

A COMPREHENSIVE REVIEW OF OIL SPILL COMBUSTION STUDIES

Ajey Y. Walavalkar and Anil K. Kulkarni
 Department of Mechanical Engineering
 The Pennsylvania State University, University Park, PA 16802, USA

Abstract

In-situ combustion of oil or water-in-oil emulsion supported on top of a water-base is a complex process. It may be examined in three stages -- before, during, and after the actual combustion. Spreading and emulsification of oil prior to combustion strongly influence the ease of ignition, rate of burning and oil removal efficiency. Surrounding physical conditions, including wind velocity, waves and the presence or absence of a containment device, such as a fire boom, determine continuation of the combustion process. The resulting smoke, residue, and aquatic toxicity should be within the acceptable limits for the cleanup measure to be a success. Discussions of the processes involved in oil spill combustion, followed by tabulated brief notes on relevant papers on each topic, are presented. The review shows that there is a need for fundamental studies, especially in the mathematical modeling area, to understand the basic mechanisms and predict the applicability of the in-situ combustion.

Introduction

The acceptability of in-situ burning as an oil spill cleanup countermeasure is growing because of its economic and environmental benefits, as well as other factors such as efficiency of removal and ease of rapid deployment. The technique has been sporadically tried in practice and investigated extensively over the past 30 years. Some of the major oil spill burn experiments and actual clean up attempts are summarized in Table 1. When feasible, it is an inexpensive technique needing fewer personnel and minimal equipment compared to other countermeasures, allowing for easier deployment. Efficiency of oil removal has been reported to be greater than 99% based on large scale in-situ oil-spill burn experiments. The removal rate is also very rapid compared to that using mechanical means. Emissions and ecological damage from the spill combustion have been found to be less severe compared to those from the conventional methods. And perhaps the most important benefit is, oil spill burn technique is a final solution as compared to mechanical recovery. Other techniques require transportation, storage and disposal after the initial cleanup phase (Fingas and Laroche, 1990; Evans and Tennyson, 1991).

In-situ burning of oil or water-in-oil (w/o) emulsion supported on top of a water-base, such as the ocean, is a complex process, and in general, may be examined in three stages -- before, during and after the actual combustion. Events and considerations prior to actual spill combustion, which are very important in determining the efficacy of this technique as a cleanup countermeasure, include the

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Table 1: Selected Historical Oil Spill Burns: (adapted from Fingas and Laroche, 1990)

Year	Country Location	Description	Oil Type	Major Conclusions
1967	Britain	Torrey Canyon	Crude	Cargo tanks difficult to ignite with military devices
1970	Sweden	Othello/ Katelaysia ¹	Bunker C	Success in burning amongst ice
1975	Canada	Balena Bay-experiment	Crude	Demonstrated ease of burning oil on ice
1978-82	Canada	Series of experiments ²	Several	Found limitations to burning was thickness
1981	Canada	McKinley Bay-experiment	Crudes	Noted difficulty in burning emulsions
1983	USA	Beaufort Sea-experiment ³	Crudes	Ability to burn in broken ice
1986-91	USA	NIST-experiments	Various	Science of burning, rates, soot, heat transfer
1989	USA	Exxon Valdez ⁴	Crude	One burn demonstrated practicality and ease
1992	USA	Texas Marsh Burn ⁵	Light Crude	Resulted in very little impact on the environment
1993	USA	Brunswick fresh water marsh ⁶	JP-5 Aviation fuel	The burn emphasized advantage of in-situ burn over mechanical recovery techniques for spills in less accessible areas
1993	Canada	NOBE ⁷	Crudes	Oil removal efficiency over 99%. Extensive emission sample analysis showing no major environmental damage.

(1: Chemical Week, 1970; 2: Energetex Engr., 1978; 3: O'Rourke, 1976; 4: Allen, 1990; 5: Gonzalez and Lugo, 1994; 6: Euphemia, 1994; 7: Fingas *et al.*, 1995c)

evaporation or weathering of oil, emulsification with water, thickness of oil slick, ignition source, surrounding physical conditions such as presence or absence of the containment structures (like a fire boom, ice, ship, or embankment) and surrounding dynamic conditions (including waves and wind conditions). Figures 1 and 2 show two of the many possibilities of the physical conditions encountered in oil spill combustion. Figure 1 shows a schematic of the leaking oil from a drilling platform trapped in a fire containment boom, which is later taken further away for fire safety and burned. Figure 2 shows burning oil trapped in a surrounding ice bank.

