Appendix V

Review of the Processes and Factors for Estimating Time Windows for In-situ Burning of Spilled Oil at Sea

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Abstract. This appendix discusses processes and factors for estimating time period windows of in-situ burning of spilled oil at sea. Time periods of in-situ burning of Alaska North Slope (ANS) crude oil are estimated using available data. Three crucial steps are identified. The first step is to determine the time it takes for the evaporative loss to reach the known or established limitation for evaporation and compare this time period with estimated time of ignition at the ambient wind and sea temperatures. The second step is to determine the water uptake of the spilled oil and compare it with the known or established limitation for water-in-oil content. The third step is to determine the necessary heat load from the igniter to bring the surface temperature of the spilled oil to its flash point temperature so that it will burn at the estimated time of ignition of the slick.

Keywords: In-situ burning, oil spills, processes, factors, time periods, windows-of-opportunity, igniters, gelled gasoline, heat load.

Introduction

Historical Perspective

In-situ burning of oil is defined as the "controlled" burning of spilled oil either on water, or wetlands and marshes, in which the direct burning of the oil is a more effective process for removing oil from the aquatic environment than other available technologies. Initially the interest in in-situ burning came from the experience of some of the early large accidental oil spills in which the oil that contaminated shorelines caused extensive environmental damage and resulted in very high clean-up costs.

An example of early success with in-situ burning during the *Exxon Valdez* clean-up was when 15,000 to 30,000 gallons of the spilled oil was held in a fire boom and

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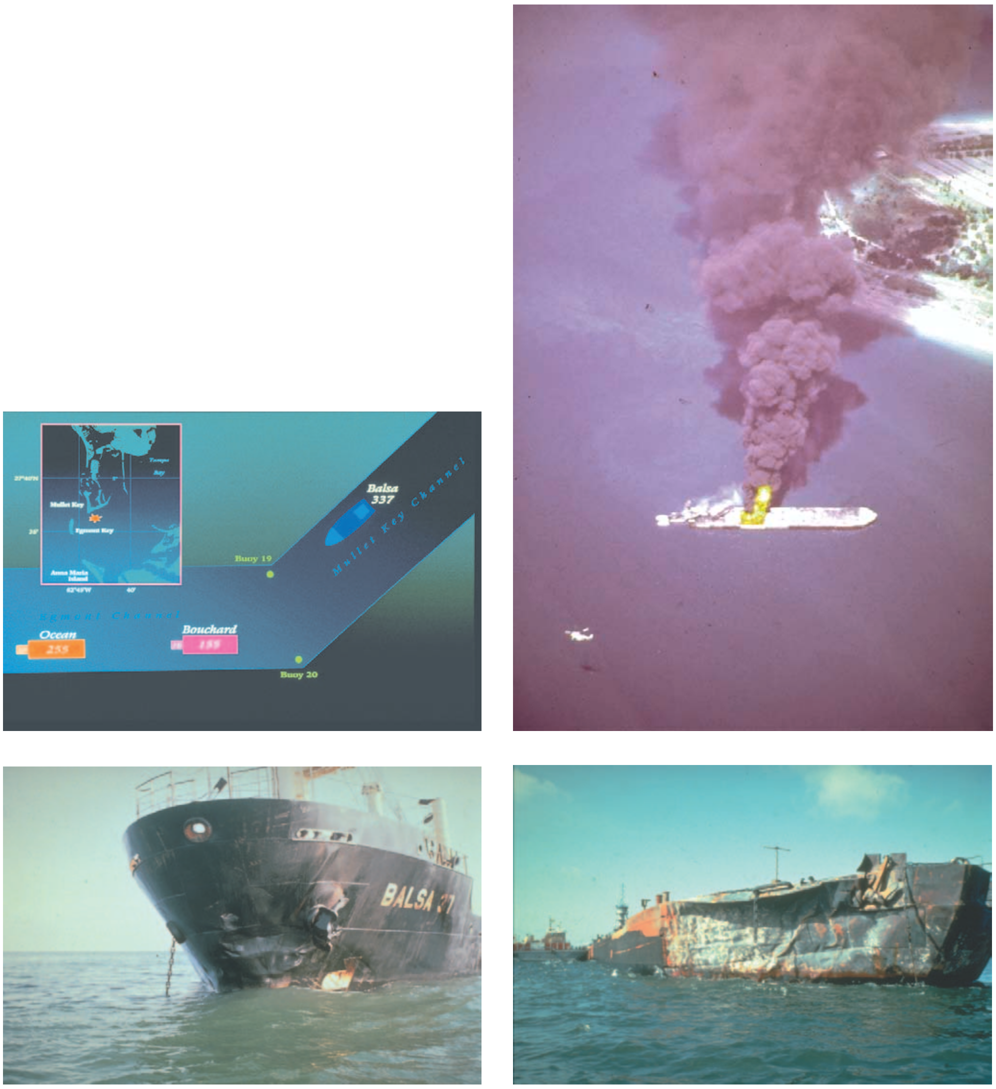
burned in about 75 minutes with an estimated 98% efficiency leaving about 300 gallons of a stiff, taffy-like burn residue that could be picked up easily upon completion of the burn (Allen, 1990).

In August 1993, a large-scale open ocean burn was conducted 42 km (25 nmi) east of the port of St. John's, Newfoundland. This in-situ burn project was commonly called the Newfoundland Oil Burn Experiment (NOBE). This field trial and demonstration project was conducted with the participation of some 35 agencies from Canada and the US with sponsors from government, the oil industry and private institutions as led by Environment Canada. The projects objectives were to: (1) obtain critical data and information on burn parameters and to collect and analyze chemical emissions needed for comparison with data sets and models that are currently based on laboratory and medium-scale tests; (2) obtain samples for analysis of the smoke plume, water, and gaseous emissions needed to determine whether the environmental impact of burning is acceptable; (3) gain experience from conducting a large-scale oil burning experiment in realistic open ocean conditions to demonstrate contained burning as a spill response technique; and (4) develop a response protocol that will establish operational strategies for burning and safety procedures under a variety of environmental and operational conditions (Fingas et al., 1994). Findings were that they were able to burn spilled oil in two tests at rates between 600 and 900 liters a minute with >99% efficiency. Some compounds in the oil of concern were detected up to 150 meters downwind. Only particulate matter/soot was a concern near the burn area and of no concern 500 meters downwind. Results of aquatic toxicity testing were too low to be measured. PAHs were found to be lower in the soot than in the starting oil and were consumed by the fire to a large degree (Fingas, 1995a, b).

Subsequently, LaBelle et al. (1994) suggested that the 1993 oil spill (*Bouchard B-155*) off Tampa Bay merited consideration for in-situ burning. Ross et al. (1995) in an unpublished MSRC report suggested that in-situ burning could be more effective than mechanical clean-up in removing oil from water. Additional benefits were the speed of the process and the minimization of waste recovered. Concern for air pollution and human health risks was the major concern.

McCourt et al. (2000) tested seventeen crude oils over a 5-year period in laboratory and controlled burns as candidates for in-situ burning. They have published a table of their results and found that, in general, oils with an API gravity of less than 20 will burn only under optimum conditions and that oils with an API gravity of greater than 35 should burn easily.

In addition, a feasibility study was conducted by Yoshioka et al. (1999) to assess if some of the past-historical oil spills (141 spills) could have been a candidate for in-situ burning using a set of criteria that they developed to make the assessment: (1) oil weathering; (2) response logistics; (3) weather; and (4) distance to populated areas. Each spill was reviewed on the basis of the established criteria and assigned a pass or fail rating. They then used a second process in which those that met the above first phase criteria were then subjected to a second phase of more critical more site-



On 10 August 1993, three ships collided in Tampa Bay, Florida: the *Bouchard B155* barge (on fire), the freighter *Balsa 37*, and the barge *Ocean 255*. The *Bouchard B155* spilled and estimated 336,000 gallons of No. 6 fuel oil into Tampa Bay. The barge *Ocean 255* after the collision is the 4th photograph. Photographs courtesy of NOAA Office of Response and Restoration.

specific data and information. Their final results identified that 10% (14 out of 141) of the historical oil spills that they reviewed were good candidates for in-situ burning.

