds can cause the oil to pile up against a boom and promote vertical circulation; and thermal instabilities may initiate convective currents. Some mixing is likely during a spill; however, the analysis of these mechanisms and the quantification of the effects are beyond the scope of this study.

The results suggest a different approach for refined products. Most common fuels, like diesel fuel, have flash points well above 26.7 °C before any evaporation occurs so no modeling is needed. Gasoline contains constituents with boiling points that fall within a relatively narrow range. Since it is mostly made up of volatile components, about 85 percent of the gasoline must evaporate before it weathers to Grade D. It seems prudent and reasonable to treat any floating gasoline as a flammable substance with a low flash point.

This study was intended to be applied to oil contained in a boom and should not be applied to cases where oil is released, spreads freely, and is subsequently boomed. When oil is released and is allowed to spread, it quickly thins to less than 1 mm. Even if the oil is stratified it weathers quickly when thin. Subsequent booming will also promote weathering through mixing.

8.0 RECOMMENDATIONS

Models of complicated natural phenomena are prone to error. Though every attempt was made to assess the possible errors and account for the largest, there was no way to estimate model errors in the absence of experimental evidence. The numerical results presented here should be verified experimentally.

The work was motivated by the USCG's need to set guidelines for vessels responding to confined oil spills. The large differences between the weathering times for completely stratified oils and well-mixed oils combined with the inherent difficulty in determining the degree of mixing during many, if not most, actual spill events poses a serious challenge to those attempting to estimate safe response times. In the absence of direct observation, the results of this study may prove useful in assessing the possible range of weathering times; however, direct measurements of flammability at the time of spill are preferred.

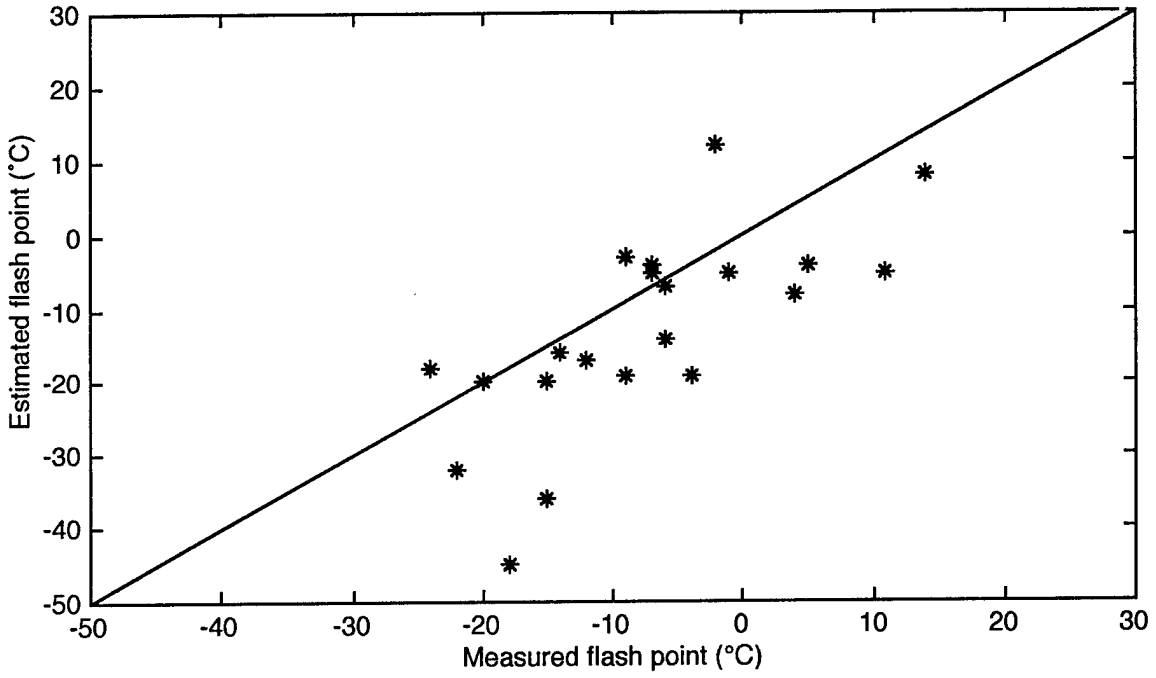

Figure 1. Measured and estimated flash points for 21 unweathered crude oils. The straight line indicates perfect agreement.