The second stage is the combustion of the oil or emulsion layer -- the primary focus of this paper. It involves several interdependent and complex physicochemical processes which are not yet fully understood. A schematic of the

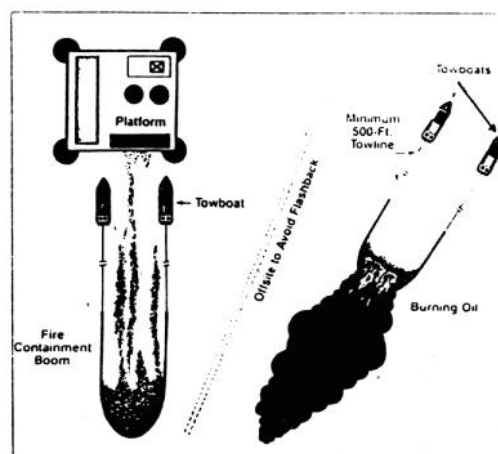


Figure 1 : Schematic of oil leaking from a well, being relocated away from the source using booms, and burned (from Fingas and Laroche, 1990)



Figure 2 : Emulsion burning against ice barrier (from Guenette *et al.*, 1995)

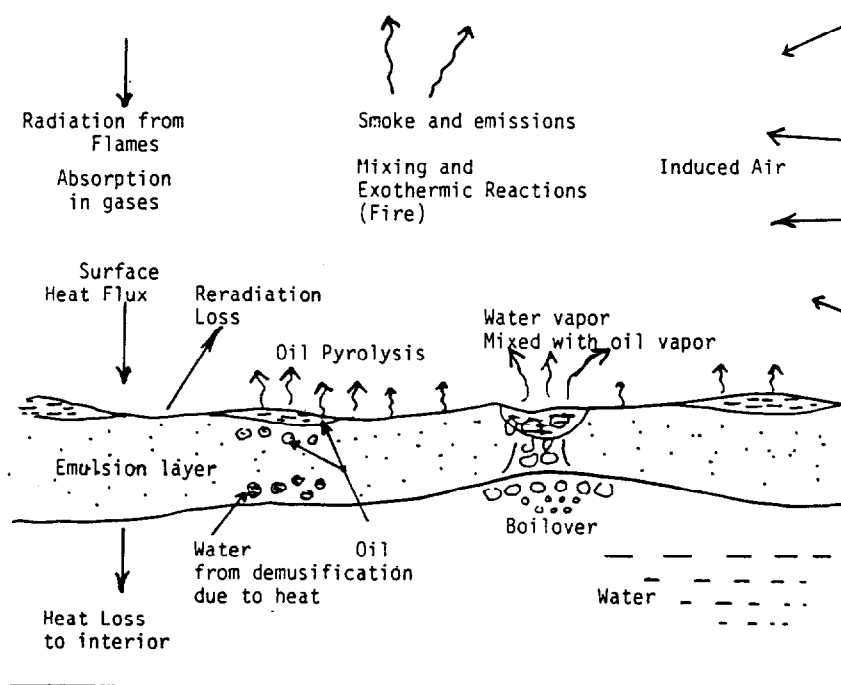


Figure 3 : Schematic showing physicochemical processes of emulsion combustion

process is depicted in Figure 3. Energy is fed back from the fire to the layer via conduction and radiation. The emulsion separates into oil and water because of the heat. Some of the water boils away, but some sinks below. The oil vaporizes and pyrolyzes, diffuses into the atmosphere, and mixes with the oxygen from air which is supplied by the diffusion aided by wind and turbulence. The mixture reacts exothermically to continue the heat feedback process to the emulsion layer. In the condensed (liquid) phase, there is heat conduction to the interior, as well as some in-depth radiation absorption. Depending on the thickness of the layer, the water substrate can boil over. If the oil/emulsion layer is too thin (typically less than 2 to 3 mm, depending on the oil type) the fire may extinguish. The separation of the oil and water in emulsion layer, and the boilover phenomenon can cause significant mixing in the condensed phase and unsteadiness of the process.

The success of oil spill combustion is often measured in terms of the fraction of the spilled oil or emulsion that is burned away. Another important

consideration, however, is the air and aquatic pollution caused by the combustion process. Figure 2 shows smoke plume from an oil spill combustion experiment. The oil spill combustion technique would be meaningless if the consequent environmental damage is significant. There is residue left from combustion, the airborne species may contain soot particles and polyaromatic hydrocarbons (PAHs), and the smoke produced may drift to nearby populated areas. This may give rise to environmental controversy as well as regulatory, legal and politically sensitive issues.

This paper attempts to present a review of studies on in-situ oil spill combustion with due consideration given to the above aspects and with an emphasis on the actual combustion studies. A summary of relevant papers in tabular form follows each section, providing a quick reference guide. Papers in the following table provide a general overview of the oil spill combustion technique.