PCCI (1999) conducted an assessment funded by the USCG to delineate the natural conditions affecting the success on in-situ burning of spilled oil using three criteria: (1) time from spill to ignition (oil evaporation and dispersion); (2) degree of emulsification as a limiting factor (water uptake); and (3) conditions that affect operations (weather). This report focused on API gravity and grouped oils and recommended that heavy crude oils (i.e., Mundulay, Merey, No. 6 fuel oil, Bunker C which range from 17 to 10 API gravity) were good candidates for in-situ burning.

In the US today, about 1/3 of the recent in-situ burning of accidentally spilled oil have been in Gulf Coast (Texas & Louisiana) coastal areas in estuaries and marshes where the focus has been on preventing long-term environmental damage to estuarine organisms and marsh plants by burning the oil. A comprehensive summary of the environmental effects of in-situ burning of some 30 inland and upland marsh oil spills was funded and published by the American Petroleum Institute (Dahlin et al., 1999). An example is the pipeline oil spill in Upper Copano Bay, Texas (Tunnell et al., 1995). In many of these cases, in-situ burning was used because the burning removed the oil quickly and prevented spreading into more sensitive areas or over large areas, and reduces the amount of oily waste for collection and disposal. In sites where limited access to the spill site reduces the feasibility of mechanical or manual recovery, burning would be a final measure or last resort, where mechanical recovery poses a greater threat to the environment (Dahlin et al., 1995) and where dispersants do not work (Walton, 2002, personal communication).

Open water in-situ burning experience from accidental oil spills is very limited. However, several recent large spills might have merited consideration of using in-situ burning to remove some of the spilled oil (the *Jessica* oil spill off the Galapagos and the Petrobras 36 Platform in the Roncador Field, Campos Basin) for the protection of the environment.

This appendix has been prepared to review in-situ burning and to focus on the mechanism and the process, and to identify the steps involved in using in-situ burning as an oil spill clean-up and response management tool and to work up a model example for an oil for which there are sufficient data and information to identify the time periods of the window-of-opportunity for this oil under selected environmental conditions.

In-situ Burning of Spilled Oil

The primary purpose of in-situ burning and any oil spill response operation is to protect the environment, wildlife resources, and human health and safety by removing oil quickly and effectively from the sea surface. Even though research and development within the area of in-situ burning has taken place for decades, there is still missing information for responders to fully estimate the time window-of-opportunity for utilization of in-situ burning as a clean-up method/technology in oil spill response with certain degree of accuracy.

API gravity has been used in feasibility studies to demonstrate the possibilities of success of in-situ burning. Even though API gravity has been used in the literature as a relative measure of volatility, it is not directly linked to vaporization and parameters determining ignitability. In-situ burning can be considered a viable oil spill response method only if data on ignitability for fresh and weathered crude oils and refined products are available, and the heat load required for ignition is known, to estimate the time periods of window-of-opportunity in contingency planning and response. For in-situ burning, this requires the development of an ignitability database based upon basic physical and chemical processes of weathered oil. It is pointless to consider the use of in-situ burning as a response in circumstances where it will not be feasible, such as where the oil will not burn. Several groups of key factors determine the success of an in-situ burning operation.

The first group of factors is related to flammability and ignitability of floating oils and are tied to oil composition and molecular weight, vapor pressure, vaporization rate, flash point, boiling point, and temperature and air movements (wind).

The second group is related to the changes in oil properties due to oil weathering during the response time, defined as the time from the onset of the spill to ignition. Weathering processes that have great influence on ignitability and effectiveness of in-situ burning are evaporation and emulsification.

The third group contains operational and technical considerations, and includes the capability of the resources (vessel and booms) to contain and thicken floating oil, durability of fire resistant booms and the capabilities of the ignition source to elevate the oil surface temperature to the fire point temperatures where burnable vapor–air mixtures can be developed.

Results from measurements of oil surface temperatures during experimental burns, coupled with dynamic flash point and evaporation data, are useful for estimation of ignitability. Current igniters are limited in their ability to produce or influence the volatilization rate of oils required to sustain burning. This limitation in current technologies may be a major reason why ignition of many weathered oils have failed, and not necessarily the weathering process itself (Walavalkar and Kulkarni, 2000). Use of in-situ burning requires knowledge and understanding of the basic processes that limit and lead to the formation of ignitable vapor–air mixtures, and how changes in oil composition will affect ignition and sustained burning.

Development of Flammable Vapor

The first group of factors is related to the chemical and physical properties of oil, in particular, factors related to flammability and ignitability. The vapor from a flammable liquid and the ease of ignition, as well as the rate of burning, is dependent upon the inter-related properties such as *vapor pressure*, *vaporization rate*, *boiling point*, and *flash point* (NFPA, 1997).

Vapor Pressure and Boiling Point

The vapor pressure is determined by the kinetic energy of molecules, and is a measure of a liquid volatility or ability to vaporize. If the liquid is in a closed container, the molecules are confined in the vapor space, and a point of equilibrium is reached when the rate of escape of molecules equals the rate of their return to the liquid. The pressure exerted by the vapor at the point of equilibrium is called the *vapor pressure*. A high vapor pressure is usually an indicator of a volatile liquid, or one that readily vaporizes and forms ignitable vapor. The pressure is often referred to as Reid Vapor Pressure (RVP). For example, for gasoline it can vary from 7.0 psi (summer) to 15.0 psi (winter), which is a result of special additives to meet governmental regulations and efficiency of combustion.

In the open air, a liquid will boil when its vapor pressure equals atmospheric pressure, and the corresponding temperature is known as *the boiling point*. When the temperature reaches the boiling point, the average kinetic energy of the liquid is sufficient to overcome the forces of attraction that hold molecules in the liquid state. A high boiling point indicates low vapor pressure and volatility at ambient temperature. Therefore, an oil's boiling point depends on its vapor pressure, which is a function of molecular weight, chemical structure and temperature.

Formation of Flammable Vapor and Vapor–Air Specific Gravity

Vapor–air specific gravity is the ratio of the weight of a vapor-in-air mixture (resulting from the vaporization of a liquid at equilibrium temperature and pressure) to the weight of an equal amount of air under the same conditions. The specific gravity (density) of a vapor–air mixture thus depends upon the ambient temperature, the vapor pressure of the liquid at the ambient temperature, and the molecular weight of the liquid (the molecular weight of a compound is the sum of the atomic weights of all atoms in its molecule). Low molecular weight oil components have higher vapor pressure, and *lower boiling points*, than higher molecular weight components of similar oils.

If an oil's temperature is well below its boiling point, the vapor pressure may be so low that the vapor–air mixture, consisting mostly of air, has a density that approximates that of pure air (vapor–air specific gravity near 1). As the temperature of the oil increases to the boiling point, the rate of vaporization increases, the vapor displaces the surrounding air, and the vapor–air mixture specific gravity approaches that of the pure vapor specific gravity. A vapor–air mixture with a density significantly above that of air will be heavier and sink (seek lower levels). The density of a vapor–air mixture is therefore often used to evaluate the potential for flame spreading.

Combustion and Ignition—Flash Point and Fire Point Temperatures

Combustion of oil is a self-sustaining reaction involving oxidation of fuel vapor by atmospheric oxygen, in which combustion takes place in the region where vapor and oxygen is mixing just above the oil surface.

Ignition of oil is the process by which self-sustaining combustion may occur if the heat flux is great enough to raise the oil to its flash point. To ignite spilled oil, thermal energy (heat) may be supplied in the vicinity of the surface to convert a sufficient part of the oil to vapor that can be mixed with air to a flammable vapor–air mixture. The minimum oil temperature that is capable of generating a flammable vapor–air mixture is called the *flash point*. The flash point of a liquid corresponds roughly with the lowest temperature at which the vapor pressure is just sufficient to produce a flammable mixture (vapor and air) at the lower limit of flammability. The flash point depends on the proportion of low molecular weight components, and is the most commonly used parameter for evaluation of flammability.

To develop a sustained burn, the temperature of the oil has to be elevated to its *fire point*, where the *vaporization rate* is sufficient to create flammable vapor–air mixtures. The fire point may be defined as the lowest temperature of the liquid at which vapor evolves fast enough to support sustained burning. The fire point is usually a few degrees above the flash point. For typical fuels, the minimum rate of vaporization required to support combustion is of the order of 2 g/m^2 (NFPA, 1997).

