

A Mathematical Model for In-situ Burning of Water-in-Oil Emulsions

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Abstract

The combustion process of a water-in-oil emulsion layer floating on top of a water body, as in case of in-situ burning of oil spilled at sea that has turned into emulsion, is modeled using comprehensive mathematical treatment. The burning process is divided into three regimes, as follows.

1. Initial regime, when the emulsion layer floating on the ocean surface receives heat flux from an external source such as an igniter or a burning oil pool;
2. Intermediate regime, from the instant when there is first appearance of oil layer on the top of the emulsion layer due to breaking of emulsion until the oil starts evaporating; and,
3. The final regime, which is characterized by the combustion of oil vapor and continues till the fire extinguishes.

In arctic regions, the ignition delay and removal efficiency may possibly be affected by the temperature of the water table (or ice) and other surrounding conditions. The purpose of this model is to find out whether the emulsion layer will burn, and if so, calculate the ignition delay, predict how long will it burn, and determine the efficiency of oil and emulsion removal by the combustion process. Important parameters include the composition of emulsion layer in % water content, layer thickness, and the incident heat flux.

1.0 Introduction

The potential benefits of in-situ burning technique make it one of the most effective oil spill clean up measures. When feasible, it is an inexpensive technique needing fewer personnel and minimal equipment compared to the other countermeasures. Efficiency of removal has been reported to be greater than 99% based on large scale in-situ oil-spill burns. 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. (Fingas and Laroche, 1990; Evans and Tennyson, 1991, Buist *et al.*, 1994).

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 leading to spill combustion, which are very important in determining the efficacy of this technique as a cleanup countermeasure, include the evaporation or weathering of oil, emulsification with water, thickness of oil slick, ignition source, surrounding physical conditions such as the presence or absence of containment structures (like a fire boom, ice, ship, or embankment) and surrounding dynamic conditions (including waves and wind conditions). The next stage is combustion of

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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 process is depicted in Figure 1. The processes in this stage are dominated by energy transfer to the layer, breakup of the emulsion layer, and subsequent burning of oil layer. The final stage is characterized by the air and aquatic pollution caused by the combustion process. The oil spill combustion technique would be unacceptable if the consequent environmental damage is significant. There is always a residue left, the airborne species may contain combustion products 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.

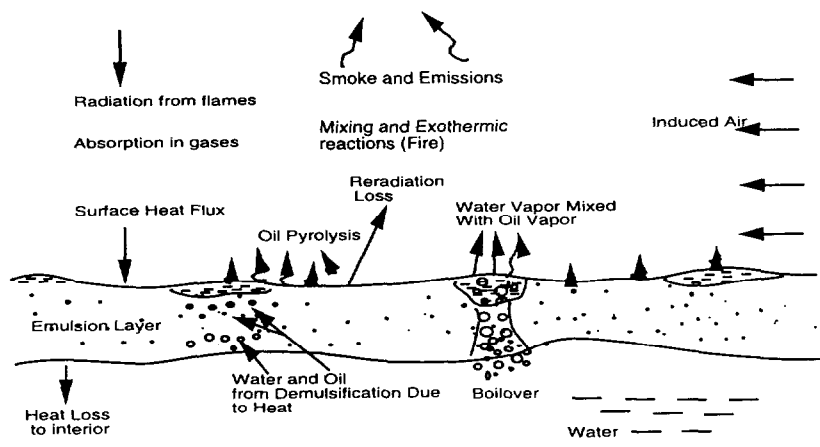


Figure 1. Schematic of Physicochemical Processes of Emulsion Combustion

The technique of in-situ oil spill combustion has been tried in practice and investigated by researchers sporadically over the past thirty years. Focus of the previous research in this field was primarily of experimental nature. A few attempts of modeling the process were limited in their scope to specific aspects of the process, such as ignition delay, steady state burn rate, or pure oil. This is the first comprehensive mathematical model for the combustion of emulsion supported by a water base.