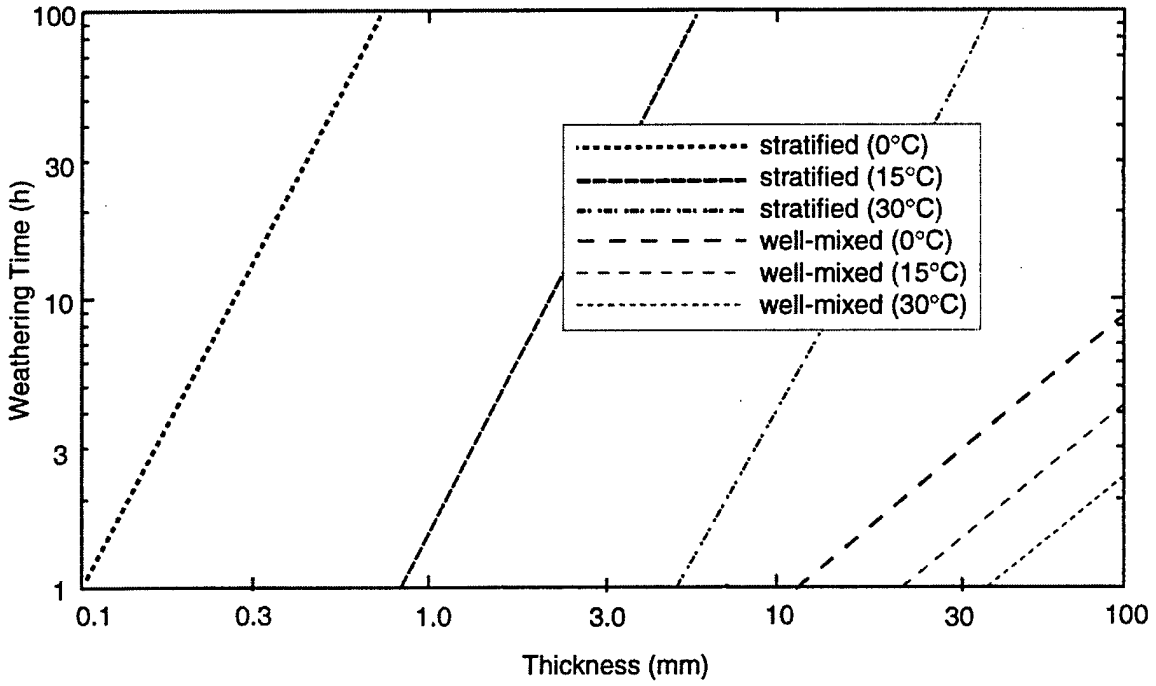

Figure 2. Weathering time required for Avalon crude to weather to Grade D.

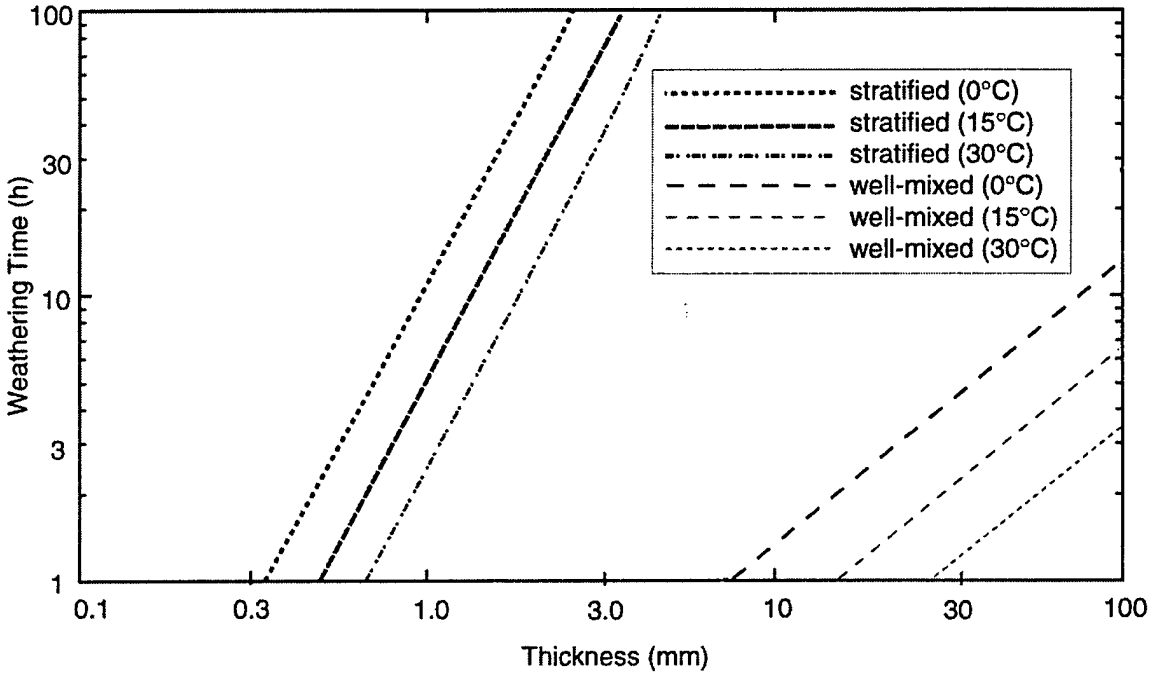

Figure 3. Weathering time required for Arabian Light crude to weather to Grade D.

