The simulation of weathering processes in three different types of oil

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Abstract. Pipeline leaks, wells damage, and water transportation accidents are some of the causes of oil spills at sea. This spill causes seawater pollution and disturbs the equilibrium of marine life. Oil spills will spread and move with the influence of currents and sea wind. Spilled oil undergoes several physical and chemical processes, including spreading, evaporation, emulsification, dissolution, and dispersion. This process results in changes in oil density, volume, and viscosity. It is important to be aware of changes in oil spill conditions because it relates to clean up efforts of oil spills at sea. This research presents some mathematical models of the oil weathering processes which include physical and chemical processes. Then a numerical simulation is performed using a finite difference method to see the changes that occur in three types of oil: heavy, medium and light oil. Simulation results show that the three types of oil have a relatively similar tendency to spread. The highest rate of evaporation and emulsion water content is shown by light oil. This resulted in higher volume and viscosity. Therefore, the process of cleaning up will require greater effort for light oil spills.

1. Introduction

Oil spills often occur due to industrial and transportation activities. The oil industry process which is commonly carried out in the coastal area allows pipe leakage or wells damage which results in contamination of seawater. In 1979, an oil well managed by the Mexican petroleum company, Pemex suffered damage and caused a large amount of oil spill into the sea. Besides, the distribution of oil between cities or countries is carried out using tankers by sea. Spill oil may occur as a result of marine transportation accidents, such as fireboats, leaking tankers, and other accidents. The largest case of oil spill was reported in 1979 in the area of Off Tobago, West Indies [1]. Some 287,000 tons of oil carried by Atlantic Empress spilled into the sea after a collision with the Aegean Captain. In 2018, a large oil spill occurred again off Shanghai, China due to the Sanchi ship accident [1].

Oil spills at sea will experience the process of spreading which is affected by the wind speed, currents, waves [2,3], gravity, and surface tension [4]. The presence of oil spills on the surface of seawater will pollute the sea and disrupt the equilibrium of marine life. Although oil spills can disappear naturally, but the time needed for this depends on the initial physical and chemical characteristics of the oil and the natural weathering process of the oil. Weathering processes are related to physical and chemical activities experienced by oil including evaporation [2, 5, 6, 7, 8, 9], dissolution [3, 5, 6, 8], dispersion [5, 7, 8], emulsification [2, 3, 5, 6, 7, 8, 9, 10], biodegradation, advection, oxidation, and sedimentation [9]. These processes also often still leave residues [11]. The cleaning process is generally carried out to accelerate the loss of oil from the surface of the sea, one of
the ways to do this is by in-situ burning, mechanical removal, bioremediation, use of sorbent and use of chemical dispersants.

This research will discuss weathering processes models that affect the physical and chemical characteristics of oil. The models are then simulated using finite difference methods. The simulation results will show changes in the physical and chemical characteristics of the oil spill which can be the basis for determining oil cleaning strategies.

2. Mathematical models of weathering processes

The character of oil spilled in the sea is greatly influenced by physical and chemical processes which occur. This process affects the area, volume, density, and viscosity of oil. The speed of the process depends on the surrounding environmental conditions, such as wind force, sea current, and wave [2], surface tension and gravity.

2.1. Spreading

According to Fay [12], the spreading process is divided into three phases, namely inertial spread, viscous spread, surface tension spread. In each phase, the oil spill area has expanded with radius shown as equation (1) - (3).

Inertia spread: \( R_i = K_i \left( \Delta V_0 t^2 \right)^{\frac{1}{2}} \)  

\[(1)\]

Viscous spread: \( R_2 = K_2 \left[ \frac{\Delta V_0^2 t^\frac{3}{2}}{\nu^2} \right]^{\frac{1}{6}} \)  

\[(2)\]

Surface tension spread: \( R_3 = K_3 \left( \frac{\sigma t^3}{\rho \nu^2 \nu} \right)^{\frac{1}{4}} \)  

\[(3)\]

\[\Delta = 1 - \frac{\rho_w}{\rho_o}\]
\[\sigma = \sigma_{wa} - \left( \sigma_{oo} + \sigma_{ow} \right)\]

\( R_i \) is the radius (m) for stage \( i \), \( K_i \) is empirical constants (1.15, 1.45, and 2.30 respectively [12]), \( i = 1, 2, 3 \), \( g \) is the gravitational acceleration (m/s\(^2\)), \( V_0 \) is the initial volume (m\(^3\)), \( t \) is time (s), \( \nu \) is the kinematic viscosity of water (m\(^2\)/s), \( \rho_w \) dan \( \rho_o \) are the density of water and oil (kg/m\(^3\)), \( \sigma_{wa} \), \( \sigma_{oo} \), and \( \sigma_{ow} \) are spreading coefficient of interfacial tension water-air, oil-air, and oil-water.

