

EVAPORATION OF OIL SPILLS

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INTRODUCTION

Evaporation is the most important change that most oil spills undergo. In a few days, light crudes can evaporate as much as 75% of the starting oil mass and medium crudes up to 40%. Heavy or residual oils may only evaporate to the extent of 10% in the first few days following a spill. Many spill models incorporate evaporation as a component of their prediction because of the large mass balance changes.

Although the process of oil evaporation is understood, the application of evaporation equations in spill models is sometimes difficult. This relates to the input data required for the equations. There are only 3 relatively well-used schemes currently employed in models. The most commonly used is that of evaporative exposure as proposed by Stiver and Mackay (1984). Difficulties with the implementation of this model are primarily in terms of input data. Model implementation requires a mass transfer coefficient and a vapour pressure for each oil. These are not routinely measured for oil and must be estimated using other techniques. The second most-commonly used method is that of applying oil fraction-cut data. These methods are applied by using the readily-available distillation curves to estimate parameters for the Mackay equations noted above or in a direct technique. The third most common method is to assume a loss rate which is estimated from oil properties and the presumption that the oil moves linearly or logarithmically to that end point.

PHYSICS AND CHEMISTRY OF OIL EVAPORATION

The basis for most of the evaporative work is the extensive study on the evaporation of water (Brutsaert, 1982; Jones, 1992). In fact, the currently-used equations still employ empirical portions of these equations. There are several fundamental differences between the evaporation of a pure liquid such as water and for a multi-component system such as crude oil. First the evaporation rate for a single liquid such as water is a constant with respect to time. Evaporative loss - by total weight or volume - is logarithmic with time for multi-component mixtures. This is due to the depletion of the more volatile components, which occurs exponentially with time. The second major difference between water evaporation is the effect of atmospheric conditions. Water evaporation is strongly dependent on wind speed and relative humidity. Air can only hold a certain water mass. Air does not contain a high level of benzene and other components and the saturation level of these in air is often well above concentrations that can be achieved from an evaporating slick. The understanding of how wind affects oil slick evaporation has not yet been achieved.

Blokker (1964) was the first to develop separate oil evaporation equations for oil evaporation at sea. His starting basis was theoretical and presuming that fuel was a one-component liquid. The ASTM distillation data with the average boiling points of successive fractions were used as the data source and a weathering curve was calculated.

Mackay and Matsugu (1973) approached the problem by adopting the classical water evaporation work and supplemented this by additional experimental data. Data on the evaporation of water and cumene have been used to correlate the gas phase mass transfer coefficient as a function of wind-speed and pool size by the equation;

$$k_m = 0.0292 U^{0.78} X^{-0.11} Sc^{-0.67}$$

where: K_m = the mass transfer coefficient in units of mass per unit time

U = wind speed, note that the power of 0.78 is the classical water evaporation-derived coefficient

Sc = Schmidt number, which is a dimensionless number representing the surface roughness

X = pool diameter

This work was extended by the same group (Goodwin, Mackay and Shiu, 1976) to show that the evaporative loss of a mass of oil spilled can be estimated using a mass transfer coefficient as shown above. Butler (1976) developed a model to examine evaporation of specific hydrocarbon components. This predicts that the fraction weathered at a given time decreases more than exponentially with increasing carbon number. Yang and Wang (1977) developed equations using the Mackay and Matsugu molecular diffusion process. A functional relationship expressing area and wind speed was developed. Drivas (1982) compared the Mackay and Matsugu equation with data found in the literature and noted that the equations yielded predictions that were close to the experimental data. Rheijnhart and Rose (1982) developed a simple predictor model for the evaporation of oil at sea. They proposed a simple relationship using empirical constants from pan evaporation experiments. Tkalin (1986) proposed a series of equations to predict evaporation at sea using similar procedures.

The most frequently used work in spill modelling is that of Stiver and Mackay (1984). The work is based on some of the earlier work by Mackay and Matsugu (1973). Additional information is given in a thesis by Stiver (1984). The formulation is initiated with assumptions about the evaporation of a liquid. If a liquid, of vapour pressure P (Pa), is spilled over an area of (m^2) , the rate of evaporation is given by:

$$N = k_a P / (RT)$$

where N is the molar flux (mol/s),

k is the mass transfer coefficient under the prevailing wind conditions (m/s),

R is the gas constant [$8.314 \text{ Pa} \cdot m^3 / (\text{mol} \cdot K)$], and

T is the environmental temperature (K).

This equation can be arranged to give:

$$dF_v / dt = k_a P_v / (V_o RT)$$

where F_v is the volume fraction evaporated,

t is time (s),
 v is the liquid's molar volume (m³/mol), and
 V_o is the initial volume of spilled liquid (m³).

or

$$dF_v = H \cdot d\theta$$

The right-hand side of the second last equation has been separated into two dimensionless groups. The group kat/V_o is termed the "evaporative exposure" and is denoted as θ . The evaporative exposure is a function of time, the spill area and volume (or thickness), and the mass transfer coefficient (which is dependent on the wind speed). "H" is a dimensionless Henry's law constant or ratio of the equilibrium concentration of the substance in the vapour phase $[P/(RT)]$ to that in the liquid (l/v) . The product θH is thus the ratio of the amount which has evaporated (oil concentration in vapour times vapour volume) to the amount originally present.