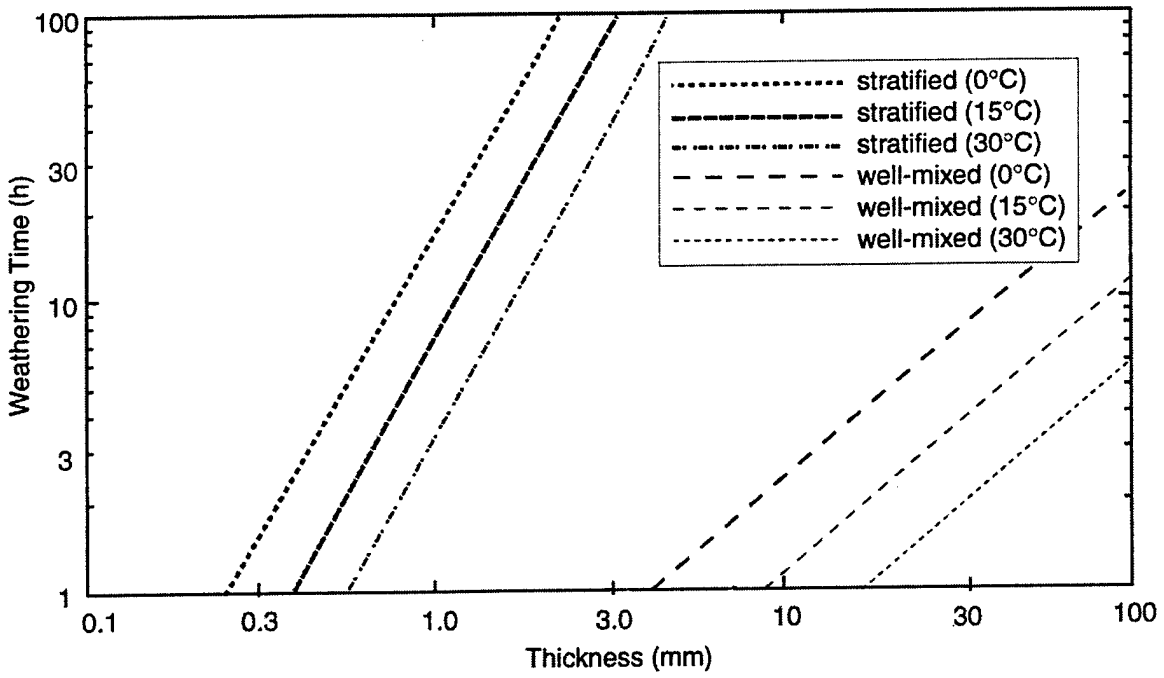

Figure 4. Weathering time required for South Pass Block 67 crude to weather to Grade D.

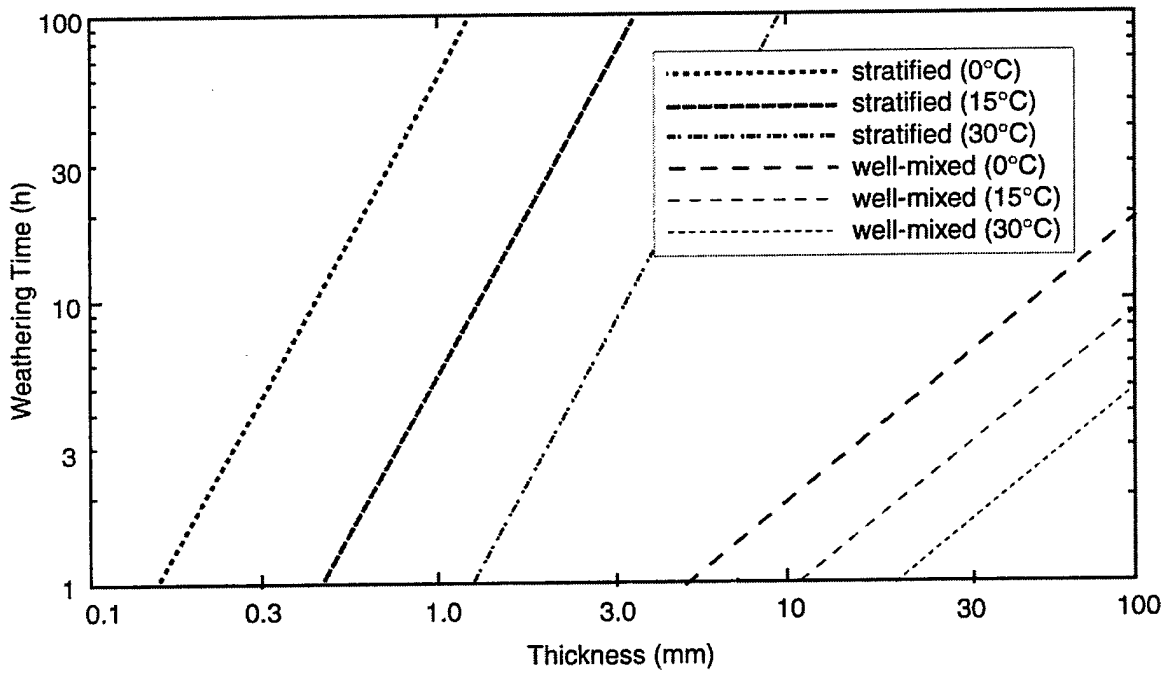

Figure 5. Weathering time required for West Texas Sour crude to weather to Grade D.