The Limits of Flammability

Ignitable vapor–air mixtures occur when the concentration of vapor in air is within two defined limiting percentages, commonly referred to as the flammable range. Within the limits of flammability, combustion of the vapor concentration will continue to propagate at the specific temperature and pressure. The limits of flammability are referred to as the lower (lean) limit (LFL) and the upper (rich) flammability limit (UFL). Below the lower flammability limit, the temperature, and vaporization rate is insufficient to form flammable vapor–air mixtures. There is also a maximum temperature above which the fuel concentration is too high to propagate flame. For in-situ burning this limit is unlikely to occur. Figure V.1 on the next page illustrates the limits of flammability and the lower and upper flash point temperatures.

The term LFL describes the minimum concentration of vapor to air below which propagation of a flame will not occur in the presence of an ignition source. When a liquid is present in a closed container with an atmosphere of vapor–air mixture above the surface, the percentage of vapor in the mixture may be determined from the vapor pressure. The percentage of oil vapor is directly proportional to the relationship between the vapor pressure of the liquid and the total pressure of the vapor–air mixture (at normal atmospheric pressure). If the vapor pressure at the flash point temperature is known, the lower flammable limit for the vapor in percent by volume at normal atmospheric pressure can be calculated.

Vapor pressure data at flash point temperatures are useful for evaluation of ignitability of floating oils. However, measurement of vapor pressure at flash point temperatures are usually not part of standard oil weathering monitoring procedures for the assessment of ignitability of floating oil.

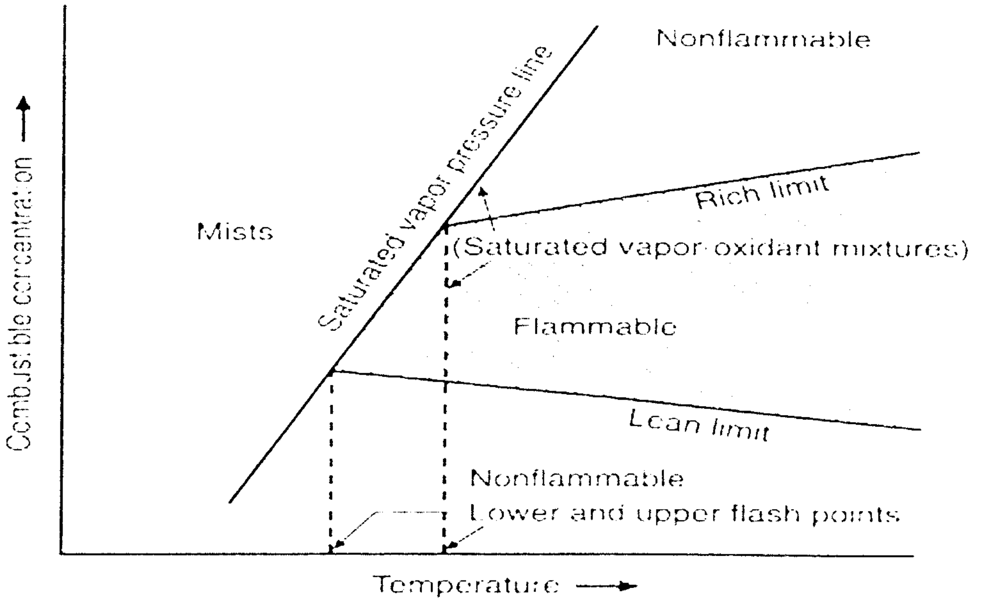


Fig. V.1. A plot presenting the limits of flammability and lower and upper flash point temperatures.

Temperature Range and Flammability of Floating Oils

Spilled oil will rapidly transfer heat until it reaches the surface seawater temperature, which can vary between −1 and 28 °C in US coastal waters, depending on location and time of the year. The difference between oil temperature and oil flash point temperature (where the vaporization rate is just sufficient to create flammable vapor–air mixtures) is the temperature increase and is related to the quantity of energy required by the ignition device to develop flammable vapor–air mixtures. Oils with flash points below the ambient sea temperature can easily be ignited and have much faster rates of flame propagation, than oils with flash points above ambient sea temperature. Oils with flash points above ambient sea temperature need to be heated to form flammable vapor–air mixtures before the flame will spread through the vapor.

Radiation, Elevation of Oil Surface Temperature and Heat Sink vs. Oil Thickness

Once the oil has been ignited, radiant heat will elevate the temperature of the oil that is adjacent to the heat source, and bring the remaining oil at the surface to above its fire point temperature. Even though, only approximately 3% of the heat from a burning oil slick is radiated back to the surface, the oil surface temperature may increase to several hundred degrees centigrade (Ross et al., 1995). Results from experimental burn tests with unemulsified Statfjord crude oil at 3 °C sea surface temperature, with thickness 5, 10, 20 and 30 mm, resulted in oil surface temperatures of approximately 150, 200, 325 and 450 °C respectively (Guénette et al., 1994). Prior evaporation of spilled oil does not diminish the potential for in-situ burning, as long as the temperature of the surface of the oil can be elevated to above the oils flash point temperature. If flash point temperatures are below the temperatures created from a fully developed burn by radiation, for example 200 °C, then sustainable burning can occur, if not then the oil may not be ignitable.

Oil thickness is important to insulate the oil slick from heat loss to the seawater below it. Studies have concluded that the oil thickness necessary to provide insulation between oil and water surface for fresh crude and light refined products is 1–3 mm, for diesel oil 3–5 mm, and for Bunker C/Fuel oil No. 6 and emulsified oils are 5–10 mm (Buist, 1999; Ross et al., 1995). The thickness of the floating oil is also critical to reduce heat loss to the surface of the sea, which can cool the oil below the flash point temperature and terminate flammability.

The increased heat loss from the surface of the oil is caused by reduced insulation from the water droplets in the oil, resulting in reduced oil surface temperature during burning.

As mentioned, oil surface temperatures, measured during experimental burns for fresh oils range from 150 to 450 °C (dependent on oil thickness). However, Ross et al. (1995) found that for emulsions, they only ranged between 100 and 250 °C. This indicates that emulsified oil with a flash point above the 250 °C will not receive sufficient heat radiation during burning to keep the surface of the oil above its flash point temperature.

Figure V.2 presents an illustration of a cross-section of an in-situ burning emulsified oil.

Refined Oils and Their Ranges of Flash Points

With refined products, the ranges of flash points are known and are used to separate out the product. This information can be used to estimate the potential for burning, because the surface temperatures of burning oils has been established. Refining is the process of separating the many groups of compounds present in crude oils. During refining, the crude is heated and changed into gases in a distillation tower. When a compound in a gaseous state cools below its boiling point, it condenses into liquid, and is drawn off the tower. The various groups of oils from the distillation tower is further processed and blended to provide commercial products to fit standard specifications such as flash point, viscosity, sulfur content and density/API gravity. Figure V.3 illustrates the distillation process, groups of refined gases and oils with boiling point ranges and c-values (Ophardt, from
http://www.elmhurst.edu/ chm/onlcourse/chm110/outlines/distill.html).

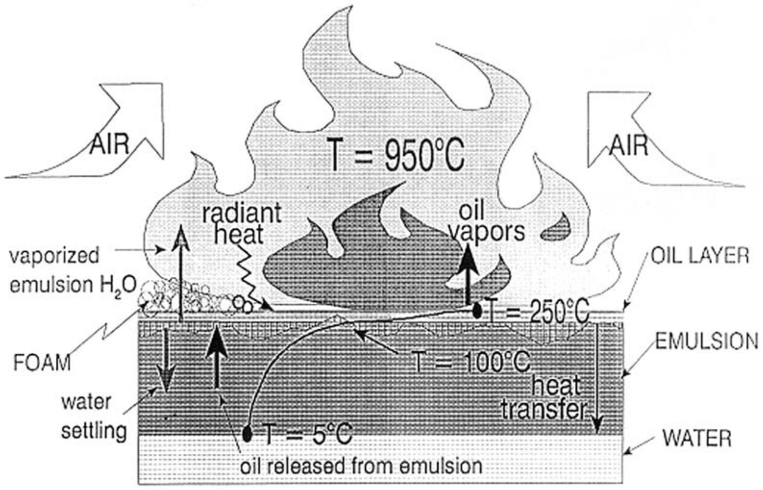


Fig. V.2. Diagram of the cross-section of in-situ burning of an emulsion to demonstrate heat transfer and burning.