Hamoda and coworkers (1989) performed theoretical and experimental work on evaporation. An equation was developed to express the effects of API° of the crude oil, temperature, and salinity on the mass transfer coefficient, K. Quin and coworkers (1990) weathered oils in a controlled environment and correlated the data with equations developed starting with Fick's diffusion law and the Clausius Clapeyron equation. Brown and Nicholson (1991) studied the weathering of a heavy oil, Bitumen. They compared experimental data using a large-scale weathering tank with two spill model outputs. The FOOS and ASA models use different approaches to the modelling of evaporation from spilled oil. Both were found to require adjustments to predict the evaporation of oil.

Bobra (1992) conducted laboratory studies on the evaporation of crude oils. The evaporation curves for several crude oils and petroleum products were measured under several different environmental conditions. These data were compared to the equations developed by Stiver and Mackay (1984). This comparison shows that the Stiver and Mackay equation predicts the evaporation of most oils relatively well until time exceeds about 8 hours, after that it over-predicts the evaporation that occurs. The 'overshoot' can be as much as two orders of magnitude of θ or as much as 5% of oil mass, at the 24-hour mark. This is especially true for very light oils. The Stiver and Mackay equation also under-predicts the evaporation of oils in the initial phases, however this is not a serious concern. Bobra noted that most oil evaporation follows a logarithmic curve (with time).

USE OF EVAPORATION EQUATIONS IN SPILL MODELS

Fallah and Stark (1976) proposed a random model to predict the evaporation of oil at sea. Grose (1979) used the Mackay and Matsugu (1973) equations with some modification. Mackay and co-workers (1980) developed an extensive oil spill model incorporating a number of process equations including evaporation. The earlier work of Leinonen and Mackay (1975) was used with the modification proposed by Yang and Wang (1977). The process is essentially that of dividing the oil in a number of different fractions and analyzing the loss of each fraction by evaporation. The mass transfer function used is the familiar one proposed by Mackay and Matsugu (1973).

Aravamudan and co-workers (1981 and 1982) developed an oil spill model

incorporating evaporation equations of their own development. These equations were based on basic physical relationships and presumed that each grouping of component densities results in a unique oil evaporation rate. Huang (1983) reviewed oil spill models and noted the state-of-the-art up to that time. Huang notes that many of the approaches are similar and can be generalized into the following:

1. The oil is assumed to be composed of a number of hydrocarbon groups;
2. The evaporative loss of a given hydrocarbon component is assumed to follow a logarithmic fashion, or a first-order kinetics;
3. The evaporation rate is assumed to be a function of the following key physical parameters: (a) spill area, (b) wind speed, (c) vapour pressure, (d) slick thickness, and (e) temperature;

Payne and co-workers (1984a, 1984b, 1988) developed an oil spill model using the pseudo-component approach. Given the boiling point and API gravity of each cut (or pseudo-component), the vapour pressure of the cut as a function of temperature can be calculated. Rasmusen (1985) developed an oil spill model for Danish waters and proposed an equation to describe the evaporative mass flux in a similar manner to that of Mackay and Matsugu (1973). Ross and Dickins (1988) used some empirical data to model the evaporation of oil under snow. Reed (1989) reports on the development of an evaporation equation. He used the familiar Mackay and Matsugu (1973) approach to estimate the mass transfer coefficient and a variant of the Stiver and Mackay (1984) approach. Lunel (1991) combined the mass transfer rates of evaporation and dissolution to deal with these competing processes simultaneously. Luk and Kuan (1992) describe an oil spill model which incorporates an evaporative equation nearly identical to that of Reed above. Spaulding and co-workers (1992) similarly use the same equations for the model OILMAP. Lehr and co-workers (1992) developed an oil spill model (ADIOS) using the evaporative algorithm developed by Stiver and Mackay (1984).

In conclusion many models exist incorporating evaporative equations. Most recent models (after 1980) use one of three approaches to model oil spill evaporation; the Mackay equation (Mackay and Matsugu (1973); Stiver and Mackay (1984)), the use of distillation cut data to simulate each fraction, and a simplified or logarithmic assumption. The equations can be implemented in a variety of ways. Often the difference in models is the manner in which the models are applied. The comparison by Bobra (1992) shows that the Stiver and Mackay equation predicts the evaporation of most oils relatively well until time exceeds about 8 hours, after that it over-predicts the evaporation that occurs. The comparison by Brown and Nicholson (1991) shows that for the heavy and mixed oils used that the Mackay and Matsugu approach was better than the distillation cut approach, however the mass transfer coefficient required adjustment. One important point to note is that there exists a large amount of actual evaporation data gathered from laboratories (eg. Bobra, 1992, Fingas - unpublished data). Another method, perhaps more accurate means, to model oil spill evaporation would be to use this data directly.

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