Weathering of oil spills accounting for oil components

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Abstract

A model is proposed to describe the weathering of oil spills taking into account the spreading, evaporation, emulsification, viscosity and density increase of the oil. The crude is described by a set of eight fractions, including paraffin, cycloparaffin, aromatic, naphtenoaromatic fractions and a high density residual. The evaporation process is computed for each fraction separately using a “pseudo-component” approach. This model is compared with another one, developed in a previous work, which treats the oil as a whole and uses evaporative exposure approach to model evaporation. The comparison of the results obtained by the two models with experimental data available in the literature shows a significant improvement when the pseudo-component approach is used, with respect to the evaporation process.

1 Introduction

The main mechanisms that govern the fate of an oil slick at sea are spreading, evaporation, dispersion, emulsification and sedimentation. Biodegradation may be the ultimate fate of much of the dissolved and dispersed oil, persisting after months and even years after the spillage. These processes are understood with different levels of confidence and they can be described by mathematical models partially based and calibrated on empirical results.
The spreading of oil released on water is probably the most dominant process in the first stage of a spill. Many oils spilled on the surface of calm water will spread in the form of a thin continuous layer as a result of gravity and net surface tension. This process influences other processes such as evaporation and dispersion, since they depend on the slick area and thickness.

When oil is released over the sea the low boiling point components will rapidly be removed, thus reducing the volume of the remaining slick. Evaporation is thus the primary initial process involved in the removal of oil from the sea surface. The rate of evaporation is determined by the physico-chemical properties of the oil and is increased by spreading, high water temperatures, strong winds and rough seas. This process is for many oils the most important mass loss process during the first hours of an oil spill. During the first 24 hours after spillage most crude oils will have lost approximately 25-30% of their lighter components.

Depending on oil composition, temperature and turbulence a process of emulsification involving the dispersion of water droplets into the oil medium may take place as oil contacts seawater. The result of emulsification is not only a large increase in volume (3 or 4 times the volume of the original stabilised oil) but also a significant increase in the density and a very large increase in viscosity.

By natural dispersion the crude oils form small droplets of oil which are incorporated in the water column. The rate of natural dispersion together with evaporation largely determine the life of an oil spill. In practice natural dispersion can be significant and account for a major part of removal of oil from the sea surface.

In a previous work a review of the available algorithms for describing the weathering processes of an oil spill was done and a set of differential equations for computing each process was selected in order to simulate the evolution of each variable. The model included the processes of spreading, evaporation, water incorporation, increase of viscosity and density.

In this paper another algorithm is presented in which the equations that proved to work well were kept. The evaporative exposure method developed by Stiver & Mackay, expressed by

\[ \frac{dF_E}{dt} = \frac{K_e A_s}{V_0} \exp \left( A - \frac{B}{T} (T_0 + T_G F_E) \right) \]

where:
- \( F_E \) = fraction evaporated
- \( T \) = temperature (K)
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\( T_0, T_G, A, B = \) constants derived from distillation data
\( t = \) time (s)
\( K_e = \) mass transfer coefficient for evaporation (ms\(^{-1}\))
\( V_0 = \) Initial spilled volume (m\(^3\))

was adopted in the formulation presented in\(^3\). The comparison made in that work with the experimental results showed that this equation overestimated the evaporation\(^3\). Therefore the present paper uses instead a pseudo-component approach.

In the pseudo-component approach oil is characterised by a set of fractions grouped by molecular weight and chemical nature. Eight fractions are considered, following Yang and Wang\(^7\), including paraffin, cycloparaffin, aromatic, naphtenoaromatic fractions and a high density residual. This approach allows different fractions of the oil to evaporate at different rates depending on the fraction considered. The mass transfer rate due to evaporation is given by\(^8\)

\[
\frac{\text{dm}_i}{\text{dt}} = \frac{K_e P_{i \text{Sat}} A_S f_i M_i}{RT_{oil}}
\]

where

- \( m_i = \) mass of fraction \( i \)
- \( t = \) time (s)
- \( P_{i \text{Sat}} = \) vapor pressure (atm)
- \( A_S = \) spill area (m\(^2\))
- \( f_i = \) fraction of spill which is constituent \( i \)
- \( M_i = \) molecular weight (gmol\(^{-1}\))
- \( R = \) gas constant (8.206\(\times\)10\(^{-5}\) atm m\(^3\) mol\(^{-1}\) K\(^{-1}\))
- \( T_{oil} = \) Oil temperature (K)

The mass transfer coefficient for evaporation is calculated, following Mackay and Matsugu\(^9\), by

\[
K_e = 0.029 W^{0.78} D_S^{-0.11} S c_i^{-0.67}.
\]

Where

- \( K_e = \) mass transfer coefficient for evaporation for fraction \( i \) (ms\(^{-1}\))
- \( W = \) wind speed (ms\(^{-1}\))
- \( D_S = \) spillet diameter (m)
- \( S c_i = \) Schmidt number of fraction \( i \)