Refined products are divided in two classes as flammable and combustible with defined flash point ranges. Class I flammable liquids are defined as those fluids with flash point below 37.8 °C and vapor pressure below 40 psi. Class I liquids are subdivided and Class IA includes liquids with flash points below 22.8 °C (73 °F) and a boiling point below 37.8 °C (100 °F). Class IB includes those having flash points below 73 °F (22.8 °C) and boiling point at or above 100 °F (37.8 °C). Class IC includes liquids with flash points at or above 73 °F (22.8 °C) and below 37.8 °C (100 °F).

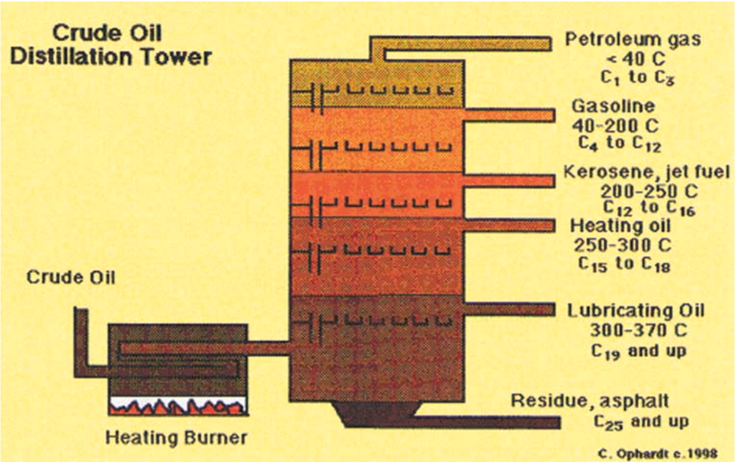


Fig. V.3. Illustration of the distillation process with groups of refined products, boiling point range and c-values (number of carbon atoms).

Combustible liquids are those with flash point at or above 37.8 °C, and are subdivided in Class II, with flash point between 37.8 °C (100 °F) and below 60 °C (140 °F), and Class IIIA with flash points between 60 °C (140 °F) and 93.4 °C (200 °F).

The highly flammable and combustible products in Class I, includes gasoline and liquid gases such as propane and butane. These products spread and evaporate very quickly and represent great fire and safety risks, and are therefore not included as products for in-situ burning. Refined product spills that could be considered for in-situ burning includes the combustible products in Group II, with flash point temperature range from 37.8 to 93.4 °C (73 to 200 °F).

Weathering of Oil

Weathering of oil influences ignitability, sustained burning, and effectiveness of in-situ burning and represents the second group of key factors. Until the studies of Wu et al. (1998), the influence of weathering and the formation of oil/water emulsions on flash and fire points had not been studied. The major weathering processes include evaporation, water-in-oil emulsification, spreading, and dispersion (oil-in-water emulsion). All of these four processes are very incident (oil spill) and oil specific, and occur progressively as oil weathers at rates, that depend on the oil composition and ambient environmental conditions. Dispersion is not a factor related to ignitability of floating oil, but is used in combination with evaporation and emulsification in mass balance calculations to estimate amounts of oil remaining on the sea surface.

Weathering effects are different for crude oils and refined products due to the differences in low molecular weight compounds, evaporation rates, flash point temperature ranges, and compounds determining the emulsification process. In order to estimate ignitability, it is important to differentiate between:

- Continuous release (fresh);
- Evaporated spilled oils (non-continuous); and
- Evaporated and emulsified oils.

Continuous release spills (fresh) will most likely keep the in-situ burning window-of-opportunity open due to the short weathering exposure before ignition. Evaporated spilled oils (non-continuous) are most likely ignitable up to 2–5 days after a spill, while evaporated and emulsified oils are difficult to ignite with current ignition technologies within 1–2 days.

Evaporation and Increase in Flash Point

The rate of evaporation of an oil slick and the volume of oil lost are dependent on

Table V.1.
Presentation of boiling point and flash point ranges for indicated refined fuels

Light refinery oils	Boiling point range (°C)	Flash point range (°C)
Gasoline	30–180	<40
Diesel	149–312	37.8–60
Kerosene	151–301	37.8–70

the vapor pressure of the oil, ambient air and sea temperature, wind, water content of any emulsion, and thickness of the oil film. The important result of evaporation is that the remaining oil at the sea surface changes the physical-chemical characteristics by increasing the flash point, boiling point, viscosity and density.

In general, most components of spilled oil with boiling points lower than 200 °C (up to C12) will evaporate within 12–24 hours, while components with boiling points up to 270 °C (less than C16) will disappear from the spill within several days. Light refinery products such as gasoline, diesel and kerosene will evaporate after some hours or a few days on the sea surface. Evaporation is defined as a percentage of volume lost. See Table V.1.

Studies of ignitability in experimental test burns have suggested that approximately 30% evaporation is the upper range for ignition of emulsions (Buist, 1999). However, because evaporation is not related to a specific flash point temperature, we suggest that it is not an appropriate measure to estimate ignitability of emulsified oils. A point of contention is that an oil can reach its flash point, but in high winds will not ignite because of the dilution of vapors. But flash point is the most appropriate measure of ignitability and will determine if an oil will burn.

The flash point temperature for various fresh crude oils are in the range of −40 to +30 °C, and increases rapidly in the first hours after being spilled. Figure V.4 presents a plot of flash point data versus time for six selected crude oils at wind velocity 5 m/s and sea temperature 15 °C. The flash point temperatures of the oils presented in Figure V.4 will increase after the first 24 hours by approximately 25–30 °C within the next 2–5 days (Strøm-Kristiansen et al., 1993).

Even though the flash point temperature for the evaporated oils still after 5 days may be ignitable, the emulsification process may prevent or make ignition difficult (see below).

Emulsification

The emulsification process makes ignition and burning of oils more difficult. The water content in emulsified oil:

- Reduces vaporization of ignitable gases;

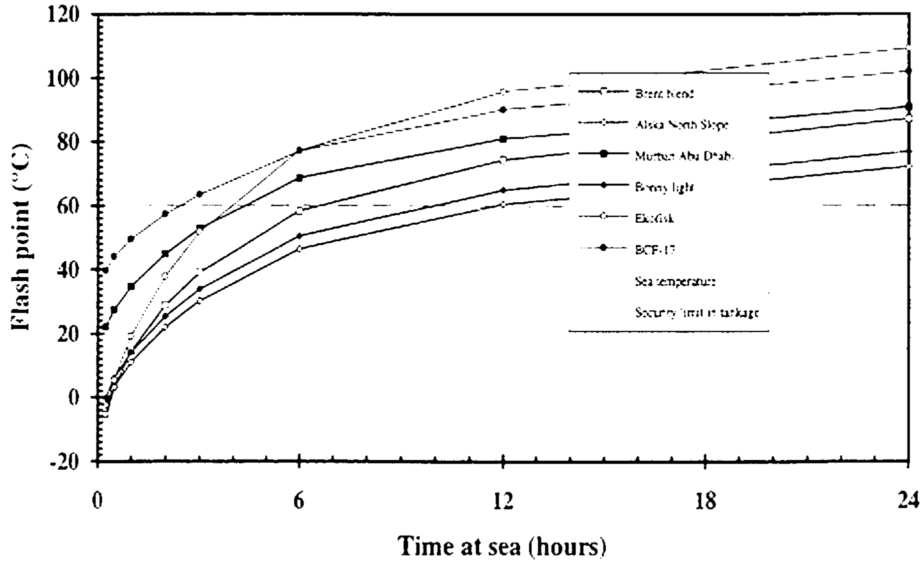


Fig. V.4. Increase in the flash point temperature within the first 24 hours at sea for six selected crude oils at wind velocity 5 m/s and sea temperature 15 °C.

- Reduces the rate of evaporation and combustible concentration of gases;
- Reduces flame temperature;
- Reduces burn rate and burn efficiency; and
- Increases the heat loss, oil viscosity and emulsion stability.

The burn efficiency depends on the water content in the oil, emulsion stability, and the flash point of the oil at various degrees of evaporation. The emulsification process is initiated at wind velocities above 2–3 m/s and may result in water-in-oil content between 20 and 70% within 6–12 hours after a spill, depending upon wind velocity and oil composition. Figure V.5 illustrates the emulsification process over time.