The first phase of inertial spread generally takes place in a short time, so the area of oil refers to the second phase. Model changes in oil area \( A \) (m\(^2\)) are shown in equation (4) [9].

\[ \frac{dA}{dt} = K_s \frac{V^3}{A} \]  

\[(4)\]

\( K_s \) is evaporation constant (150 s\(^{-1}\) [8]). The initial time and initial oil area are obtained during the transition from phase one to phase two. At that time, \( R_1 \) is equal to \( R_2 \), so an initial time \( t_0 \) (s) and initial area \( A_0 \) (m\(^2\)) are obtained as in equations (5) and (6).
$$K_1 \left( \Delta g V_0 t_0^2 \right)^{1/4} = K_2 \left( \frac{\Delta g V_0^2 t_0^3}{v^2} \right)^{1/6}$$

$$t_0 = \left( \frac{K_2}{K_1} \right)^4 \left( \frac{V_0}{\Delta g v} \right)^{1/3}$$

$$A_0 = \pi R^2 = \pi \left( K_1 \left( \Delta g V_0 t_0^2 \right)^{1/4} \right)^2$$

Substitute $t_0$ then obtained

$$A_0 = \pi \frac{K_2^4}{K_1^2} \left( \frac{\Delta g V_0}{v^2} \right)^5$$

2.2. Evaporation

Evaporation is the process by which a liquid turns into a vapor or air. The evaporation process in oil spills is influenced by oil and sea temperature [13], oil composition, solar radiation, slick thickness, spill area, and wind speed [7, 9]. The higher the temperature, the faster the evaporation occurs. Evaporation is a very important process for cleaning up oil spills at sea. Evaporation rates can be calculated analytically using the equations of Stiver and Mackay [14] in equation (7).

$$\frac{dF_e}{dt} = \frac{K_e A}{V_0} \exp \left( B_1 - \frac{B_2 \left( T_e + T_g F_e \right)}{T_w} \right)$$

$$K_e = 2.5 \times 10^{-3} W^{0.78}$$

$F_e$ is the volume fraction of oil evaporated (100 %), $K_e$ is the mass transfer coefficient of evaporation (m/s), $B_1$ and $B_2$ are evaporation constants obtained from experiment (6.3 and 10.3 [14]), $T_e$ initial boiling temperature of oil (K), $T_g$ is the gradient of oil distillation curve (K), $T_w$ is the temperature of the oil spilled (K), $W$ is the wind speed (m/s), $T_o$ dan $T_i$ calculated using NOAA formulation, $T_b = 532.98 - 3.125 API$ and $T_b = 985.62 - 13.597 API$. $API$ is the American Petroleum Institute gravity scale.

2.3. Emulsification

Emulsification can be interpreted as the process of forming emulsions from two materials that do not dissolve due to differences in polarity. When oil spills in the sea, there is a mixture of oil and seawater in the form of an emulsion. This process occurs due to wave breaking and surface turbulent which makes seawater trapped in the slick. The formation of emulsion increases the water content of oil [10]. This makes the process of oil spills cleaning up more difficult. Although oil can be lost naturally through the evaporation process, emulsification keeps the residue of pollutants [8]. Mackay et al. [15] formulate water content as in equation (8).

$$\frac{dF_w}{dt} = K_{w1} (W + 1)^2 \left( 1 - \frac{F_w}{K_{w2}} \right)$$
$F_w$ is the fractional water content of oil (100 %). $K_w1$ is emulsification coefficient (m/s) ($2 \times 10^6$ for light oil and $4.5 \times 10^6$ for heavy oil), $K_w2$ Moose viscosity constant (0.7 for crude and heavy oil [16, 17]).