The algorithms considered concern the processes that describe the weathering of an oil spill in calm weather, without taking into account the influence of waves and water currents. An overall attempt for the description of a spill will have to join these algorithms with a model to simulate the movements of the oil.
2 “Pseudo-component” Algorithm

Under environmental conditions all processes are occurring at the same time. In order to simulate these processes simultaneously the system of differential equations (2.1) to (2.7) is solved numerically. These equations describe respectively area growth, evaporation, a volume balance, water incorporation, viscosity increase and temperature variation by heat exchange between the slick and the surroundings. The density increase is calculated by (2.7). The index $i$ denotes oil fraction $i$ ($i = 1$ to number of fractions considered)

\[
\frac{dA_S}{dt} = K_i A_S \frac{1}{4/3} V^{4/3} \tag{2.1}
\]

\[
\frac{dV_{Ei}}{dt} = K_{ei} \frac{P_{sat}}{RT_{oil}} X_{mol_i} M_i \frac{A_S}{\rho_i} \tag{2.2}
\]

\[
\frac{dV_i}{dt} = -\frac{dV_{Ei}}{dt} - X_{vol_i} DV \tag{2.3}
\]

\[
\frac{dY}{dt} = 2.0 \times 10^{-6} (W + 1)^2 \left[ \frac{1 - \frac{Y}{Y_{max}}} \right] \tag{2.4}
\]

\[
\frac{d\mu}{dt} = C_{4\mu} \frac{dF_E}{dt} + \frac{2.5 \mu}{(1 - C_3 Y)^2} \frac{dY}{dt} \tag{2.5}
\]

\[
\frac{dT_{oil}}{dt} = \frac{1}{V_{oil} C_{oil}} \left[ A_S \left( (1 - a) H(t) + \frac{\sigma}{\rho_{air}} \left( \beta_{air} T_{air}^4 + \beta_{w} T_{w}^4 - 2 \beta_{oil} T_{oil}^4 \right) \right. \right.
\]

\[
+ \frac{h_{oil}}{\rho_{oil}} \left( T_{oil} - T_{oil} \right) + \left. h_{wo} \left( T_{w} - T_{oil} \right) - Q_v \right) \right)
\]

\[
+ \left( \frac{dV_w}{dt} \rho_w c_{p_w} + \frac{dV_{oil}}{dt} \rho_{oil} c_{p_{oil}} \right) \left( T_{w} - T_{oil} \right) \right]
\]

\[
\rho_v = Y \rho_w + (1 - Y) (\rho_{oil} + C_3 F_E) \tag{2.7}
\]

where

- $a$ = Albedo constant
- $A_S$ = Area of slick ($m^2$)
- $C_3$, $C_4$ = Oil dependent constants
- $C_{p_{air}}$ = Air heat capacity ($J K^{-1} \text{g}^{-1} \text{C}^{-1}$)
- $C_{p_{oil}}$ = Oil heat capacity
- $C_{p_w}$ = Water heat capacity ($J K^{-1} \text{g}^{-1} \text{C}^{-1}$)
- $D$ = Fraction of sea surface lost per hour
- $D_S$ = Spillet diameter ($m$)
- $V_{dp}$ = Dispersed volume ($m^3$)
- $V_{dp_i}$ = Dispersed volume of fraction $i$ ($m^3$)
- $V_{c_i}$ = Evaporated volume of fraction $i$ ($m^3$)
- $V_i$ = Volume of fraction $i$ ($m^3$)
- $V_w$ = Water volume ($m^3$) in oil
- $X_{mol_i}$ = Molar fraction $i$
- $X_{vol_i}$ = Volume fraction $i$
- $Y$ = Fraction of water content
\[ H(t) = \text{Solar radiation (Jm}^{-2}\text{s}^{-1}) \]
\[ h_{oa} = \text{Heat transfer coefficient between oil and air (Jm}^{-2}\text{k}^{-1}\text{s}^{-1}) \]
\[ h_{ow} = \text{Heat transfer coefficient between oil & water (Jm}^{-2}\text{k}^{-1}\text{s}^{-1}) \]
\[ K_1 = \text{Constant with default value of 150 s}^{-1} \) (Mackay et al., 1980) \]
\[ M_i = \text{Molar weight of fraction } i \text{ (kg mol}^{-1}) \]
\[ P_i = \text{Vapor pressure for fraction } i \text{ (Pa)} \]
\[ Q_e = \text{Evaporation heat loss (Js}^{-1}\text{m}^{-2}) \]
\[ \beta_a = \text{Emissivity of air} \]
\[ \beta_o = \text{Emissivity of oil} \]
\[ \beta_w = \text{Emissivity of water} \]
\[ \mu = \text{oil viscosity (cP)} \]
\[ \rho_{air} = \text{Density of air (kg m}^{-3}) \]
\[ \rho_i = \text{Density of fraction } i \text{ (kg m}^{-3}) \]
\[ \rho_{oil} = \text{Density of original crude oil (kg m}^{-3}) \]
\[ \rho_w = \text{Density of sea water (kg m}^{-3}) \]
\[ \sigma = \text{Boltzmann Constant} \]
\[ \dot{V}_{oil} = \frac{dV_{oil}}{dt} \text{ Rate of upwelling dispersed oil droplets [m}^3\text{s}^{-1}] \]
\[ \dot{V}_{w} = \frac{dV_{w}}{dt} \text{ Rate of water uptake [m}^3\text{s}^{-1}] \]