Table 2 : Oil Spill Combustion Overview Papers

Allen, 1991	A description of in-situ burning of spilled oil with basic combustion considerations. Representative situations where in-situ burning could be considered viable are described.
Buist <i>et al.</i> , 1994	A comprehensive review of in-situ burning as an oil spill response technique and a list of fourteen ideas for top R&D consideration.
Evans and Tennyson, 1991	A general overview of in-situ burning as an oil spill response technique.
Evans, 1989	Discussion and summary of past work on in-situ oil spill burning. Provides a basis for decisions on applicability of a broad range of available research in liquid fuel combustion to particular problems of oil spill combustion in Arctic regions.
Fingas and Laroche, 1990	An overview of in-situ burning of oil spills and emission. Overview of studies shows that emissions are not of serious concern.
La Belle, 1994	Behavior and movement of spilled oil under prevalent sea and weather conditions are described in light of 1993 spill off Tampa Bay. Feasibility of in-situ combustion of such spills is discussed considering actual and publicly perceived hazards associated with burning.
Shigenaka and Barnea, 1993	Considerations for health hazards, safety, ecological effects, and environmental effects of in-situ burning.
Tennyson, 1994	An overview of historical research perspectives.
Thompson <i>et al.</i> , 1979	A practical guide oriented toward the needs of potential user. Decision elements provided which can be used as a guide for technical evaluation of a particular oil spill situation.

Oil Spreading and Emulsification

As soon as the oil spills on water, it starts spreading. For small amounts of oil spilled onto clean water, the initial spreading was found to be dominated by the surface tension effects. If large amounts of oil are spilled, even onto previously oiled surfaces, the spreading occurs by gravity inertial mechanisms (Brown and Goodman, 1995). The oil layer thickness decreases as it continues to spread, and a continuous film of oil as thin as 0.01 to 0.1 mm may be formed by light crudes and 0.05 to 0.5 mm by heavy crudes (Fingas and Laroche, 1990). Most of the crude and refined oils will burn on water if the layer thickness, depending on the type of oil, is at least 1 to 3 mm. Oil layers thinner than a critical thickness will cause excessive heat loss to water and leave either insufficient energy to pyrolyze it or cause boilover of water under the layer (Arai *et al.*, 1988). Thus, spreading dynamics are very important when considering the implementation of oil spill combustion as a cleanup countermeasure.

Oil starts forming emulsion with water in a matter of few hours. Formation of w/o emulsions (water droplets trapped in continuous oil phase) is the major difficulty in the clean-up techniques of oil spills, including in-situ burning. Under some conditions, w/o emulsions can form rapidly and contain up to 80% volume of water. The rate of formation and the stability of these emulsions are dependent on prevailing sea conditions and on the physical and chemical properties of oil. One of the most important characteristics of emulsion is its greatly enhanced viscosity compared to oil or water. As the oil weathers, the lighter components evaporate. In a few days, light crude oils can be reduced by up to 75% of their initial volume and medium crudes by up to 40% of their volume due to evaporation. The temperature and volume of spilled oil are the two most important parameters in this regard (Fingas, 1994). As the lighter components of oil escape, the emulsifiers --asphaltenes, resins and waxes --which are present in oil and are soluble in lighter components of oil, precipitate out and aid emulsification (Bobra, 1992).

In order to burn the emulsified oil, the two phases usually need to be separated. The breaking of emulsions can be achieved by chemical agents, sometimes referred to as demulsifiers, and heat (Strom-Kristiansen *et al.*, 1995). The stability of a w/o emulsion and its response to an emulsion breaker and heat depend on the chemical composition and physical properties of the oil from which it is formed; however, stable emulsions are formed only with high water content. Extensive studies on the properties of emulsion, emulsification process, initial dynamics and combustibility of emulsions have been carried out (Lewis and Walker, 1995; Bobra, 1992; Fuji, 1995; and Buist *et al.* 1995).

Table 3 : Studies on Oil Spreading and Emulsification

Blokke, 1966	Quantitative methods to calculate rate of spreading and evaporation of oil spillage on water.
Bobra, 1992	Experimental study of mechanisms leading to stabilization of water-in-oil emulsions by asphaltene, resins and waxes.
Brown and Goodman, 1995	Oil spreading mechanisms are presented based on video observations of spills in a containment boom.
Fingas, 1995	An experimental method is proposed for measuring evaporation of oil products.
Fingas, 1994	Data on evaporation of oil spills analyzed and an equation for prediction of evaporation proposed.
Fingas <i>et al.</i> , 1995b	Literature review of studies on emulsion stability treating agent effectiveness tests.
Guenette, <i>et al.</i> 1994	Extensive testing of three crude oils for different weathering conditions, water content and thicknesses in 1.2 m diameter pool. Burning rate efficiency and several other parameters measured.
Lewis and Walker, 1995	Review of processes involved in formation and breaking of emulsions at sea.
Strom-Kristiansen <i>et al.</i> 1995	Bench-scale laboratory study for four different oils and crudes on demulsification by heat, emulsion breakers, and the two combined. The combination was found to be very effective in demulsification.
Tokura <i>et al.</i> , 1988	Measurement of thermal conductivity of crude oil as input data for numerical models.