2.0 A Brief History of Modeling Attempts

A key mechanism for a sustained combustion of the oil or 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, 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. Based on this general principle, a simple energy balance for the oil layer burning on top of water was proposed by Thompson *et al.* (1979),

$$Net\ Energy = 0.02\ Q_{comb} - Q_{Lo} - C_{po}\ (T_{ov} - T_o) \quad (1)$$

This equation assumes that 2% of heat of the combustion is returned to fuel in order to compensate for the heat of evaporation and sensible heat. Since crude oils have several components (light and heavy) which have a range of vaporization temperatures (T_{ov}), the Net Energy can be positive, negative, or zero for the individual components. From a sustained combustibility point of view, crude oils were categorized as :

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

The above model provided a practical approach to classifying fuels. However, a more accurate energy analysis was needed to predict ignition time and burning rate under specific conditions. A detailed energy balance for 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:

$$r = \frac{\dot{q}'' - U_0 \Delta T}{\rho_o \Delta H_{v,o} + \rho_o C_{p,o} (T_e - T_o) - \rho_w \Delta H_{v,w} f_w / (1 - f_w)} \quad (2)$$

where $f_w(t)$ is the fraction of water in emulsion at time t , U_0 is the overall heat transfer coefficient, and ΔT is the average temperature drop across the slick. This is a steady state, zone model which allows computation of burning rate based on averaged quantities. Putorti and Evans (1994) made transient analysis of surface heating of viscous oils under external radiation flux under three heat loss conditions at the surface. The model comprised of the following governing equation,

$$k_o \frac{\partial^2 T}{\partial y^2} + (1 - C_o) \dot{q}'' \beta e^{-\beta y} = \rho_o C_{p,o} \frac{\partial T}{\partial t} \quad (3)$$

which is a similar to the general form of governing equation used in the present model. The model was limited to a pure oil layer floating on water receiving incident radiant heat flux. Ignition delay was computed under various heat flux conditions. It was concluded, after comparing the results to experiments, that the heat transfer at the surface is dominated by convective loss, and its proper accounting allowed an accurate prediction of ignition time.

The focus of the present work is on the transient burning of water-in-oil emulsions with an emphasis on computation of timeline for the important events in the process, such as the onset of breakup of the emulsion into oil and water, ignition delay, complete consumption of the emulsion layer, total burnout period, and the residue left.

3.0 Physical Model

Combustion of an oil emulsion layer floating on top of a body of water is a complex phenomenon, as depicted in Figure 1. To make it mathematically tractable, a simpler, one-dimensional process is assumed. Heat is transferred from a source, such as an igniter or adjacent fire, to the emulsion layer. As the emulsion heats up, there is thermal breaking of the emulsion, resulting in separation of water and oil. With further heating, water vaporizes and the oil floats up. The condensed phase now consists of oil layer, emulsion layer and the water base. At the free oil surface, there is partial absorption of incident heat flux, in-depth radiation absorption, heat loss to the surroundings by radiation and convection, and conduction in the condensed phase. As the top layer of oil receives heat, it heats up, vaporizes, and pyrolyzes. The pyrolysis gases mix with the oxidizer from the air and the mixture is ignited by available ignition source or fire above the oil layer. The oil burning process is sustained by partial energy feedback from the combustion. In addition to pyrolysis, the energy is distributed as the sensible heat of raising the temperature of the condensed phase, reradiation and convection to the surroundings, latent heat of water evaporation and oil vaporization, and heat loss into the water. The process ends after the emulsion layer is completely consumed and there is excessive heat loss into the water which can not support oil vaporization.

For the modeling purpose, the overall burning process is divided into three regimes as follows.

1. *Initial Regime* ($t = 0$ to t_1): The model starts with the application of external heat flux to an emulsion layer floating on top of ocean surface. Entire slick is at a uniform temperature equal to the surrounding temperature. A constant radiation heat flux source is incident on the emulsion surface. The emulsion layer is heated and eventually the top surface reaches the emulsion-breaking temperature. This marks the end of initial regime.