Equation (2.1) is used to model the process of spreading. It expresses the rate of change of surface area based on the gravity-viscous formulation of Fay\(^{10}\) and Hoult\(^{11}\) as modified by Mackay et al.\(^{12}\), the most widely used spreading model for calm water.

The evaporation process is calculated by equation (2.2) which is similar to equation (1.2), but expressed in volume evaporated.

A volume balance is made by equation (2.3) which accounts for the volume lost by evaporation and by dispersion into the water column. The fraction of sea surface oil dispersed into the water column is simply calculated as a lost fraction of surface oil per hour given by\(^{12}\):

\[ D = D_a D_b \] (2.8)

where \( D_a \) is the fraction of surface oil dispersed per hour, and \( D_b \), the fraction of dispersed oil not returning to the slick are expressed by:

\[ D_a = 0.11(W + J)^2 \] (2.9)

\[ D_b = \left(1 + 50 \mu \frac{1}{2} h s_i \right)^{-1} \] (2.10)

Where
- \( \mu = \text{viscosity (cP)} \)
- \( h = \text{slick thickness (cm)} \)
- \( s_i = \text{oil-water interfacial tension (dyne cm}^{-1}) \)
Water incorporation is computed by equation (2.4) following Mackay et al.\textsuperscript{12}.

The viscosity change is calculated as the sum of both the change on viscosity due to water incorporation and the change due to mass loss by evaporation. These two processes are computed by equation (2.5).

Equation (2.6) intends to calculate the actual oil temperature which may be different from the surroundings\textsuperscript{9,13}. It represents a heat budget where it is considered heat transfer between air and oil, emitted and received radiation from the upper boundary of the slick and from the lower boundary, input of solar radiation, evaporative heat loss and heat transfer between oil and water. However, a sensitivity analysis on the effect of the parameters used in equation (2.6) should be done, since in most cases these parameters have to be estimated or simply taken from the literature to perform the calculation.

The density is calculated by equation (2.7), assuming that the crude is an ideal mixture\textsuperscript{13}:

\[
\rho_{oil} = \sum_{i=1}^{8} Xvol_i \rho_i
\]

(2.11)

3 Numerical Example

The case simulated was the experimental oil release carried out in 1982 on Haltenbanken near the Norwegian coast involving the spillage of 100 tons of Statfjord crude oil in the North Sea, that was monitored over a period of seven days\textsuperscript{15}. The crude physical properties used are presented in the Table 1 below.

<table>
<thead>
<tr>
<th></th>
<th>Density</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude</td>
<td>g/cm(^3)</td>
<td>40°C (cSt)</td>
</tr>
<tr>
<td>Statfjord</td>
<td>0.832</td>
<td>3.64</td>
</tr>
</tbody>
</table>

For the “pseudo-component” calculation a wind speed of 28.8 Km/h and a temperature of 11 °C was used. Since Statfjord crude is a fairly volatile crude, the percentages of different groups of hydrocarbons in Table 3 were used to represent the oil composition, using the fractions shown in Table 2, chosen to model the oil\textsuperscript{7}. According to Whittle et al.\textsuperscript{14} the values in Table 3 are the average composition for a light crude.
The system of differential equations above was solved by the fourth order Runge-Kutta method. The programme was developed in Fortran 77.

The results of the simulation are shown in Figure 1 and Figure 2 with the experimental points from Buchanan & Hurford\textsuperscript{15}. The results obtained by the “evaporative exposure” algorithm\textsuperscript{3} are also shown in order to have a comparison.