Ignition

If the oil layer thickness (greater than a critical value), degree of emulsification (preferably lower), weathering (as little evaporation as possible) and surrounding physical conditions (wind velocity and waves not too strong) are suitable, the spilled oil may be ignited. Use of proper igniters and ignition methods is necessary to initiate sustained in-situ combustion of spilled oils. Heavy oils require longer heating times and a hotter flame to ignite compared to lighter oils. Typical methods used for ignition in field experiments have been pyroclastic igniters, Dome igniters, laser igniters, and Helitorch igniters with gelled gasoline. The "Dome igniter," developed by Dome Petroleum, is a relatively simple device consisting of cans and propellants having a burn time of approximately ten minutes. The pyroclastic igniter was developed by Environment Canada and the Canadian military. A 25-second delay, after pulling on a firing pin which strikes a primer cap, allows for manual tossing and setting of the igniter on the oil slick surface. The flame from the edge of the igniter lasts for two minutes (Allen, 1986). Attempts to develop a laser ignition device have also been made. A device called "Helitorch" is used extensively for the purpose of ignition. It is

a helicopter-slung device which distributes packets of burning, gelled fuel. Typical burning globules have a burning time of four to six minutes (Evans, 1989). Gelled crude oil was found to be a better igniter than gelled gasoline (Guenette *et al.*, 1995). The combination of gelled gasoline and crude oil has also been found to be effective for the ignition of weathered crude emulsions (Buist *et al.* 1995).

It has been shown in lab studies that ignition delay increases with the evaporation of lighter components and water content of the emulsion (Buist *et al.*, 1995). In 3 m pool spill experiments the ignition delay was found to increase with 0.5 power of spill volume. Ignition time for evaporated oils was found to be less than 90 seconds and was not affected by slick thickness. Emulsions of fresh crude ignited in 25 seconds. Demulsifiers were found to enhance ignition and flame spread. The minimum ignitable thickness for emulsions tended to be greater than that of water-free oil slicks (in the range of 5 to 10 mm). Sensitivity of emulsion burning to wind is also more than that of water-free oil burning. A guide for ignition of weathered and emulsified fuels was presented by Putorti *et al.* (1994), using measured ignition characteristics of diesel pools of various sizes.

Table 4 : Studies on Ignition

Arthur D. Little, Inc., 1969	Types, use and effectiveness of wicking agents for oil slick burning are discussed.
Energetex Engr., 1978	Development and testing of a portable oil slick burner using a wicking system and a gaseous fuel to be used on Arctic oil spills.
Putorti <i>et al.</i> , 1994	Measurement of ignition time for weathered oils and oil emulsions when heated by thermal ignition using 100 mm diameter pool in a Cone Calorimeter; water content was found to have no effect on ignition time.
Tam and Purves, 1980	Burning of three petroleum fractions floating on water in confined and unconfined layers, at two thicknesses and in various wave and ice conditions. Ten promoter materials screened to improve ease of ignition and burn efficiency.
Thornton, 1977	Incendiary devices and wicking agents developed for burning all spills on ice and snow.
Tully, 1969	Cab-O-Sil is effective wicking agent with slicks down to 2 mm thickness.
Woodyard, 1970	Use of fumed silica as wicking agent to enhance burning at sub-freezing temperatures.

Burning Rate and Efficiency of Removal

Once the oil or emulsion layer is ignited, sustained burning can be achieved if energy feedback at the surface is at least equal to the heat losses and latent heat of vaporization. Typically, the oil layer thickness reduces at a rate of approximately 2 mm/min (for heavy crudes) to 3 mm/min (for lighter oils). (3 mm/min is approximately $0.07 \text{ gal/min.ft}^2$, 4100 L/d.m^{-2} , or 100 gal/day.ft^2 .) The burn rate decreases during the final stage, due to the increased rate of heat loss to water substrate. However, it does not vary significantly with different oil types, degrees of weathering and water content (Fingas and Laroche, 1990).