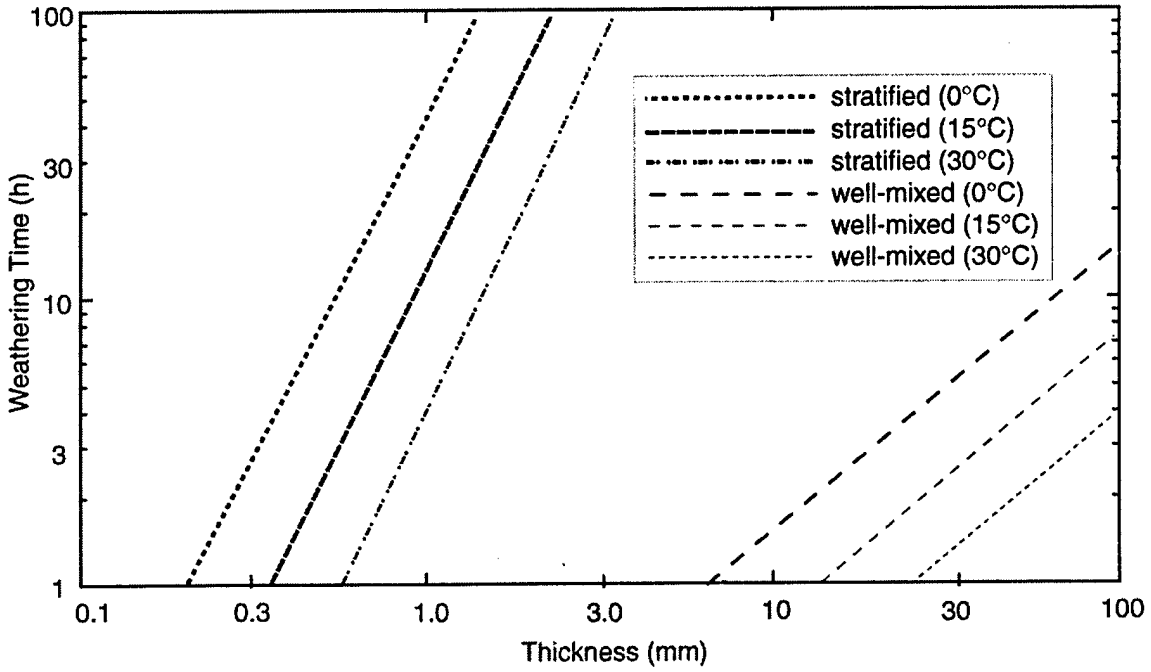

Figure 6. Weathering time required for Point Arguello Light crude to weather to Grade D.

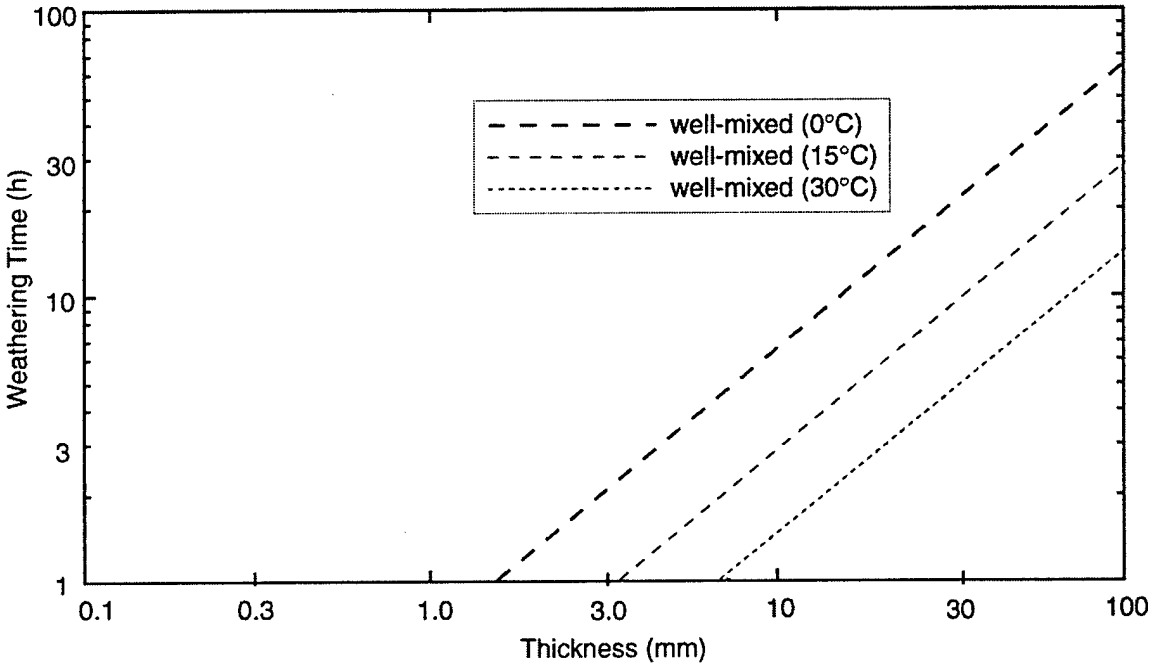

Figure 7. Weathering time required for gasoline to weather to Grade D.