Table 2 Basic data used in the numerical example\textsuperscript{7}.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Description</th>
<th>Density (g ml\textsuperscript{-1})</th>
<th>Boiling Point (°C)</th>
<th>Molecular weight</th>
<th>log(Vapor Pressure) (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Paraffin</td>
<td>0.66-0.77</td>
<td>69-230</td>
<td>86-170</td>
<td>9.64-1417.61/(202.17+7)</td>
</tr>
<tr>
<td>2</td>
<td>Paraffin</td>
<td>0.77-0.78</td>
<td>230-405</td>
<td>184-352</td>
<td>7.01-1825.04/(149.76+7)</td>
</tr>
<tr>
<td>3</td>
<td>Cycloparaffin</td>
<td>0.75-0.9</td>
<td>70-230</td>
<td>84-164</td>
<td>6.91-1441.79/(204.70+7)</td>
</tr>
<tr>
<td>4</td>
<td>Cycloparaffin</td>
<td>0.9-1.0</td>
<td>230-405</td>
<td>156-318</td>
<td>6.99-1893.78/(151.82+7)</td>
</tr>
<tr>
<td>5</td>
<td>Aromatic (mono - dicyclic)</td>
<td>0.88-1.1</td>
<td>80-240</td>
<td>78-143</td>
<td>6.91-1407.34/(208.48+7)</td>
</tr>
<tr>
<td>6</td>
<td>Aromatic (poli-cyclic)</td>
<td>1.1-1.2</td>
<td>240-400</td>
<td>128-234</td>
<td>6.97-1801.00/(162.77+7)</td>
</tr>
<tr>
<td>7</td>
<td>Naphtheno-aromatic</td>
<td>0.97-1.2</td>
<td>180-400</td>
<td>116-300</td>
<td>6.97-1789.85/(164.56+7)</td>
</tr>
<tr>
<td>8</td>
<td>Residual</td>
<td>1-1.1</td>
<td>400</td>
<td>300-900</td>
<td>(P_x=0)</td>
</tr>
</tbody>
</table>

Table 3. Average composition of the light crude used in the numerical example (Whittle \textit{et al.}\textsuperscript{14}).

<table>
<thead>
<tr>
<th>Group</th>
<th>% wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-alkanes</td>
<td>23.3</td>
</tr>
<tr>
<td>Isoalkanes</td>
<td>12.8</td>
</tr>
<tr>
<td>Cycloalkanes</td>
<td>41.0</td>
</tr>
<tr>
<td>Aromatics</td>
<td>6.4</td>
</tr>
<tr>
<td>Naphtheno-aromatics</td>
<td>8.1</td>
</tr>
<tr>
<td>Heterocycles (resins) and asphaltenes</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Figure 1 Simulation results for an oil spill of 100 tons of Statfjord crude oil. a) Evaporation curves; b) Water content curves. The broader lines are calculated by the “pseudo-component” algorithm. The narrow lines were calculated by the “evaporative exposure” algorithm. Experimental points from Buchanan & Hurford.

Figure 2 Simulation results for an oil spill of 100 tons of Statfjord crude oil. a) Density curves; b) Viscosity curves. The broader lines are calculated by the “pseudo-component” algorithm. The narrow lines were calculated by the “evaporative exposure” algorithm. Experimental points from Buchanan & Hurford.

4 Discussion

The plots in Figure 1 and Figure 2 show that both algorithms give good predictions for the water content, density and viscosity increase. Slight differences are observed in respect to the calculated density, which arise from the fact that in the “pseudo-component” algorithm the initial density was calculated by equation (2.11) with the assumptions that it
implies. First it considers that oil is an ideal mixture, what may be far from the reality, and second the calculation is based on densities of the fractions considered, that are a model of the chemical composition of the oil but not the real composition. Despite all these assumptions, the calculation gives reasonable values.

The most important difference that is observed in the results is the calculated fraction evaporated plotted in Figure 1a. The simulation using the pseudo-component approach gives results much closer to the experimental points than evaporative exposure simulation. Since the evaporation process represents a significant loss of volume during the first hours after spillage such a difference in calculation leads to a significant difference in the predicted volume remaining in the oil slick.

In this case the “pseudo-component approach” gave better results as showed in Figure 1a, but it should be noticed that the oil composition was based on average percentages for a light crude oil. It cannot be said that the improvement found is applicable to all situations. A study is mentioned where it was found that for heavy and mixed oils the pseudo-components approach is worse than the approach developed by Mackay & Matsugu (1973). This approach uses essentially the same basis of the evaporative exposure approach (Stiver & Mackay, 1984). More information is needed to evaluate the performance of both methods.

5 Conclusions

In principle, the more information used in the description of the oil the more accurate the simulation of the weathering process should be. Thus whenever information is available about the composition of the crude, the pseudo-component approach is attractive. Whenever there is a lack of knowledge of the real physicochemical parameters of the crude oils, also because their composition varies with time for crudes with the same origin, the evaporative exposure method becomes attractive. It can give an estimate of the fraction evaporated, making use of little information about the crude.

6 Acknowledgements

This work was performed under the scope of the project “Computer System for the Evaluation of the Environmental Impact of Polluting Maritime Accidents”, which was financed by the Portuguese Directorate-General for Environment (Direcção-Geral do Ambiente), under contract no. PEAM/SIA634/95.
7 References