The mechanism of w/o emulsion combustion is far more complex than oil. It has been postulated that it is not the emulsion that burns; rather a layer of oil, separated out and floating on top of emulsion, burns (Guenette *et al.*, 1995). Thus the controlling factor in emulsion burning is the removal of water. It can be done either by breaking the emulsion (especially for unstable emulsions) or boiling it out (emulsion must reach 100 C). In an extensive experimental study on liquid fuel layer combustion on water, Inamura *et al.* (1992) estimated that a considerable amount of heat can be "lost" to the water via in-depth radiation absorption and conduction, making the water boil, breaking through the oil layer and affecting the oil combustion.

Some observations of emulsion burning reveal that (i) incident heat helps separate water and oil in emulsion (Strom Kristiansen *et al.*, 1995); (ii) when water content exceeds 25% the emulsion is difficult to ignite (Buist *et al.*, 1995); (iii) for a stable emulsion, water must be removed by boiling before igniting; (iv) emulsions above 50% can be successfully ignited and burned only if demulsifiers are introduced in the emulsion (Guenette *et al.*, 1995); (v) burn efficiencies with emulsions, even with water content as high as 50%, are in excess of 90%; (vii) emulsions under certain conditions show a peculiar behavior of combustion characterized by flashing and then extinguishing over a large surface in a repetitive manner (Buist *et al.*, 1995).

The efficiency of burning is the percentage of the original oil that is removed by burning. As there are finite heat losses to the water surface, the burn efficiency is always less than 100%. However, experiments on small, as well as large, scale have revealed that well over 90%, and often more than 99% of the oil can be burnt. For example, the burning efficiency in the recent large scale NOBE (Newfoundland Offshore Burn Experiment) was found to be over 99% (Fingas *et al.*, 1995a) and in the case of the Exxon Valdez oil spill, the burning efficiency was over 98% (Allen, 1990). Burn efficiency decreases with increasing water content and evaporation. However, when the oil is emulsified, the combustion efficiency may drastically reduce (Buist *et al.*, 1995).

The oil spill combustion is unsteady when the burning oil spreads and also when the flames advance over a relatively stagnant oil layer. If the spill area is ignited at its periphery, the flames spread outward along with the oil layer, and inward aided by the fire-induced air convection. Flame spread alone accounted for a rate of

approximately 1 m/min on a four-hour aged Alberta Sweet mixed blend with 0.25 m/s wind. Flame spread rate over a fresh crude was approximately four times faster than the weathered oil. It was also found that the spread rate on 38% evaporated oil was very slow, and almost zero on 40% w/o emulsion. The burning oil was found not to spread significantly faster on water than the cold oil. Flame spread almost always keeps up with the spread of oil. The other unsteady combustion phenomenon observed on burning emulsion exhibited a very peculiar behavior of intermittent flashover and extinction of the fire. It is believed to occur because the rate of water-free oil layer production may be less than the rate of oil removal by burning. Or, this can be due to foaming of the emulsions (Buist *et al.*, 1995).

The key mechanism for a sustained combustion of the oil or w/o emulsion layer (the fuel) on water is the energy balance at the surface. If sufficient energy from combustion is fed back to the fuel layer, the evaporation and pyrolysis of fuel continues; if excess energy is available from combustion, flame spread and more intense burning occurs; and if insufficient energy is available, the fire extinguishes. A simple energy balance for the oil layer burning on top of water was proposed by Thompson *et al.* (1979),

$$\text{Net Energy} = 0.02 H_c - H_p - C_p (T_{bp} - T_{amb})$$

where H_c is the heat of combustion, H_p is heat of evaporation, C_p is specific heat, and T_{bp} and T_{amb} are boiling point and ambient temperatures, respectively. This equation assumes that 2% of heat of the combustion is returned to the fuel to compensate for the heat of evaporation and sensible heat. For crude oils, which have a range of boiling points, a break-even point at distillation is defined when the net energy is zero. From a sustained combustibility point of view, crude oils are categorized as :

- #1 (most combustible in the form of an oil slick): Over 67% of the mixture by volume has positive Net Energy.
- #2 (moderately combustible): between 40% and 67% of the mixture by volume has positive Net Energy.
- #3 (not combustible) : Less than 40% of the mixture by volume has positive Net Energy.

The above energy balance provides a practical approach to classifying fuels and has some scientific basis. However, a more detailed energy analysis is needed to accurately predict ignition and burning rate under specific conditions, such as the one proposed by Putorti, (1994). He made transient analysis of surface heating of viscous oils under external radiation flux under three simplified heat loss conditions at the surface. It was found, after comparing the results to experiments, that the heat transfer at the surface is dominated by the convective loss, and its proper accounting allows an accurate prediction of ignition.