2. *Intermediate Regime*: ($t = t_1$ to t_2): Continued input of heat does not raise the temperature of the emulsion surface, instead, it provides the energy required for emulsion breaking which causes the first appearance of oil on top of the emulsion. Thus, there are three layers in this regime, oil, emulsion and water. The oil layer grows and the emulsion layer thins out. Now the oil layer receives incident heat flux. The oil, not being optically thick, absorbs only a part of the incident heat flux at the surface and some of the radiation energy is absorbed in-depth. A part of the heat flux that reaches oil-emulsion interface without getting absorbed in oil, is completely absorbed at the oil-emulsion interface. The temperature of the oil layer increases while the oil-emulsion interface temperature remains constant at the emulsion breaking temperature. When the oil surface temperature reaches vaporization temperature, the intermediate regime ends.

3. *Final Regime*: ($t = t_2$ to t_3): The vaporized oil burns because of the presence of the fire, energy is released by oil combustion, and a part of it is fed back to the oil. The incident heat flux increases rapidly to the prescribed maximum value, q_{\max} (which depends on the type of crude oil, fire size, wind velocity, and other combustion conditions). The surface temperature of the oil now stays at the oil vaporization temperature. The vaporization causes the oil layer to deplete while the breaking up of

emulsion layer causes the oil layer to grow. The process continues until the emulsion layer completely depletes, oil layer continues to burn, and finally extinction occurs because the loss of heat to the water becomes greater than the heat feedback to the oil surface.

4.0 Mathematical Model

4.1 Assumptions: Initially, it was assumed that a specified thickness of emulsion layer was floating on the water surface, which was at 273 K, a typical arctic condition. The energy transfer is from the external source or ignitor into the condensed phase, and in the interior, it is by one dimensional conduction. Representative properties for emulsion were assumed to be weighted average of the oil and water properties, and constant throughout the time of operation. When the oil begins to vaporize, a prescribed maximum heat flux, q_{max} , is reached; and after that, the heat flux remains constant. Emulsion is assumed to separate into oil and water at the boiling point of sea water of 380 K, and the oil evaporates at 555 K. The latent heat of emulsion breakup is set equal to the latent heat of liquid water vaporization times the water fraction. Wind and ocean turbulence effects are neglected. Emulsion is assumed to be optically thick but oil is allowed in-depth radiation absorption. The sea water base is modeled as a semi-infinite medium.

4.2 Model:

4.2.1 Initial Regime

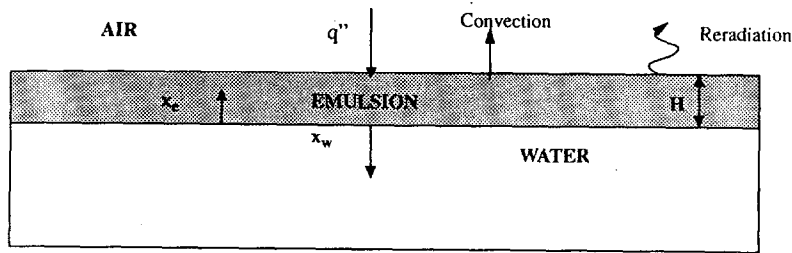


Figure 2. Initial Regime

Governing Equations:

$$\frac{\partial T_{e1}}{\partial t} = \alpha_e \frac{\partial^2 T_{e1}}{\partial x_e^2} \quad (4)$$

$$\frac{\partial T_{w1}}{\partial t} = \alpha_w \frac{\partial^2 T_{w1}}{\partial x_w^2} \quad (5)$$

Initial Conditions:

$$@ t = 0, T_{e1} = T_i \quad (6)$$

$$T_{w1} = T_i \quad (7)$$

Boundary Conditions:

$$@ x_e = H, k_e \frac{\partial T_{e1}}{\partial x_e} = -\dot{q}'' + h_e (T_{e1} - T_\infty) + \sigma \epsilon_e (T_{e1}^4 - T_i^4) \quad (8)$$

$$@ x_e = 0, x_w = 0, k_e \frac{\partial T_{e1}}{\partial x_e} = -k_w \frac{\partial T_{w1}}{\partial x_w} \quad (9)$$