An emulsion is generally unstable in the early period of a spill and becomes more stable with evaporation and increased viscosity (Fingas et al., 1998). Important compounds in oils that determine water-in-oil emulsification and emulsion stability are resins, waxes and asphaltenes, and some suspended particles in the ocean. The term stability is used to define an emulsions capability to maintain water content. When the water droplet size in emulsified oils have reached a sufficiently small size so that the forces of gravity cannot naturally separate them, the emulsion is termed stable. Figure V.6 is a microscopic view of water droplet size in an emulsion after 1 and 24 hours.

The emulsification process is reversible and crude oil emulsions can be broken by radiant heat and/or chemically by demulsifiers (emulsion breakers). Laboratory testing has indicated that some stable crude oil emulsions, within 2–5 days after a spill, dehydrate when the emulsion temperature is elevated to approximately 50 °C.

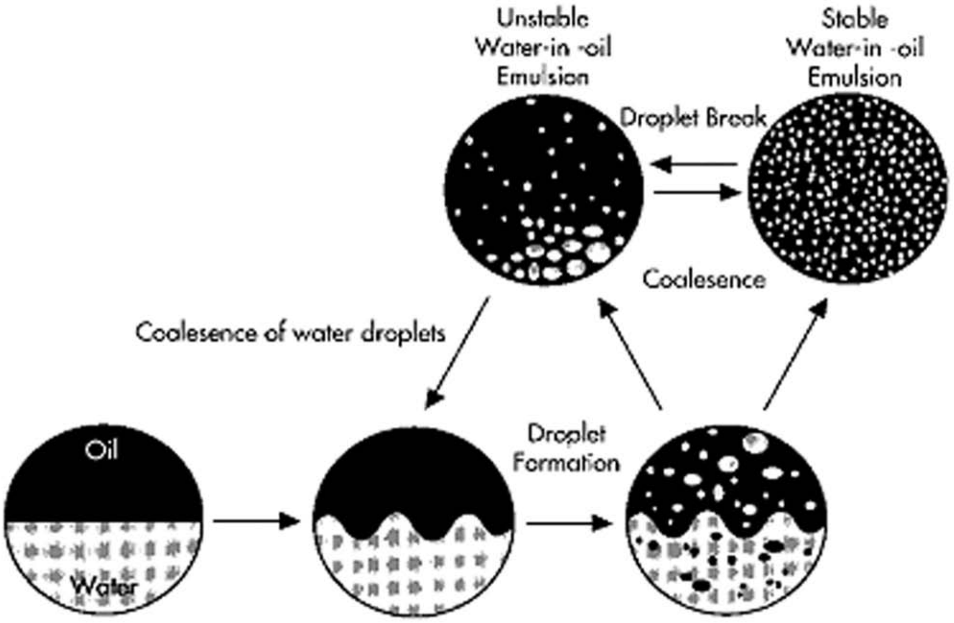


Fig. V.5. Illustration of the formation of an emulsion as a spilled oil weathers into a stable water-in-oil emulsion, which can incorporate up to 70–80% water in oil over time (Lee, 1999).

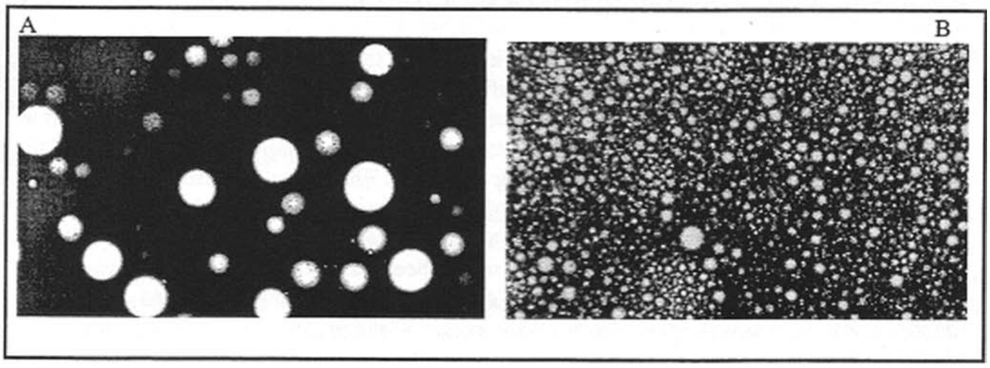


Fig. V.6. Microscopic view of water droplet size in an unstable emulsion after 1 hour at sea (left), and after 24 hours following stabilization (right) of the same oil (Strøm-Kristiansen et al., 1993).

Lighter refined products like gasoline, jet kerosene, diesel, and heating oils do not emulsify to any degree that affect ignition and in-situ burning. Heavier fuel oils emulsify to approximately 40–50% or 60% water content in very windy conditions and less during calmer conditions (Strøm-Kristiansen at al., 1994).

In-situ burning of emulsions develops vapor and steam at the surface (generally with no combustible content) when the temperature of the oil emulsion approaches the boiling point of water. Water vapor or steam absorbs radiant heat from the igniter or burning oil. The water vapor or steam and smoke generated may therefore reduce the heating of the oil surface and make ignition and sustained burning of emulsions difficult, and in particular, for oils with flash points above 100 °C.

Ignition of emulsions with higher stability, viscosity, limited insulation and lower oil surface temperature, require higher radiant heat load igniters and extended ignition time to increase oil temperature to its flash point and flame temperature to expedite burning.

Stable emulsions are more difficult to ignite than medium and low stability emulsions. A microscope view of a stable emulsion indicates that approximately 70% of the oil surface area is covered by water droplets, surrounded by a thin oil film, that limits the vaporization of ignitable vapor. The limit of ignitability and sustained burning of oils that have formed various degrees of stable emulsions needs to be determined by quantitative and qualitative tests using standardized test methods.

Even though data are not now available to predict, with a high degree of accuracy, the exact time window-of-opportunity (±60 minutes) for in-situ ignition and burning, windows have been estimated by using correlating data. Such data indicate that stable emulsions are difficult to ignite with more than 25% water, while unstable crude oil emulsions with 60% water content can sometimes be easily ignited (Guénette et al., 1994).

Water Removal Processes During Burning

The processes of reducing the water content from oils of various degrees of emulsification (stability) are different (Guénette at al., 1994; Strøm-Kristiansen at al., 1994). For unstable emulsions, the water drains off the oil by gravity separation, while water in stable emulsions form steam at the surface, reducing the flame temperature and radiant heat.

Operational and Technical Considerations

The third group of factors includes the capability of the resources (vessel and booms) to contain floating oil in various wind and sea states, the durability of fire resistant booms and the capabilities of the ignition source to elevate the temperature of the surface of the oil to the flame point temperature where ignitable vapor can be developed.

It has been observed that wind speed and direction can have a positive effect on flame spreading. However, excessive wind can make ignition and sustained burning difficult, and waves can prevent ignition of marginally ignitable oils and stable emulsions by creating thinner oil layers at the top of the crest and by speeding up the rate of emulsification.

Operational Considerations

Listed below are the major advantages and disadvantages presented in the ASTM standard guide for in-situ burning (ASTM F1788-97).

Advantages of in-situ burning include the following:

- Rapid removal of oil from the water surface;
- Requirement of less equipment and labor than many other techniques;
- Minimal storage and disposal requirement for the recovered burn residue;
- Significant removal of volatile emission components; and
- May be the only solution possible, such as in oil-in-ice situations?

Disadvantages of in-situ burning include the following:

- Creation of a smoke plume;
- Residues of the burn must be dealt with;
- Time in which to ignite the oil may be limited;
- Oil must be a minimum thickness to burn, which may require containment; and
- The fire may spread to other combustible materials.

The valid arguments for considering in-situ burning as a response measure are that it extends the options for response by decreasing the dependency on recovered oil and water storage and disposal needs and costs. The latter remains a limiting factor for large catastrophic spills at sea. From an operational point of view, major concerns have been related to the likelihood of conducting a successful in-situ burning operation. Factors of concern are:

- Response in a timely manner to meet the window-of-opportunity;
- Difficulties associated with igniting emulsified oil slicks;
- Relies of heavy smoke and soot;
- Distance of burning oil to populated areas (smoke and secondary fires);
- The fate of unburned residue; and
- Thermal durability and seaworthiness of fire resistant booms.

Even though ignition of weathered and emulsified oil may be difficult, application of ignition and combustion promoters, such as diesel or other liquids with lower flash points than the spilled oil, may extend or open the time window. The emulsification process can be reversed by the use of heat and/or emulsion breakers (Strøm-Kristiansen et al., 1995). A promising “break and burn” technique utilizing emulsion breakers and heat has been successfully demonstrated during tank and field tests in Canada (Buist et al., 1996), Spitsbergen (Guénette et al., 1994) and the UK (Thornborough et al., 1997). However, break and burn application technologies (spray guns and mixers) to extend the time window from vessels are not currently available for practical operations.