Once the oil layer is ignited, the sustained burning rate can be determined by examining the energy transfer processes at the surface at steady state. A detailed

analysis oil emulsion layer was presented by Guenette *et al* (1994) which was based on the work of Brzustowski and Twardus (1982). The burn rate for oil emulsions was given by:

$$r = \frac{q_r'' - U_o \Delta T}{\rho_o \Delta H_{v,o} + \rho_o C_{p,o} (T_e - T_o) - \rho_w \Delta H_{v,w} f_w / (1 - f_w)}$$

where q_r'' is the radiative heat transfer from the flame to the oil layer; r is the burning rate of the oil layer; ρ_o and ρ_w represent the density of oil and water respectively; $\Delta H_{v,o}$ and $\Delta H_{v,w}$ are heats of vaporization of oil and water, respectively; $f_w(t)$ is fraction of water in emulsion at time t ; $C_{p,o}$ is heat capacity of oil; T_e and T_o are temperatures of emulsion and oil respectively; U_o is the overall heat transfer coefficient; and ΔT is the average temperature drop across the slick.

A comprehensive analysis of the spill combustion has not yet been attempted. Even simplified models are not extensively explored compared to the efforts devoted to the experimental approach. Often the emphasis is on finding empirical, engineering solutions, and the scope is limited to specific aspects of the process, such as ignition delay or burn rate. Thus, there is a strong need for developing more accurate models to understand and predict the oil spill combustion process.

Table 5 : Studies on Burn Rate, Burn Efficiency and Flame Spread

Allen, 1990	Exxon Valdez oil spill controlled burning tests; 98% efficiency obtained.
Berridge <i>et al.</i> , 1968	Mixing affects the extent and rate of removal. Burning agents on ice pool slicks did not affect burning rate but changed the residue. Average burn rates were 3-5 gal/min with faster rates for thicker slicks.
Brzustowski and Twardus, 1982	A one-dimensional, quasi-steady model of oil slick burning that does not include liquid-phase processes. Model predicts minimum thickness for ignition, the unburned residue, the burning time and the effects of wind on all of these factors.
Buist <i>et al.</i> 1995	Extensive burn tests on Alaska North Slope emulsions on various scales, including 0.13 m ² , 1.3 m ² , 3.3 m ² and 69 m ² pools. Burn efficiencies of over 96% were observed for emulsions having up to 60% water.
Coupal, 1976	Combustion of oil on water with a wicking agent for Bunker C and Cuerta crude; burn efficiencies of up to 85% noted.
Evans <i>et al.</i> , 1987	Results of measurements performed on 0.4 m and 0.6 m diameter pool fires by burning Prudhoe Bay crude oil on thermally deep layer of water. Emission studies also carried out.

Table 5 Continued

Evans <i>et al.</i> , 1989a	Burning rate measurements made on a 1.2 m diameter pool on n-decane, toluene and Alberta Sweet Crude.
Evans <i>et al.</i> , 1992	Experiments on crude oil burning on water using effective pool diameters from 0.4 to 17 m; burning rate was 0.55 ± 0.1 mm/s.
Evans <i>et al.</i> , 1990	Laboratory tests on 1 m diameter pool fires on crude oil
Fuji, 1995	Burn tests on 0.30 m diameter and 3.5 sq m pools for emulsified Murban crude on artificial sea water; also, chemical additives were tested
Glaeser, 1971	Data on spreading behavior of crude oil on water and ice surfaces, interaction of oil and ice, aging characteristics of oil, and effectiveness of burning and absorption for removal.
Guenette <i>et al.</i> , 1994 and 1995	Conducted extensive field experiments in basins cut into sea ice on 4 sq m to 300 sq m over four years. Effect of waves, extent of evaporation, ice and layer thickness on ignition and burning rate was analyzed.
Hillstrom, 1970	Use of activated carbon to enhance burning, forming an aggregated structure within fuel and acting as a wick to draw the oil to the surface.
Smith and Diaz, 1985	Small and large scale experiments conducted to explore range of conditions in which Prudhoe Bay Crude can be burned in broken ice and to determine efficiencies of such burns.
Walton <i>et al.</i> , 1993	6 m and 15 m square pools had burn rates of 0.062 ± 0.003 mm/s whereas 0.046 mm/s for 1.2 m diameter fire.
Wong and Kashyap, 1994	Fluid mechanical model presented to obtain shape of a boom in a tow (to assist in estimating burning rate).
Yumoto, 1971	Experimental determination of ratio of radiation and convection transfers to total heat transfer from flame to fuel surface. Burn rate mainly dependent on radiation.