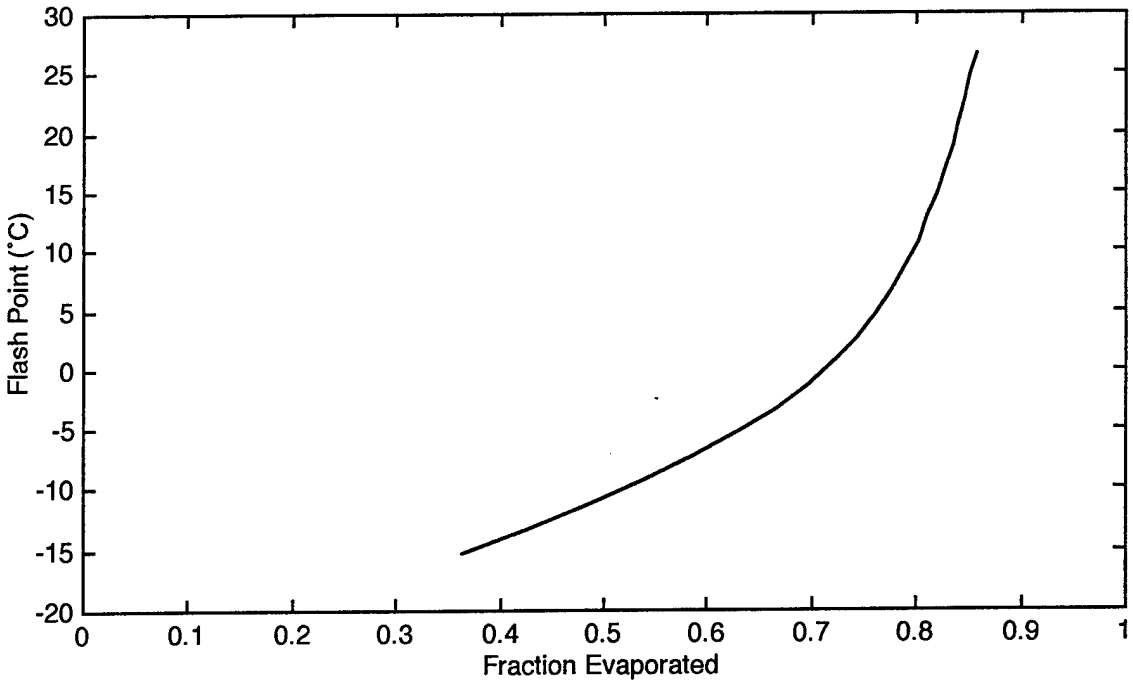

Figure 8. Flash point of gasoline as a function of mass fraction evaporated.

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APPENDIX A
FINITE DIFFERENCE FORMULATION

A numerical model was developed to find the time required for the flash point of an oil to reach or exceed 26.7°C (t_w) under various spill and environmental conditions. A correlation proposed by Butler et al. (1956) was used to estimate the flash point of weathered oils from the concentrations of the individual components,

$$\frac{\sum_i \left[\left(\frac{1}{L} \int_0^L C_i(z,t_w)dz \right) \cdot MW_i \cdot P \right]}{\sum_i \left(\frac{1}{L} \int_0^L C_i(z,t_w)dz \right)} = 104.7. \qquad \text{(A-1)}$$

The problem was reduced to finding the concentration of the components as a function of time and position. When oil weathers following a spill, the most volatile components evaporate from the surface at the fatest rate. Concentration gradients are established and drive a vertical diffusion within the oil layer. The vertical diffusion was modeled using the one-dimensional material balance equation with no sinks or sources (Hines and Maddox, 1985),

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (U^M \cdot C_i)}{\partial z}. \qquad \text{(A-2)}$$

At the oil-water interface (z=0) a zero-flux boundary condition was used:

$$\frac{\partial C_i}{\partial z}(0,t) = 0. \qquad \text{(A-3)}$$

At the oil-air interface (z=L) the liquid-phase flux was set equal to the evaporative flux; this was represented by a mixed boundary condition:

$$D_i \frac{\partial C_i}{\partial z}(L,t) + \left(h_i \cdot C_i(L,t)\right) = 0. \qquad \text{(A-4)}$$

where,

$$h_i \equiv \frac{K_{m,i} \cdot P_i}{R \cdot T_{air} \sum C_i(L,t)} \quad . \qquad \text{(A-5)}$$

The initial molar concentrations were the initial conditions derived from the distillation data:

$$C_i(z,0) = C_i^o. \qquad \text{(A-6)}$$

The following approximations were used:

i. advection was negligible (U^M=0);

ii. oil thickness was constant (L=constant);

iii. diffusivity was uniform.

An implicit finite-difference algorithm, specifically a "Backward-time, Centered-space" scheme (Hoffman, 1992), was used to solve the coupled diffusion equations for the concentrations of the components as a function of position and time. The vertical dimension was represented by z; the oil-water interface was at z=0, and the oil-air interface was at z=L. M evenly-spaced nodes were used. The first node was located at the oil-water interface; the M^{th} node was located at the oil-air interface.

The finite difference formulation of the diffusion equation took the form,

$$\frac{C_{i,m}^{p+1} - C_{i,m}^{p}}{\Delta t} = \frac{D_{i,m}^{p}}{\Delta z^2}\left(C_{i,m+1}^{p+1} - 2C_{i,m}^{p+1} + C_{i,m-1}^{p+1}\right) \qquad \text{(A-7)}$$

where i was used to specify the component, m the spatial node, and p the time increment.