$$@ x_w = \infty, T_{w1} = T_i \quad (10)$$

Part I ends when the $T_{e1} = T_{eb}$ @ $x_e = H$

At end of Part I, $t = t_1$, $H = H_i$

4.2.2 Intermediate Regime

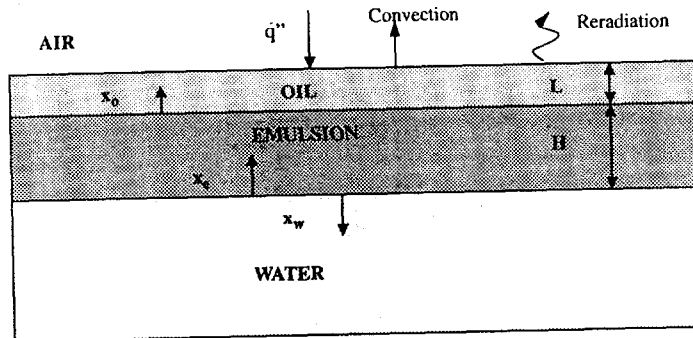


Figure 3. Intermediate Regime

Governing Equations:

$$\frac{\partial T_{o2}}{\partial t} = \alpha_o \frac{\partial^2 T_{o2}}{\partial x_o^2} + \frac{C_0 \dot{q}'' \beta e^{-\beta(L-x_o)}}{\rho_o C_{po}} \quad (11)$$

$$\frac{\partial T_{e2}}{\partial t} = \alpha_e \frac{\partial^2 T_{e2}}{\partial x_e^2} \quad (12)$$

$$\frac{\partial T_{w2}}{\partial t} = \alpha_w \frac{\partial^2 T_{w2}}{\partial x_w^2} \quad (13)$$

Initial Conditions:

$$@ t = t_1, T_{o2} = T_{eb} \quad (14)$$

$$T_{e2} = T_{e1} \quad (15)$$

$$T_{w2} = T_{w1} \quad (16)$$

$$L = 0 \quad (17)$$

$$H = H_i \quad (18)$$

Boundary Conditions and Auxiliary Equations at The Boundaries:

$$@ x_o = 0, T_{o2} = T_{eb} \quad (19)$$

$$@ x_o = L,$$

$$k_o \frac{\partial T_{o2}}{\partial x_o} = - (1 - C_0) \dot{q}'' + h_o (T_{o2} - T_i) + \sigma \epsilon_o (T_{o2}^4 - T_i^4) \quad (20)$$

$$@ x_e = 0, x_w = 0, k_e \frac{\partial T_{e2}}{\partial x_e} = -k_w \frac{\partial T_{w2}}{\partial x_w} \quad (21)$$

$$@ x_e = H, T_{e2} = T_{eb} \quad (22)$$

$$@ x_w = \infty, T_{w2} = T_i \quad (23)$$

$$@ x_o = 0, x_e = H,$$

$$-C_1 Q_{Le} \rho_o \frac{dL}{dt} = \rho_e Q_{Le} \frac{dH}{dt} = -k_o \frac{\partial T_{o2}}{\partial x_o} + k_e \frac{\partial T_{e2}}{\partial x_e} - a C_0 \dot{q}'' e^{-\beta L} \quad (24)$$

Part II ends when $T_{o2} = T_{ov}$ @ $x_o = L$

At end of Part II, $t = t_2, H = H_2, L = L_2$

4.2.3 Final Regime

Governing Equations:

$$\frac{\partial T_{o3}}{\partial t} = \alpha_o \frac{\partial^2 T_{o3}}{\partial x_o^2} + \frac{C_0 \dot{q}'' \beta e^{-\beta(L-x_o)}}{\rho_o C_{po}} \quad (25)$$

$$\frac{\partial T_{e3}}{\partial t} = \alpha_e \frac{\partial^2 T_{e3}}{\partial x_e^2} \quad (26)$$

$$\frac{\partial T_{w3}}{\partial t} = \alpha_w \frac{\partial^2 T_{w3}}{\partial x_w^2} \quad (27)$$