2.4. Dissolution

Dissolution, in this case, is the process of releasing compounds present in oil. The dissolution of crude oil in seawater increases levels of seawater pollution. But because dissolved compounds can also be evaporated and the evaporation process is faster than dissolution, the dissolved oil content in water-soluble is relatively small [8]. The dissolution rate can be estimated using equation (9) [18].

$$\frac{dF_d}{dt} = \left( \frac{K_d}{h} \right) A \left( \frac{C_s}{\rho_m} \right)$$

(9)

$F_d$ is the volume fraction of oil dissolved in seawater (100 %), $h$ is oil spill thickness (m), $\rho_m$ is oil molar density that can be calculated using $\rho / m$. The dissolution constant $K_d$ (m/s) in equation (10) [18] and solubility of oil $C_s$ (kg/m$^3$) in equation (11) [19] [19]

$$K_d = 0.035u^{0.8}D_s^{0.67}v^{0.47}A^{0.1}$$

(10)

$$C_s = S_0 \exp(-0.1t)$$

(11)

$u$ is water velocity (m/s$^2$), $D_s$ is diffusion coefficient of oil in water (m$^2$/s), $S_0$ is initial solubility of oil in water (0.03 kg/m$^3$ [20]).

2.5. Dispersion

Dispersion is a mixture in which fine particles of one substance are scattered throughout another substance. By knowing the dispersion process of an oil spill, we can estimate the lifetime of an oil spill. The rate of natural dispersion depends on environmental parameters and oil-related parameters, such as oil thickness, density, surface tension and viscosity [17, 22]. Loss of oil from the surface slick due to natural dispersion can be computed by equations original proposed by Mackay et al. [15].

$$D = \frac{0.11(W + 1)^2}{1 + 50 \mu^2 hS_i}$$

(12)

$D$ is dispersion rate (m/s), $\mu$ is dynamic viscosity (Pa.s), $S_i$ is the interface tension of oil-water (N/m)

2.6. Volume, Density, Viscosity

Weathering Processes which occur in oil spills result in changes in oil composition which include volume, density, and viscosity. This is mainly due to the evaporation, emulsification, and dissolution processes. Research conducted by HaoXie [10] shows emulsification and evaporation can increase viscosity and fluid volume. Evaporation and dissolution leads to an increase in volume and density. The following equations (13) - (14) are used to predict volume and density [22].

$$V = \frac{V_o(F_e + F_d - 1)}{F_w - 1}$$

(13)

$$\rho = F_w \rho_w + \left( \rho_o + K_w2F_e \right)(1 - F_w)$$

(14)

The change in viscosity due to evaporation process was modeled as:

$$\mu = \mu_0 \exp(K_e F_e)$$


\( \mu_0 \) is initial dynamic viscosity (Pa.s), \( K_c \) is oil-dependent constant (1 for light oil and 10 for heavy oil [23]). The effect of emulsification in viscosity was predicted using the following Mooney Equation variant:

\[
\mu = \mu_0 \exp \left( \frac{2.5F_w}{1 - 0.65F_w} \right)
\]

Thus, changes in viscosity due to evaporation and emulsification can be determined as equation(15) [23]:

\[
\mu = \mu_0 \exp \left( K_c F_e \frac{2.5F_w}{1 - 0.65F_w} \right)
\]

(15)

3. Numerical Simulation

The mathematical model of oil weathering processes, which is shown in equations (4), (7) - (9), and (12) - (15), is solved numerically using forward finite-difference methods. The finite difference model used as shown in equation (16)

\[
\left. \frac{df}{dx} \right|_{x_j} \approx \frac{f(x_j + \Delta x) - f(x_j)}{\Delta x} + o(\Delta x)
\]

(16)

The simulation is carried out for 25 hours with the initial volume of each type of oil as much as 1000 m³. The wind speed is assumed to be 5.28 m/s and the speed of seawater currents of 2.83 m/s. The density of seawater is 1029 kg/m³ at a temperature of 303.15° K. Three types of oil used come from three different sources, namely: Mississippi Canyon Block 807 Gulf of Mexico, Louisiana, USA (heavy oil), Alaska North Slope Prudhoe Bay, Alaska, USA (medium oil), and Brent Blend North Sea, United Kingdom (light oil). Parameters relating to each type of oil are shown in Table 1 [24]:

| Table 1. Oil Parameter                  | Heavy oil | Medium Oil | Light Oil |
|----------------------------------------|-----------|------------|-----------|
| Oil density (kg/m³)                    | 946.1     | 866.3      | 835.1     |
| Kinematic viscosity (10⁻³ m²/s)        | 5.0735    | 13.275     | 7.1848    |
| Dynamic viscosity (cP)                 | 4.8       | 11.5       | 6         |
| API gravity                            | 17.5      | 30.89      | 37.8      |
| Interface tension of oil-water (10⁻³ N/m) | 26.6    | 20.2       | 22.5      |
| Moose viscosity constant               | 0.7       | 0.8        | 0.9       |

4. Result and Analysis

The following are the results of weathering processes simulation on three types of oil, namely light oil, medium oil, and heavy oil, using parameters as shown in the previous chapter. The results obtained indicate an oil character change from time to time due to processes of spreading, evaporation, emulsification, dissolution, dispersion, and the changes of volume, density, and viscosity.