Effects of Surrounding Physical Conditions

Short waves, in general, do not affect the ignition of emulsion drifting in the burning region. However, swells of the order of 30 cm high and 3 m long can reduce burn efficiency and make ignition impossible. Heat radiated from fire could ignite emulsions with 50% water in a current of 0.3 m/s and waves 15 cm in height (Guenette *et al.* 1995). Air temperature (-11°C to 2°C), water temperature (-1°C to 17°C) and ice coverage were shown to have negligible effect on burning of oil. It was found that for wind over 30 knots, the fire would not spread, however, at higher wind speeds the fire continued in windward direction.

Under creation conditions, the water sublayer starts boiling, penetrates the fuel layer and ejects water drops into the surroundings. This is the boilover phenomenon. Oil layer thinner than a critical thickness will cause excessive heat loss to water and leave either insufficient energy to pyrolyze it, or cause boilover of water under the layer. If the oil layer is sufficiently thick, the heat from the combustion is absorbed in depth, causing boilover of water forming droplets of oil which burn above the surface. To maintain a sufficient thickness of oil layer, a practical consideration is to contain the oil in an area restricted by a boom, vessel, shoreline, ice or other means, so that it does not spread itself too thin to burn. Since booms are portable, there is considerable interest in developing fire-resistant booms for containment of oil slick.

Table 6 : Effects of Surrounding Physical Conditions and Water Base

Allen and Simpson, 1986	Testing of four fire containment booms with 24 hour exposure to burning crude oil. Seven burn tests in waves up to 0.6 m in height and with currents of 0.2 m/s to 0.6 m/s.
Arai <i>et al.</i> , 1988	Boilover phenomenon was studied using a specially designed burner system for nine different single-component and six different multi-component fuels. Results for 4.8 cm diameter ethyl benzene pool fire show that for boilover, temperature gradient across the fuel vanishes.
Brown and Goodman, 1986	A series of experiments evaluating the effects of wind herding, oil weathering, oil thickness and ice lead geometry on burn efficiency
Guenette <i>et al.</i> , 1995	Effects of wind velocity, waves, evaporation, water content and ice coverage on burn efficiencies are studied on oil mixtures in field experiments in basins ranging from 4 to 300 sq.m.
Inamura <i>et al.</i> , 1992	A one-dimensional model developed to predict the time required for boilover to begin. It was found that, significant amount of heat is transferred from the fuel open surface to fuel-water interface by Rayleigh convection.
Lazes, 1994	Evaluates effects of more than a dozen oil burn tests on fire booms.
McMinn, 1973	Burning of oil on ice and snow is discussed. Under conditions of limited snowfall and wind velocity below 14 knots, 80% of spilled petroleum can be burned without promoters.
Meikle, 1977	Proposed two equipment ideas for containment -- buoyant net to trap oil in its mesh for burning and lightweight fire proof boom.

Smoke, Residue and Aquatic Toxicity

A large amount of research has been carried out in the field of emissions from the in-situ fires. Polyaromatic Hydrocarbons (PAHs) are found to be lower in the soot than in the starting oil and are consumed by the fire to a large extent. The burn products are typically CO₂- 75%, water vapor- 12%, soot- 10%, CO- 3% and other products including PAHs- 0.2% (Tennyson, 1994). The work conducted up until now has not shown any serious air pollution problems from the oil spill combustion emission. The most damaging pollution in an oil spill occurs when lighter compounds are evaporated from the spill. The laboratory test burns have indicated that residues from thick, batch type in-situ burns of heavier crudes will sink. The research on the aquatic toxicity has revealed very little, if any, toxicity from the oil burn. Perhaps the most extensive aquatic and air pollution studies conducted on large scale oil spill combustion were in NOBE (Newfoundland Offshore Burn Experiment) in 1993 (Daykin *et al.*, 1995; Fingas, *et al.*, 1994a). Smoke measurements and air sampling was done using miniblomp and helicopter deployed instrumentation (Walton *et al.*, 1994a,b). It was found that up to 150 m downwind at ground level, emissions were of concern; however, beyond 500 m, they were negligible. Large eddy simulation of the smoke trajectory from this and other experiments have been made with success (McGrattan *et al.*, 1994; Baum *et al.*, 1994).

Table 7 : Studies on Smoke, Residue And Aquatic Toxicity

Baum <i>et al.</i> , 1994	Large eddy simulation model of smoke plumes generated by large outdoor pool fires. Assessment of potential environmental hazard posed by burning marine oil spills.
Benner <i>et al.</i> , 1990	Alberta Sweet crude in 2-, 3-, 5-, 10- and 30-mm layers on water was burned and smoke samples were collected at elevated and ambient temperatures and analyzed for 18 PAHs.
Buist <i>et al.</i> , 1995b	Physical properties of residues from burning small slicks of eight different oils on water are studied and are compared to the original oil properties. Oils used were unweathered and artificially weathered. 5 cm, 10 cm and 15 cm of oil thicknesses were burned on salt water at 15 °C and residues were measured for density, water content, pour point and viscosity. Chemical analyses of oils and residues were carried out.
Day <i>et al.</i> , 1978	Estimates of soot, CO, SO, and metals emissions based on literature and experiments. Downwind concentrations of combustion products calculated using conventional plume dispersion equations with superposition of plume in time and space from a number of burning pools.