Initial Conditions:

$$@ t = t_3 \quad T_{o3} = T_{ov} \quad (28)$$

$$T_{e3} = T_{e2} \quad (29)$$

$$T_{w3} = T_{w2} \quad (30)$$

$$L = L_2 \quad (31)$$

$$H = H_2 \quad (32)$$

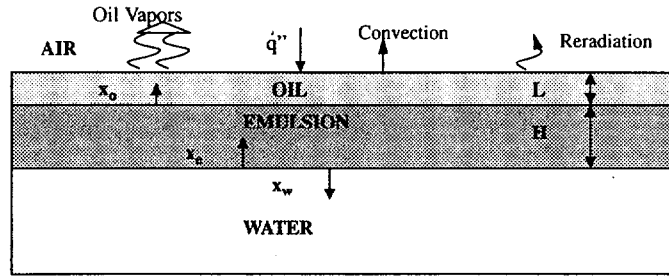


Figure 4. Final Regime

Boundary Conditions and Auxiliary Equations at The Boundaries:

$$@ x_o = 0, \quad T_{o3} = T_{eb} \quad (33)$$

$$@ x_o = L, \quad T_{o3} = T_{ov} \quad (34)$$

$$@ x_e = H, \quad T_{e3} = T_{eb} \quad (35)$$

$$@ x_e = 0, x_w = 0, \quad k_e \frac{\partial T_{e3}}{\partial x_e} = -k_w \frac{\partial T_{w3}}{\partial x_w} \quad (36)$$

$$@ x_w = \infty, \quad T_{w3} = T_i \quad (37)$$

$$@ x_o = 0, x_e = H,$$

$$-C_1 Q_{Le} \rho_o \dot{L}_p = \rho_e Q_{Le} \frac{dH}{dt} = -k_o \frac{\partial T_{o3}}{\partial x_o} + k_e \frac{\partial T_{e3}}{\partial x_e} - a C_0 q'' e^{-\beta L} \quad (38)$$

$$@ x_o = L,$$

$$k_o \frac{\partial T_{o3}}{\partial x_o} = -(1 - C_0) q'' + h_o (T_{o3} - T_i) + \sigma \epsilon_o (T_{o3}^4 - T_i^4) + \rho_o Q_{Lo} \dot{L}_d \quad (39)$$

$$\frac{dL}{dt} = \dot{L}_p + \dot{L}_d \quad (40)$$

4.3 Numerical Solution Scheme:

The emulsion layer was divided into 0.5 mm grid for numerical computation and the grid for water base was stretched to accommodate the semi-infinite medium using coordinate transformation. The oil grid spacing was calculated such that one emulsion grid formed one grid length in oil after break up. From the resulting set of

equations, a general equation is selected for finite differencing, as follows :

$$\frac{\partial T}{\partial \tau} + \frac{\partial T}{\partial t} = \alpha C_{i1} \frac{\partial^2 T}{\partial x^2} + C_{i2} \frac{\partial T}{\partial x} + \frac{a C_0 q'' \beta e^{-\beta(L-x)}}{\rho_o C_{po}} \quad (41)$$

where, $C_{i1} = C^2 (1-x)^4$ and $C_{i2} = -4\alpha_w C^2 (1-x)^3$ for water base and $C_{i1}=1$ and $C_{i2}=0$ for oil and emulsion layers. Also $a=1$ for oil layer to account for indepth absorption and $a=0$ for emulsion and water layers. The pseudo time derivative added to the governing equation is driven to zero by attaining steady state in pseudo time (τ), each step in real time (t) assuring a converged solution. Explicit finite differencing is used with two point differencing in time and central differencing in space. The code was written in Fortran, compiled and run on SGI Irix 6.2 system. Typical run time for the code was around 20 minutes.

5.0 Results

Numerical results were obtained for the following conditions :

External Heat Flux : Initially 20 kW/m^2 (from $t = 0$ to t_2), increasing to q_{\max} of 50, 75 or 100 kW/m^2 as the oil starts burning. This range was selected because for pool fires under various conditions, measurements have shown that the flux level can be up to 145 kW/m^2 (Holen, et al. 1990). Heat flux in present calculations was increased gradually to q_{\max} by adding 2% of the heat of combustion of the vaporizing oil to the base value of 20 kW/m^2 .

Emulsion composition : 30%, 45% and 60% water in oil by volume

Emulsion layer thickness, H : 2 cm, 3 cm, 5 cm.