At z=0 (m=1), the zero flux condition was written in a finite-difference form:

$$\frac{C_{i,2}^{p+1} - C_{i,0}^{p+1}}{2\Delta z} = 0. \qquad \text{(A-8)}$$

so $$C_{i,0}^{p+1} = C_{i,2}^{p+1}. \qquad \text{(A-9)}$$

This was substituted into the finite difference expression for m=1:

$$\frac{C_{i,1}^{p+1} - C_{i,1}^{p}}{\Delta t} = \frac{D_{i,1}^{p}}{\Delta z^2}\left(C_{i,2}^{p+1} - 2C_{i,1}^{p+1} + C_{i,2}^{p+1}\right). \qquad \text{(A-10)}$$

At z=h (m=M), the mixed boundary condition was written in finite-difference form:

$$\frac{C_{i,M+1}^{p+1} - C_{i,M-1}^{p+1}}{2\Delta z} = -\frac{h_i}{D_{i,M}^{p}} C_M^{p+1}. \qquad \text{(A-11)}$$

so $$C_{i,M+1}^{p+1} = C_{i,M-1}^{p+1} - \frac{2h_i \Delta z}{D_{i,M}^{p}} C_M^{p+1} \qquad \text{(A-12)}$$

This was substituted into the finite difference expression for m=M:

$$\frac{C_{i,M}^{p+1} - C_{i,M}^{p}}{\Delta t} = \frac{D_i}{\Delta z^2}\left(C_{i,M-1}^{p+1} - \frac{2h_i \Delta z}{D_{i,M}^{p}} C_{i,M}^{p+1} + C_{i,M-1}^{p+1} - 2C_{i,M}^{p+1}\right). \qquad \text{(A-13)}$$

Based on the known concentrations at some time step, p, the concentrations at the following time step, p+1, were solved using the following set of equations, where 1<m<M:

$$C_{i,1}^{p} = \left(1 + \frac{2D_{i,1}^{p}\Delta t}{\Delta z^2}\right) C_{i,1}^{p+1} + \left(-\frac{2D_{i,1}^{p}\Delta t}{\Delta z^2}\right) C_{i,2}^{p+1} \qquad \text{(A-14)}$$

$$C_{i,m}^{p} = \left(-\frac{D_{i,m}^{p}\Delta t}{\Delta z^2}\right) C_{i,m-1}^{p+1} + \left(1 + \frac{2D_{i,m}^{p}\Delta t}{\Delta z^2}\right) C_{i,m}^{p+1} + \left(-\frac{D_{i,m}^{p}\Delta t}{\Delta z^2}\right) C_{i,m+1}^{p+1} \qquad \text{(A-15)}$$

$$C_{i,M}^{p} = \left(-\frac{2D_{i,m}^{p}\Delta t}{\Delta z^{2}}\right) C_{i,M-1}^{p+1} + \left(1 + \frac{2D_{i,m}^{p}\Delta t}{\Delta z^{2}} + \frac{2h_{i}\Delta t}{\Delta z}\right) C_{i,M}^{p+1}. \qquad \text{(A-16)}$$

Below is an example of system with four nodes written in the form of a matrix equation:

$$\begin{bmatrix} (1+2\alpha_{i,1}) & (-2\alpha_{i,1}) & 0 & 0 \\ (-\alpha_{i,2}) & (1+2\alpha_{i,2}) & (-\alpha_{i,2}) & 0 \\ 0 & (-\alpha_{i,3}) & (1+2\alpha_{i,3}) & (-\alpha_{i,3}) \\ 0 & 0 & (-2\alpha_{i,4}) & (1+2\alpha_{i,4}+\beta_{i}) \end{bmatrix} \begin{bmatrix} C_{i,1}^{p+1} \\ C_{i,2}^{p+1} \\ C_{i,3}^{p+1} \\ C_{i,4}^{p+1} \end{bmatrix} = \begin{bmatrix} C_{i,1}^{p} \\ C_{i,2}^{p} \\ C_{i,3}^{p} \\ C_{i,4}^{p} \end{bmatrix} \qquad \text{(A-17)}$$

where
$$\alpha_{i,m} \equiv \frac{D_{i,m}^{p}\Delta t}{\Delta z^{2}}, \qquad \beta_{i} \equiv \frac{2h_{i}\Delta t}{\Delta z}. \qquad \text{(A-18)}$$

Both h_i and D_i are functions of time, and D_i can change by orders of magnitude over the course of the study. To address the time dependence, the matrix equation for the individual components was solved sequentially for each time step, and the values of h_i and D_i were updated at the end of each time step. In general, D_i is also a function of position; however, an average diffusivity based on the spatially averaged composition yielded very similar results to those found with spatially resolved diffusivity.