Igniters and Missing Specifications

Many different ignition devices have been tested over the last several decades without providing responders with information required for evaluation of ignitability. Igniter heat loads and burning time limitations are factors that have resulted in many failures to ignite an oil slick. Evaporated and emulsified oils require longer ignition time and higher heat loads than fresh and less weathered oils. Methods to improve ignition devices to extend the time window for in-situ burning have successfully included mixing of gelled fuel and emulsion breakers to rapidly remove water by gravity settling, resulting in reduced formation of steam during ignition and burning. However, key data that are not available for evaluation of igniters include: *heat loads* (*heat production*), *heat flux* (ΔT °C) *created on the surface of the oil*, *oil surface area heated*, and *data on oil temperature increase* to evaluate if the igniter is capable of closing the gap between the sea temperature and flame point temperature.

Fire Resistant Booms

Unconfined slick spreading will rapidly result in oil layers of less than 1 mm, and the minimum oil thickness for ignition has been found to be 1–3 mm (Buist, 1999). This is also the thickness when a flame starts to extinguish due to heat loss to the underlying water. Floating oil, therefore, needs to be contained in fire resistant oil booms prior to ignition and burning and oil depths maintained at greater than 3 mm. A boom towing aspect of the burn operation is not significantly different from conventional oil containment booms; fire resistant booms have the same towing speed, oil loss, and sea state limitations. Oil thickness measured in regular containment booms during experimental oil spills in the North Sea varies from 50 to 600 mm, and should therefore provide sufficient insulation to ignite and burn oil.

Testing of fire resistant booms in recent years clearly indicate that most of the current refractory fabric-based fire resistant booms are not capable of withstanding high temperatures (up to 2000 °F) in waves, and wave conformance is limited and less than that for regular booms. In the past, the lack of fire resistant booms has been a limiting factor in the success of in-situ burning. However today, the newly developed water-cooled booms have been found to meet new ASTM requirements for testing fire resistant booms (Bitting, 1999). The photograph below is from the Newfoundland Offshore Burn Experiment (NOBE) [August, 1993] illustrating a controlled in-situ burn of experimental spilled oil in offshore open ocean waters. For more information on the NOBE Burn experiment see the following overview citations (Fingas, et al., 1994, 1995) and the following Environment Canada Website:
http://www.etcentre.org/main/e/pubs/biennial/birep1996.html#16.2

Photograph from the NOBE Burn Experiment (August, 1993). Courtesy of Joe Smith of Ross Environmental, Seattle, Washington, and Environment Canada.

Effect of Wind

Wind velocities in excess of 20 knots make ignition of spilled oil difficult for three reasons: (1) the vapor–air mixture is rapidly diluted below flammable concentrations; (2) the flame from the ignition source may extinguish; and (3) the wind effect cools the oil surface temperature below the oils flash point temperature. Figure V.7 illustrates the tow speed and wind velocity values where in-situ burn operation is likely.

Modeling Tools to Predict Ignitability and Sustained Burning

Crude oil weathering, or the changes in oil properties and behavior caused by different prevailing conditions, has been extensively studied in recent years. A combination of standardized, "step-wise" laboratory investigations, combined with verified (field studies) numerical modeling, has enabled the models to be calibrated to improve the accuracy of predictions in changes in flash point, evaporation, boiling point and emulsification for many different oil types (Strøm-Kristiansen et al., 1993). Models are not perfect and need further refinement, but today, they provide useful information to estimate windows-of-opportunity. These predictions have been used to assess the applic-

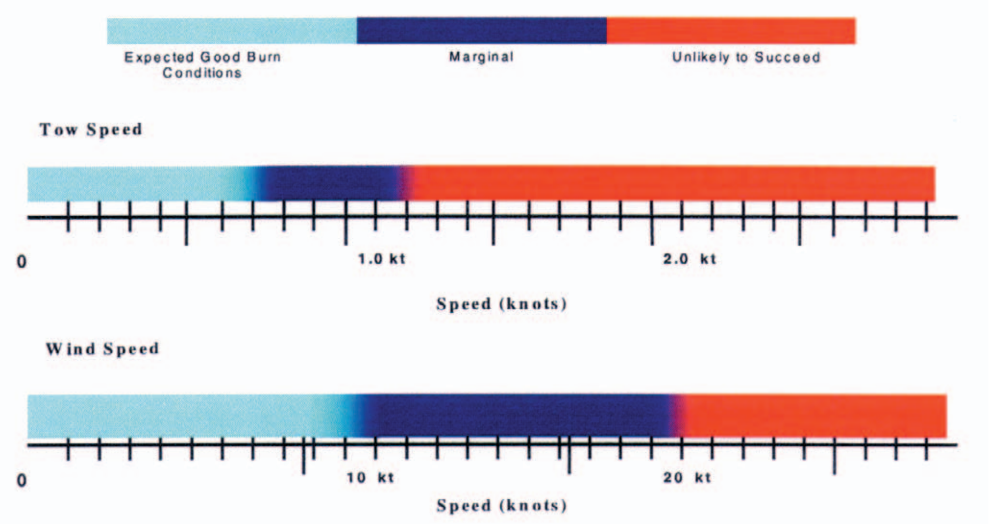


Fig. V.7. Tow speed and wind velocity values where in-situ burn operation is likely (PCCI, 1999).

ability of response techniques such as dispersants as a "time window-of-opportunity" for dispersant use (Lewis and Aurand, 1997).

Models to predict time windows-of-opportunity for in-situ burning are not currently available because standardized test methods for ignitability of emulsions, or ignition devices capability to raise oil surface temperature to flash point temperatures, are not available. In this appendix, however, flash point, evaporation, and emulsion data available in IKU Oil Weathering Model, have been used to indicate the potential of ignitability of floating oils (Daling et al., 1997). But without linkage to ignition source data on expected increase of oil temperature, the data are of limited value to predict feasibility of in-situ burning.

The Principles of Burning Oil Slicks at Sea

Although the general principles and limitations of in-situ burning are well known, the possibilities and limitations of in-situ burning and estimation of the "time window-of-opportunity" are incident and oil specific (Strøm-Kristiansen, 1993). The feasibility of in-situ burning can only be realistically assessed if the influences of oil composition, prevailing conditions and capabilities of the ignition source to elevate oil temperature to its flash point temperature are known.

All mineral oils, even the heaviest, will burn if the circumstances are correct for ignition and sustained burning (Strøm-Kristiansen, 1993). However, previous in-situ burn studies have indicated that a thin film of crude oil from which almost all of the most volatile and flammable components have evaporated, and which has incorporated water to form a water-in-oil emulsion, cannot be set alight very easily, if at all, while it is on the sea. However, results from emulsion breaking studies have indicated that elevation of surface temperature to approximately 50 °C is sufficient to break many crude oil emulsions. For Bunker C oil, research has found that the combination of emulsion breakers and heat is required to break them (Strøm-Kristiansen, 1994).

Experimental spills have demonstrated that fresh or relatively unweathered crude oil can easily be ignited and that they can burn well leaving only a very small amount of residue. It is also known that spilled oil, in general, becomes difficult or impossible to ignite when the oil:

- Layer thickness drops below a critical minimum (>2–3 mm);
- Has lost a substantial proportion of its more volatile and flammable components by evaporation; and
- Has formed an emulsion by incorporating water.

Ignition of Highly Flammable Liquids

When oil with a flash point below seawater temperature is spilled on the sea, the most volatile components will evaporate rapidly at rates that depend on the vapor pressure of the spilled oil, slick thickness and the prevailing temperature (sea and air) and wind speed. The vapor will ignite if an ignition source (accidental or intentional) is present and the flammable vapor concentration exceeds the minimum vapor–air concentration. The flammable vapor concentration in the air is being constantly diluted by the effect of the wind. The minimum concentration of flammable vapor that is required for ignition will therefore persist for a period of time and depend on several factors such as:

- The proportion of readily volatile and flammable components originally present in the oil (broadly the fraction that boils below 150 °C—the gasoline fraction).
- The thickness of the oil slick and the way that this decreases during spreading (or increases due to subsequent containment).
- The rate at which the flammable components are being transferred into the vapor phase (the mass flux, which depends on the proportion of molecular weight oil components, temperature and wind speed).
- The rate at which the flammable vapor concentration in air is being diluted to below the minimum flammable concentration by the wind.