Numerical computations were carried out to determine, among other variables, the distribution of temperature in the layers as a function time, the ending times for the three regimes, t_1 , t_2 , and t_3 , residual thickness of oil layer, efficiency of removal,

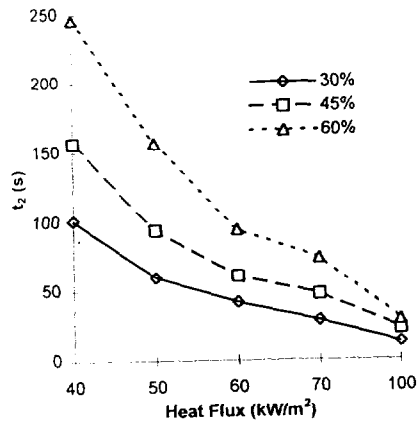


Figure 5. Ignition Delay a Function of Incident Heat Flux For Three Different Types of Emulsions

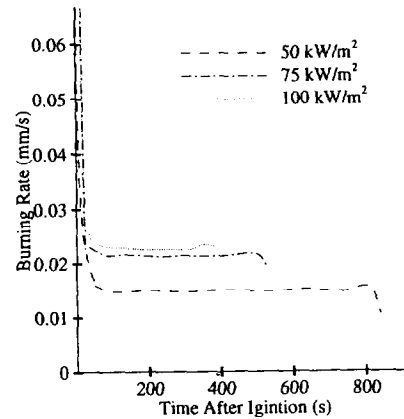


Figure 6. Transient Burning Rate of Oil Layer at Various External Heat Fluxes

oil burning rate in mm/s of surface recession, and the time to burnout.

Ignition delay, which is the same as the time at the end of intermediate regime (t_2), is shown in Fig. 5 for three fluxes and various compositions of the emulsion. In this set of runs, the external heat flux was held constant throughout (i.e., it did not start from 20 kW/m^2 and changed to q_{\max}). The ignition delay decreases with increasing external flux, as expected. It also decreases with higher water content in the emulsion at a given flux. This occurs because the incident heat is utilized to separate oil from emulsion layer by evaporating the water. The corresponding values obtained by Putorti and Evans (1994) for pure oil (0% water content) were 260 s at a flux of 20 kW/m^2 and 40 s for 50 kW/m^2 , which are similar in magnitude to the present results.

The transient burning rate of oil in mm/s of surface recession is shown in Fig. 6 as a function of time for the three heat fluxes. Soon after the vaporization of oil begins, the oil layer thickness is the highest. The burning rate is high because the loss into the interior is minimum. As the oil layer starts thinning, the conduction loss to the emulsion layer and the transmission of radiation through the oil layer leaves less energy for vaporization; consequently the burning rate drops and then becomes steady. Near burnout, the rate drops to zero because of the losses, leaving a thin residual of oil layer. The steady burning rate value is greater for higher heat fluxes as expected. The burning rate observed experimentally by Walton *et al.*, 1993 was 0.046 mm/s for pool burning fires of plain oil under slightly different conditions, which is in the same range of the present results.

The oil layer continued to burn as the emulsion layer was separating into oil and water. When the emulsion layer completely depleted (at $t = t_3$) only a small amount of oil layer was left (less than 2 mm), and it extinguished in less than 20 s

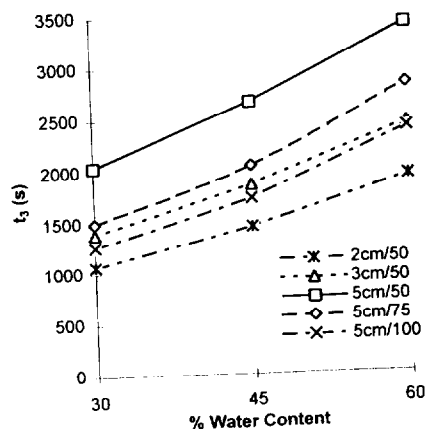


Figure 7. Time to Burnout a Function of Water Content in Emulsion For Three Different Emulsion Layer Thicknesses at Three Incident Heat Fluxes