APPENDIX B
SERIES SOLUTION TO THE DIFFUSION EQUATION

The spacing of the nodes and size of the time steps in the finite difference formulation were adjusted so that the numerical errors were reduced to insignificance. The numerical errors were tested by comparing the finite-difference results with those obtained using an infinite series solution for the special case where the molecular diffusivity was constant. The following is a description of the series solution to this problem:

The following approximations were used to find the infinite-series solution:

i. advection was negligible ($U^M=0$);

ii. the molar concentration at the oil-air interface was constant over the time domain ($\sum C_i(L,t) = \text{constant}$);

iii. oil thickness was constant (L=constant);

iv. diffusivity was constant over time;

v. diffusivity was uniform.

Applying these approximations yielded the following partial differential equations and auxiliary conditions:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2}, \qquad \text{(B-1)}$$

with initial condition: $$C_i(z,0) = C_i^o, \qquad \text{(B-2)}$$

boundary condition at z=0: $$\frac{\partial C_i}{\partial z}(0,t) = 0, \qquad \text{(B-3)}$$

and boundary condition at z=L: $$D_i \frac{\partial C_i}{\partial z}(L,t) + \left(h_i \cdot C_i(L,t)\right) = 0, \qquad \text{(B-4)}$$

where,

$$h_i \equiv \frac{K_{m,i} \cdot P_i}{R \cdot T_{air} \sum C_i(L,t)} \quad . \tag{B-5}$$

These equations were reformulated in terms of dimensionless variables:

$$\frac{\partial \gamma_i}{\partial \tau} = \frac{\partial^2 \gamma_i}{\partial \xi^2} \tag{B-6}$$

where

$$\gamma_i \equiv \frac{C_i}{C_i^o}; \qquad \xi \equiv \frac{z}{L}; \qquad \tau_i \equiv \frac{D_i t}{L^2}. \tag{B-7}$$

The boundary condition at z=0 became:

$$\frac{\partial \gamma_i}{\partial \xi}(0,\tau) = 0. \tag{B-8}$$

And the boundary condition at z=L became:

$$\frac{\partial \gamma_i}{\partial \xi}(1,\tau) + Bi \cdot \gamma_i(1,\tau) = 0. \tag{B-9}$$

where the mass Biot number is a measure of the relative importance of diffusion versus evaporation and is defined

$$Bi_i \equiv \left(\frac{h_i \cdot L}{D_i}\right). \tag{B-10}$$

The initial condition became:

$$\gamma_i(\xi, 0) = 1 \tag{B-11}$$

In the initial formulation of the problem, the components were coupled through the boundary conditions. Approximation (ii) permitted them to be uncoupled. In this treatment, the Biot number was held constant. The equations for each component could then be solved independently.

For each time step the concentration of each component was calculated and averaged over the volume of the spill. These average concentrations were used to test the flash point condition. If the flash point was below 26.7°C (80°F) the time was incrementally stepped.

The solution of the partial differential equation for each component follows (the subscript specifying the component is omitted):

First the solution was separated into a product of a time and spatial function:

$$\gamma(\xi,\tau) = Y(\tau)Z(\xi). \tag{B-12}$$

Following a separation of variables, the equation in time was

$$\frac{dY}{d\tau} + \lambda^2 Y = 0 \qquad \text{with solutions: } Y = B \cdot e^{-\lambda^2 \tau}. \tag{B-13}$$

The equation in space was a Sturm-Liouville problem with eigenfunction solutions:

$$\frac{dZ}{d\xi} + \lambda^2 Z = 0 \tag{B-14}$$

with solutions:

$$Z = E\cos\lambda_n\xi + F_n \sin\lambda_n\xi. \tag{B-15}$$

The boundary condition at z=0 required that $F = 0$. From the other boundary condition the eigenvalues were found:

$$\frac{d(\cos\lambda_n\xi)}{d\xi}(1) + Bi \cdot \cos\lambda_n = 0. \tag{B-16}$$

The eigenvalues are the roots of the following equation:

$$\lambda_n \tan\lambda_n = Bi. \tag{B-17}$$

For very large values of Bi (Bi>1000), the eigenvalues approach $(2n-1)\pi/2$. For very small Bi the eigenvalues approach zero except the first which approach $\sqrt{Bi}$.

The solution to the partial differential equation was a product of the temporal and spatial parts

$$\chi(\xi,\tau)=\sum_{n=1}^{\infty}B_n e^{-\lambda_n^2\tau}\cos\lambda_n\xi. \tag{B-18}$$

The initial condition and the orthogonality of the eigenfunctions were used to find the coefficients in the expansion. Writing the initial condition, multiplying both sides by $\cos\lambda_m\xi$, and integrating over the domain:

$$\int_0^1 d\xi\cos\lambda_m\xi=\int_0^1 d\xi\cos\lambda_m\xi\sum_{n=1}^{\infty}B_n\cos\lambda_n\xi \tag{B-19}$$

so

$$B_n=\frac{4\sin\lambda_n}{2\lambda_n+\sin 2\lambda_n}. \tag{B-20}$$

The concentration of each component averaged over the oil was used to test the flash point:

$$\frac{1}{L}\int_0^L C_i(z)dz=C_i^o\int_0^1 d\xi\sum_{n=1}^{\infty}B_n e^{-\lambda_n^2\tau}\cos\lambda_n\xi. \tag{B-21}$$