If a low energy ignition source, such as a spark or open flame is introduced into the vapor at this stage, ignition of the vapor–air mixture will occur. The flames will radiate heat, which will rapidly evaporate more flammable vapor from the oil, and the burn will become self-sustaining. The fire will burn until almost all the oil has been consumed.

Many crude oils contain a sufficiently high proportion of the volatile components to produce the flammable vapor at prevailing ambient temperatures. Fresh crude oils have been successfully ignited even at thickness as low as 0.8 mm.

Ignition Leading to Self-Sustained Burning

When the flash point of the spilled oil is above the seawater temperature, the spilled oil needs to be heated to its flash point temperature. During the rapid evaporation phase, the volatile and flammable components (the gasoline fraction) will evaporate from the crude oil and dispersed to below the minimum flammable concentration without burning. The risk of accidental ignition by a low energy ignition source will have passed.

Less readily volatile components of the crude oil (those with boiling points higher than 150° C—the kerosene fraction and higher) can be easily and rapidly evaporated by the application of moderate amounts of heat from an ignition source such as a flaming rag. When these components have been evaporated in sufficient local concentration, ignition from the same source that provided the heat will be possible. Localized burning of the freshly liberated vapor will then occur and this will, in some circumstances, be sufficient to generate more flammable vapor which will subsequently ignite, and lead to sustained burning.

Ignition Not Followed by Sustained Burning

If the oil does not contain a high enough proportion of readily volatile components, or is present in too thin a layer to be able to provide a sufficiently high flammable vapor concentration locally, the flammable vapor may briefly ignite, but rapidly extinguish.

Technologies to increase the heat energy (i.e., the amount and duration of heat radiated onto the oil slick) of the ignition source by using more igniter fuel or bigger and more persistent igniters (such as the Helitorch) may be able to generate sufficient local vapor concentration for ignition. However, if the oil layer is too thin and the heat loss to great to produce sufficient vapor, the ignition will be transient or unsuccessful.

Failure to Ignite

It has been found that some thin films of lightly weathered oils and even thick layers of emulsified oils are impossible to ignite, even when high energy, long duration ignition sources are used.

This can occur with thin oil layers, where the heat radiated from the ignition source passes through the oil and is absorbed by the underlying water. Subsequently the oil absorbs only a small proportion of the heat, and the increase in temperature is not sufficient to elevate the oil temperature to its flash point.

Thick layers of emulsion (containing up to 70% volume of water) may also cause failures to ignite, because the radiant heat from the igniter is consumed by evaporating the water. The water vapor (non-flammable) released from the emulsion result in the dilution of the concentration of burnable vapor–air mixture.

Considerations for Conducting In-situ Burning

The following considerations are a summary of the limitations and requirements for in-situ burning, and have been established based on a number of experimental spills and laboratory investigations:

A. *Minimum slick thickness*
  - 1–3 mm for fresh crude oils.
  - 3–5 mm for diesel and weathered crude oil.
  - 5–10 mm for Bunker C and emulsified oil.

B. *Oil weathering*
  - Evaporative losses of appropriately 30% (except for highly refined products).
  - Combination of evaporation and emulsification with water content of less than 25–50%, depending on emulsion stability and ignition source.

C. *Weather conditions*
  - Wind velocity of less than 10–12 m/s.
  - Waves of less than 1 m for non-emulsified oils, and less for emulsions.
  - Current speeds of less than 0.5 m/s.

Although all of these factors are known to influence ignitability, they represent relative trends without specific time windows estimates needed for contingency planning and decision-making processes. An absolute assessment of ignitability can only be made once a suitable method to measure ignitability has been devised.

Estimation of Time Windows

The time window is defined as the period where response methods and technologies are most effective in oil spill response. The estimation of time windows is a highly integrated process, where the selection of response technologies is more efficient, technically correct, cost effective, environmentally sensitive and appropriate. The estimation of time windows integrates environmental, dynamic oil weathering and performance effectiveness data for oil spill response technologies derived from laboratory, mesoscale, and experimental field studies.

The objectives behind the development of time windows are to:

- Increase the effectiveness of selected clean-up technologies by using them in the correct time windows;
- Increase the cost effectiveness and efficiency of the response;
- Reduce the environmental impact of spilled oil;
- Prepare a scientific foundation for the response decision-making process; and
- Direct researchers and technology manufacturers in their effort to improve response community knowledge, technologies, and clean-up capabilities.

To properly estimate the window for ignitability, the following must be known:

- The type of oil that has been spilled;
- The oil and seawater surface temperature at the time of ignition;
- Data for wind, sea state, currents, etc.;
- The required increase in oil surface temperature determined for ignition; and
- Expected increase of oil surface temperature during sustained burning, are the most important factors/parameters to assess ignitability.

The failure to determine the heat flux (ΔT °C) of igniters by research over the past decade has severely limited the ability to use them in a wide range of in-situ burning options. For example, an igniter that only has the capability (which is currently unknown) to provide a heat flux to the oil/water surface of 50 °C is ineffective when 100 °C is needed. However, because the data on heat flux are not available, use of igniters today is by trial and error.

ANS In-situ Burning Windows—A Model Example

To demonstrate the method to estimate windows, data for this example have been selected as an example, and the input data may not represent the total range of limits for this specific oil. As more data and understanding are available, these estimates for windows can be refined.

To demonstrate an estimation of time periods of in-situ burning, given the combined effect of evaporation and emulsification, the following scenario with mid-scale testing have been prepared (Buist, 1999):

- Spilled oil is Alaskan North Slope (ANS);
- Sea temperature 5 °C;
- Wind velocities 10 and 5 m/; and
- Ignitability up to approximately 20.4% evaporation and 25% water content (60% with emulsion breaker).

The ignitability data used in this scenario are also for ANS crude oil and comes from laboratory, meso, and field experimental burns (Guénette, 1994). The above oil and conditions have been selected because of available data.

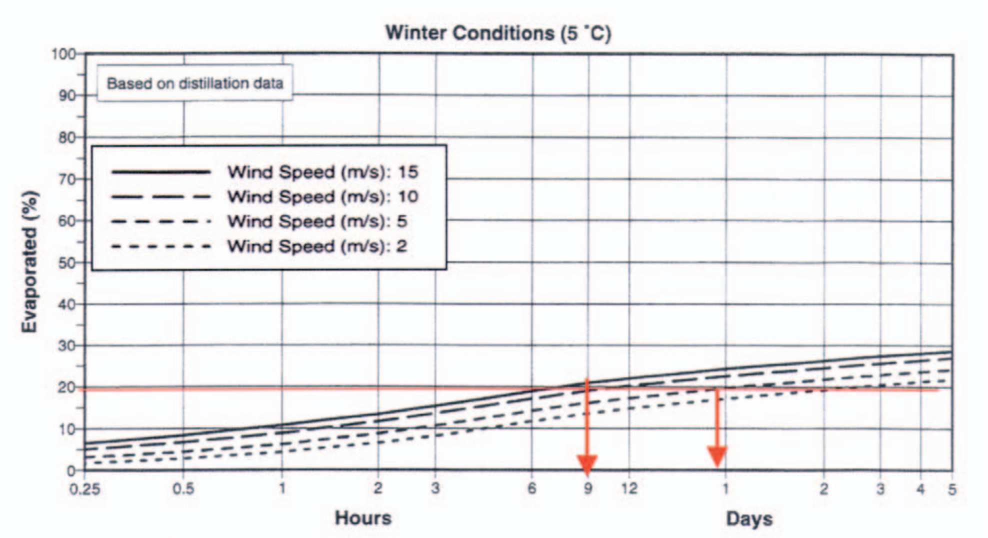


Fig. V.8. A dynamic plot of evaporative loss for ANS over time at indicated wind speeds.

The *First Step* is to estimate the time available, before evaporation exceeds the estimated time period for ignition for the spilled oil and compare this time with the needed time for response.