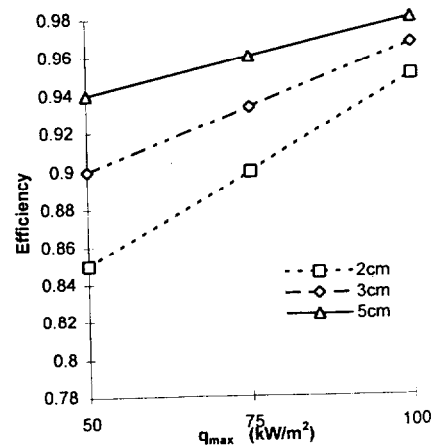


Figure 8. Oil Removal Efficiency a Function of Incident Heat Fluxes For Three Different Emulsion Layer Thicknesses

after t_3 . Hence, the t_3 is used as the time to burnout. It is plotted in Fig. 7 as a function of the % water in emulsion for three thicknesses, 2 cm, 3 cm, and 5 cm at a fixed maximum external flux, and for three maximum external fluxes of 50, 75 and 100 for a 5 cm thick emulsion layer. The burnout period is greater for higher water content in emulsion and for larger thickness; and it decreases for increasing external heat fluxes. The higher water content makes it difficult for oil to separate out and burn, hence the longer burnout period. The effects of thickness and heat flux are obvious.

It was found that the residual oil layer, which remained because the excessive heat loss to the interior did not allow it to reach the evaporation temperature, was relatively thin (approximately 1 mm) under most conditions. This is consistent with experimental observations. It indicates that the efficiency of removal (defined as the amount of oil burnt divided by the amount of oil in original emulsion layer) increases with larger initial emulsion layer thickness, as shown in Fig 8. For the largest initial emulsion layer thickness, the removal efficiency remained over 94% at all the fluxes studied. These efficiencies are consistent with the experimental measurements of emulsion burning efficiency. (Buist *et al.*, 1995; Fuji, 1995)

The present model illustrates the parametric effects of external heat flux, emulsion layer thickness and composition on such important quantities as the ignition delay, total burnout period, efficiency of removal, and transient burning rate. There is a strong need for a systematic experimental study to verify applicability of the model. Also, accurate property data for actual crude oils and a realistic assessment of weathering and other conditions is needed for applying the model to practical situations. Once validated, the present model can give reasonable idea as to whether an emulsion layer under given conditions can burn, and if so, how long will it take and what will be its effectiveness.

6.0 Summary and Conclusion

This paper presents a comprehensive mathematical model for the combustion of water-in-oil emulsion layers floating on top of a water body, as in case of in-situ burning of oil spilled at sea that has turned into emulsion. The model was solved numerically using a finite difference, pseudo-time algorithm.

It was found that the total burnout period decreased with increasing external heat flux, lower % water content and smaller layer thickness. The ignition delay also decreased with increasing external heat flux and lower % water content, but it was insensitive to the emulsion layer thickness. The efficiency of removal was greater at higher heat fluxes and for emulsion layers of larger thickness. The burning rate was higher at higher flux levels. The numerical results were in the same range as previous experimental and analytical results obtained under somewhat different conditions. It appears that such a model can provide significant insight before applying oil-spill combustion technique to real life situations.

7.0 Nomenclature

- C_o Fraction of incident heat flux not absorbed at the surface
- C_1 Inverse of oil content of emulsion, on mass basis
- C_{po} Specific heat of oil

H	Emulsion thickness
h	Convective heat transfer coefficient
k	Thermal conductivity
L	Oil thickness
\dot{L}_p	Rate of oil layer production due to emulsion breaking
\dot{L}_d	Rate of oil layer depletion due to oil evaporation
\dot{q}''	Incident heat flux
q_{\max}	Maximum heat flux incident on the slick
Q_{comb}	Energy released by combustion of oil
Q_{Le}	Energy consumed in emulsion breaking
Q_{Lo}	Energy consumed in oil vaporization
Q_{Lw}	Energy consumed in water vaporization
t	Time
T_{eb}	Emulsion breaking temperature
T_{ov}	Oil vaporization temperature
T	Temperature
x_e	Emulsion coordinates
x_o	Oil coordinates
x_w	Water coordinates

7.1	Greek Symbols
α	Thermal diffusivity
β	Inverse absorption depth
ε	Emissivity
ρ	Density
σ	Stefan-Boltzmann constant

7.2	Subscripts
e	Emulsion
o	Oil
w	Water
1	For part I
2	For part II
3	For part III
i	Initial conditions

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