4.1. Spreading

The simulation results in figure 1 show that the area of the oil spill has increased over time. Initially, heavy oil had a wider area than the other two types of oil because its kinematic viscosity was the smallest. With the same amount of volume, heavy oil tends to spread faster. This condition then changed due to an increase in the volume of light oil and medium oil which resulted in an increased
The increase in volume is due to the evaporation and emulsification process which will be shown in the next simulation results.

**Figure 1.** Comparison of oil spreading

4.2. Evaporation and Emulsification

Evaporation is influenced by temperature, oil spill area, and wind speed. Figure 2 shows an increase in evaporation in all three types of oil. From the simulation results, it appears that the value of API is very influential in the evaporation process. Light oil has the highest API value so that the initial boiling temperature of the oil and the gradient of oil distillation are low. This results in a high rate of evaporation in light oil. The three types of oil each experienced evaporation of 25% for heavy oil, 39% for medium oil, and 52% for light oil. This process results in the evaporation of oil components from the surface of seawater and leaves a residue in the form of high molecular weight compounds. Heavy oils that contain nonvolatile and high molecular weight components tend to be more difficult to evaporate compared to light oil that consists of low molecular weight components.

The emulsification process allows water to enter into oil which results in the formation of an emulsion. Figure 3 shows that heavy oil reaches the water limit faster than the other two types of oil which is between 3-5 hours. While the medium oil and light oil each take 7-15 hours and 10-15 hours. Light oil which is composed of low molecular height components contains more water in its emulsions. This condition caused the process of cleaning up oil spills on light oil that takes longer than the other two types of oil.

**Figure 2.** Comparison of evaporation rate

**Figure 3.** Comparison of emulsion water content
4.3. Dissolution and Dispersion

Compared to other processes, the dissolution process has a smaller effect, between 1.5% to 2%, as shown in figure 4. The dissolution process releases the activated oil components at sea level. Simulation results show that heavy oil pollutes seawater more than light and medium oils. The dispersion process is strongly influenced by the speed of the wind and dynamical viscosity of the oil. A wind speed of 5.28 m/s given in this simulation resulted in an oil dispersion rate of around 4.3 m/s (figure 5). Small differences that occur in the three types of oil are influenced by the magnitude of dynamical viscosity and oil thickness.

![Figure 4. Comparison of dissolution rate](image1)

![Figure 5. Comparison of dispersion rate](image2)

4.4. Volume, Density, and Viscosity

![Figure 6. Rasio of volume](image3)

![Figure 7. Rasio of density](image4)

![Figure 8. Rasio of viscosity](image5)

Evaporation, emulsification, dissolution, and dispersion processes affect the volume, density, and dynamical viscosity of the oil. As a result of these processes, there was a 5 times increase in the...
volume of light oil, 3 times in the volume of medium oil, and 2.5 times in the volume of heavy oil (figure 6). The amount of water that enters the emulsification process greatly affects the increasing volume and density of the oil. Figure 7 shows that the ratio of oil density in the initial conditions and after undergoing a chemical process is increasing to reach 1.21 times. Furthermore, the evaporation process that evaporates light particles in the oil leaves a residue in the form of high molecular weight which increases the dynamical viscosity of the oil. As a result, oil spills become thicker and more concentrated. Figure 8 shows a very significant increase in dynamical viscosity of oil, where the ratio reaches 375 for light oil, 315 for heavy oil, and 215 for medium oil.

5. Conclusion
Based on the simulation results it can be concluded that the oil characteristics affect the rate of evaporation, emulsification, dissolution, and dispersion. The high rate of evaporation and emulsification results in large changes in volume, density, and viscosity. The biggest change is shown in light oil, therefore the cleaning process will take longer than other types of oil. The oil cleansing process also depends on the movement of oil spills that are affected by wind and seawater currents. Further research is needed to determine the movement of oil spills in the sea.

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