Table 7 Continued

Daykin <i>et al.</i> , 1995	Chemical analyses of background samples (sea water only), pre-burn samples (sea water and unburned oil) and post-burn samples (sea water and burned oil) from NOBE to identify 24 target PAHs and to determine total petroleum hydrocarbons. Five toxicity tests were carried out concluding that no major contamination or toxicity generation was caused by in-situ burning.
Evans and Walton, 1990	Measurements of 1.2 m diameter Murban crude oil pool fires. 10% of crude oil was converted to smoke with carbon content in excess of 90%.
Evans <i>et al.</i> , 1988	Burning behavior of Alberta Sweet, LA Rose and Murban crude oils using 1.2 m diameter pool. Chemical analysis of products of combustion of Alberta Sweet oil in 0.6 m diameter pool fires.
Evans <i>et al.</i> , 1989a	Measurements of optical properties and particulate agglomeration of smoke from Alberta Sweet blend mix crude oil fires using 1 m ³ aging chamber.
Evans <i>et al.</i> , 1990	Field scale measurement techniques for fire radiation, smoke yield, particulate sampling and plume trajectory.
Evans <i>et al.</i> , 1991	Instrument packages developed to determine the amounts of combustion products from 15m x 15m crude oil pool fires.
Evans, 1994	Measured smoke production from burning of crude oils in the laboratory, in meso-scale experiments and in an off-shore experiment are presented.
Fingas <i>et al.</i> , 1994b	Thirty meso-scale burns between 1991 and 1992, and NOBE in 1993, were analyzed for PAH content of soot, metals in residue and soot samples, particulates in soot, and other components. More than 50 compounds were quantified, several at levels of concern, up to 150 m downwind at ground level. Emissions were found to be of no concern beyond 500 m downwind.
Fingas <i>et al.</i> , 1994a	Emission samples from NOBE showed that CO, CO ₂ , and SO ₂ , are not of major concern. Volatile organic compounds, though abundant, were less than emitted from non-burning spill.
Ghoniem <i>et al.</i> , 1993	Computational model for simulation of large scale smoke plumes from oil spill fires with a focus on descent and dispersion of wind driven plumes in a homogeneous atmosphere and smoke deposition of flat terrain.
McGrattan <i>et al.</i> , 1994	Large Eddy Simulation numerical model to predict the concentration of particulate matter downwind of a large fire. Validity of the model checked by data from NOBE, Alaskan Clean Seas Burning of emulsions and US Coast Guard/NIST Mesoscale burns. Data are found to match the predicted concentrations.

Table 7 Continued

Mitchell <i>et al.</i> , 1991	Study concerned with efforts to reduce smoke emission from burning of crude oil by the use of ferrocene and its derivatives. Excellent soot-inhibiting results obtained. Smoke volume reduced by 90%.
Notarianni <i>et al.</i> , 1993	Scaling of smoke yield from laboratory to large scale fires based on results from pool fire experiments from 0.85 m to 17.2 m in diameter.
Walton <i>et al.</i> , 1993	Smoke particulate yields from 15 m square and 1.2 m diameter fires found to be approximately 11% of oil burned on mass basis. Predictions of plume trajectory using Large Eddy Simulation technique.
Walton <i>et al.</i> , 1994a	Developed and tested a smoke sampling package, with real time sampling of CO, with infrared gas analyzer and volatile organic compounds with a photoionization detector, to be deployed on a helicopter winch cable.
Walton <i>et al.</i> , 1994b	Smoke measurements during NOBE using helium filled miniblomp tethered to a vessel operated approximately 300 m downwind.

Conclusions

This paper presents a comprehensive review of studies on in-situ oil spill combustion. In-situ burning of oil or water-in-oil emulsion supported on top of a water-base, such as the ocean, is a complex process, and in general, may be examined in three stages before, during and after the actual combustion. Prior to combustion, the important factors are weathering and emulsification. The burn rate and efficiency depend on the extent of emulsification and the evaporation of oil. The combustion produces smoke and other emissions; however, most studies indicate that these are not of great concern when compared to the alternative cleanup measures. The review shows that there is a need for fundamental studies, especially in the mathematical modeling area, to understand the basic mechanisms and to predict the applicability of the in-situ combustion.

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