Interchanging the order of integration and summation and carrying out the integration on the right-hand side (RHS):

$$\frac{1}{L}\int_0^L C_i(z)dz=C_i^o\sum_{n=1}^{\infty}B_n\frac{\sin\lambda_n}{\lambda_n}e^{-\lambda_n^2\tau} \tag{B-22}$$

so

$$\overline{C}_i \equiv \frac{1}{L}\int_0^L C_i(z)dz = C_i^o \sum_{n=1}^{\infty} \frac{4\sin^2\lambda_n}{2\lambda_n^2 + \lambda_n \sin 2\lambda_n} e^{-\lambda_n^2 \tau}. \qquad \text{(B-23)}$$

This series converges quickly so only a few terms were needed to adequately represent the series. Of course, there was an error associated with truncating the series, but it was readily measured and reduced. By comparing a 100 term expansion to the known value at τ=0 it was determined that 100 terms were adequate in evaluating the series. The series converges more quickly as with larger values of τ, so the 100 term expansion was treated as exact for all τ.

For large values of the Biot number (Bi>1000), and values of τ larger than 0.1, the spatially averaged concentration of a component was simply:

$$\overline{C}_i = \frac{8C_i^o}{\pi^2} e^{-\left(\frac{\pi}{2}\right)^2 \tau}. \qquad \text{(B-24)}$$

For small values of the Biot number the eigenvalues approach the square root of the Bi number. For values of τ larger than 0.1, the spatially averaged concentration of a component was simply:

$$\overline{C}_i = C_i^o e^{-h_i t/L}. \qquad \text{(B-25)}$$

This covers all cases: diffusion limited evaporation (large Bi), boundary layer limited evaporation (small Bi), and intermediate cases (.01<Bi<100).

The time required for the flash point of an oil to reach or exceed 26.7°C (t_w) based on the series solution concentrations was found to be in good agreement with that found using the finite difference formulation.

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APPENDIX C
PROPERTY DATA FOR OILS

The following data was extracted from the Environment Canada database (Jokuty, 1996) for use in this study.

Oil name:	Avalon Crude
API gravity:	36
Flash Point:	14 °C
Viscosity at 0 °C:	575 cP
Viscosity temperature constant ($k_{\eta,T}$):	20760 K
Viscosity evaporation constant ($k_{\eta,E}$):	18.42

Distillation Data:	Temperature (°C)	Fraction
	40	0.01
	60	0.02
	80	0.03
	100	0.06
	120	0.09
	140	0.12
	160	0.15
	180	0.19
	200	0.22
	250	0.31
	300	0.40
	400	0.58
	500	0.74
	600	0.87
	700	0.94

Oil name:	Arabian Light Crude
API gravity:	31.8
Flash Point:	-20 °C
Viscosity at 0 °C:	31 cP
Viscosity temperature constant ($k_{\eta,T}$):	4171 K
Viscosity evaporation constant ($k_{\eta,E}$):	7.934

Distillation Data:	Temperature (°C)	Fraction
	40	0.02
	80	0.05
	100	0.08
	120	0.12
	140	0.16
	160	0.19
	180	0.23
	200	0.26
	250	0.36
	300	0.45
	400	0.64
	500	0.80
	600	0.91
	700	0.99

Oil name:	South Pass Block 67 Crude
API gravity:	16.4
Flash Point:	-1 °C
Viscosity at 0 °C:	89 cP
Viscosity temperature constant ($k_{\eta,T}$):	4329 K
Viscosity evaporation constant ($k_{\eta,E}$):	2.263

Distillation Data:	Temperature (°C)	Fraction
	40	0.01
	60	0.02
	80	0.04
	100	0.08
	120	0.12
	140	0.16
	160	0.21
	180	0.26
	200	0.31
	250	0.42
	300	0.53
	400	0.72
	500	0.86
	600	0.95

Oil name:	West Texas Sour Crude
API gravity:	30.2
Flash Point:	-14 °C
Viscosity at 0 °C:	113 cP
Viscosity temperature constant ($k_{\eta,T}$):	11347 K
Viscosity evaporation constant ($k_{\eta,E}$):	7.057

Distillation Data:	Temperature (°C)	Fraction
	40	0.02
	80	0.04
	100	0.07
	120	0.09
	140	0.13
	160	0.15
	180	0.19
	200	0.22
	250	0.31
	300	0.40
	400	0.57
	500	0.73
	600	0.85
	700	0.92

Oil name:	Point Arguello Light Crude
API gravity:	30.3
Flash Point:	-6 °C
Viscosity at 0 °C:	70 cP
Viscosity temperature constant ($k_{\eta,T}$):	6073 K
Viscosity evaporation constant ($k_{\eta,E}$):	12.21

Distillation Data:	Temperature (°C)	Fraction
	60	0.01
	80	0.02
	100	0.04
	120	0.06
	140	0.07
	160	0.10
	180	0.13
	200	0.15
	250	0.23
	300	0.31
	400	0.48
	500	0.66
	600	0.80
	700	0.91

Product name: Gasoline

Viscosity at 0 °C: 0.5 cP

Distillation Data:	Temperature (°C)	Fraction
	40	0.26
	60	0.30
	80	0.44
	100	0.70
	120	0.84
	140	0.85
	160	0.88
	180	0.95
	200	0.98