Figure V.8 illustrates a dynamic plot of evaporative loss of ANS crude oil at 15, 10, 5, and 2 m/s wind velocity predicted by the IKU Oil Weathering Model (Strøm-Kristiansen, 1993) using available laboratory data (Buist, 1999). The time it takes for the spilled oil to reach the point where evaporative loss exceeds ignition (20.4%) with current ignition technologies, is indicated in Figure V.8 by red arrows for 10 and 5 m/s wind velocities and is approximately 9 and 22 hours respectively.

The *Second Step* is to determine the water uptake of the spilled oil. Without the use of an emulsion breaker, the maximum water content in the emulsion was 25% for ignition and burning (Buist, 1999), marked in blue in Figure V.9. Results from laboratory and field testing has shown that an emulsion of ANS can be ignited and burned with 60% water content (marked in red) by using an emulsion breaker in combination with gelled gasoline.

Figure V.9 presents a dynamic plot of changes in water content at four wind velocities with marked horizontal lines for 25 and 60% water content. The time it takes to reach 25% water content at 10 and 5 m/s wind velocities are up to 4 and 12 hours respectively. For emulsion with 60% water content, the burn time increases to approximately 22 and 70 hours by using the break and burn method marked in red. However, the evaporative loss limits the ignition at maximum 22 hours (see Figure V.8). The “break and burn” method, therefore, increased the time window for the 60% water-in-oil emulsion from 4 to 22 hours, and from 12 to 22 hours at 10 and 5 m/s wind velocity respectively.

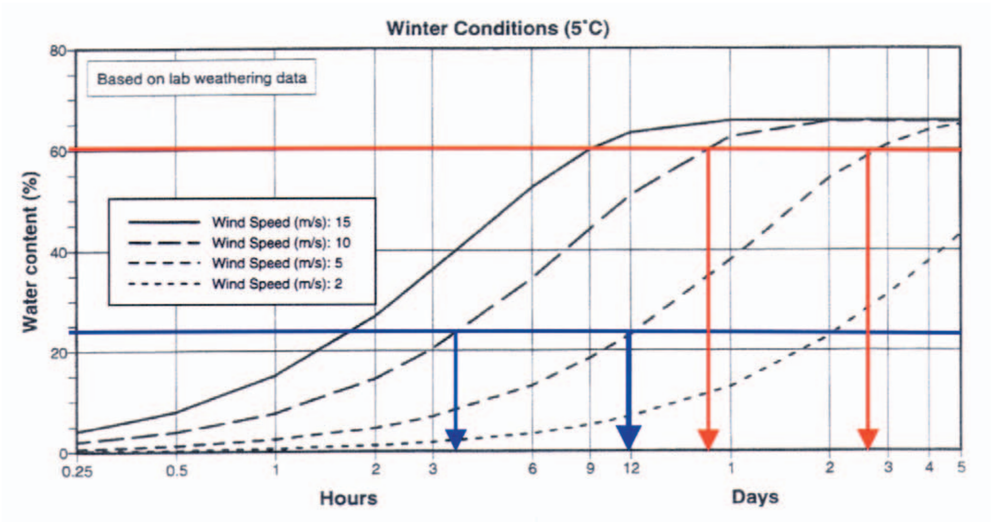


Fig. V.9. A dynamic plot of changes in water content (%) for four wind velocities (15, 10, 5, and 3 m/s) for indicated time periods.

The *Third Step* is to determine if the heat flux (ΔT °C) from the igniter and ignition method is sufficient to bring the surface temperature of the spilled oil to its flash point temperature so that the oil will burn. This means that the sea and flash point temperatures of the 20.4% evaporated spilled oil must be known.

In the example below, it is known from field test results that the use of gelled gasoline ignited and burned the 20.4% evaporated and 25 and 60% emulsified ANS crude oil at 5 °C sea temperature (Guénette, 1994). Because the evaporative loss corresponds to its flash point temperature at 20.4% evaporation, the flash point can be found by comparing the oil weathering models" predicted flash point at 9 and 22 hours at wind velocities of 10 and 5 m/s respectively (Figure V.8).

Figure V.10 presents a dynamic plot of changes in flash point during oil weathering for ANS crude oil. The sea temperature (marked in blue) and the estimated flash point temperature at 20.4% evaporation (marked in red) are plotted in the figure and show that the flash point at ignition was approximately 58 °C. Even though the heat flux at ignition is unknown, the minimum increase of oil surface temperature of 53 °C (58 °C flash point minus 5 °C sea temperature) was exceeded.

Discussion of Caveats

In this review and model example, we have attempted to bridge the gap between available data and information from open water in-situ burning experiments and the technical literature from laboratory and field mesoscale studies, and we are aware

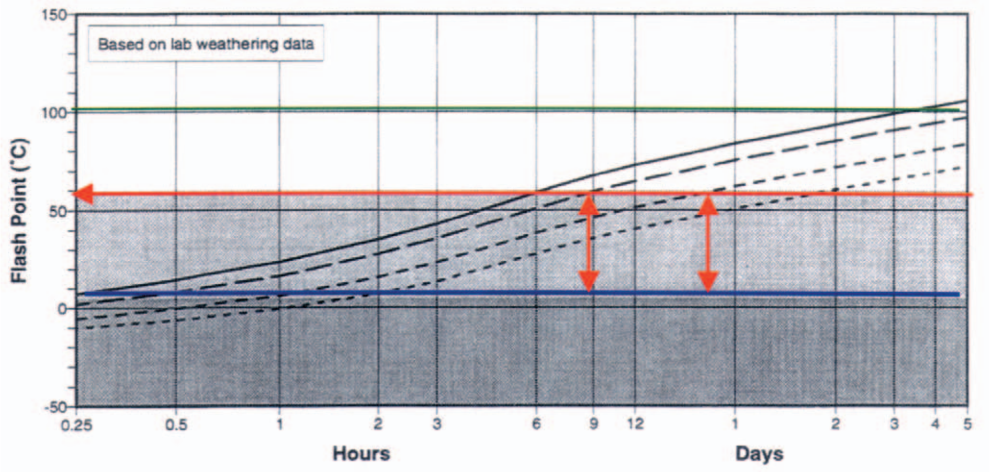


Fig. V.10. A dynamic plot of changes in ANS crude oil flash point temperatures at various wind velocities (15, 10, 5 and 2 m/s) for indicated time periods (9 and 22 hours) where in-situ burning was successful.

that the estimate time periods (windows-of-opportunity) in this appendix are based on limited research and flash point data, and that the ability to burn an oil is a complicated combination of factors as we have discussed.

It should be noted that the burning limitations for ANS is an example of the method to estimate time windows, and that the evaporated loss with its corresponding flash point temperature may not represents the actual limitation of ignition. The main reasons is because data points above 20.4% evaporation are limited, test methods for experimental burns are different, the effectiveness of chemicals (demulsifiers) varies, and the method of ignition does not provide net heat flux (ΔT °C), and corresponding data of temperature increase capabilities.

It appears, however, that the success of in-situ burning is dependent upon the successful ignition of a slick. In the future, the heat flux (ΔT °C) of commercial igniters should be determined and calibrated to provide ignitability capability data. Higher heat flux igniters capable of increasing the oil surface temperature to temperatures measured during experimental burns of evaporated oils (150–450 °C—dependent on oil thickness), and for evaporated and emulsified oils (100–250 °C), clearly indicate the potential to extend the time window.

Summary

Three Steps have been identified to estimate the in-situ time period windows-of-opportunity:

Step 1. The *First Step* is to determine the time it takes for the evaporative loss to reach the known or established limitation for evaporation and compare this time period with estimated time of ignition at the ambient wind and sea temperature.

Step 2. The *Second Step* is to determine the water uptake of the spilled oil.

Step 3. The *Third Step* is to determine the necessary heat load from the igniter to bring the surface temperature of the spilled oil to its flash point temperature so that it will burn.

This flash point of the emulsified spilled oil must be known (as also the evaporation rate and the water content) and the ability of the igniter to produce enough heat flux to bring the surface of the oil to the temperature where sustained burning will occur.

If the oil spill planners and responders do not have the specific data discussed above, and resources (booms and igniters), they may be unable to estimate and utilize time windows of in-situ burning to maximize the effective response to an oil spill. The estimation and use of time windows is consistent with the regulations of OPA 90.

Readers interested in more information on in-situ burning of spilled oil need to study the references cited below. The authors of this appendix will continue to explore management strategies for ISB of spilled oil, as opportunities and funding become available, to support the utilization of the windows-of-opportunity strategy in oil spill response to reduce clean-up costs and environmental damage.

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