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The Simulation of the Oil Weathering Processes in Marine Environment

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Abstract. The aim of this paper is modeling the essential oil weathering processes. This is achieved by providing a two dimensional numerical model to simulate the oil slick spreading using finite volume approach and an oil weathering model (OWM) to consider the mass transfer processes. This model is consisted of important weathering processes such as evaporation, vertical dispersion, emulsification and dissolution. Several equations are introduced by previous researchers to predict the natural oil disappearances and the changes of oil properties after spillage. Therefore, by reviewing the most applicable expressions and comparison their results and available experimental data or analytical solutions, the suitable equations have been introduced. By using the oil depreciations as sink term in oil dynamic equation, the final model is able to simulate the oil weathering processes.

Keywords: oil spill, oil weathering processes, mathematical modelling.

1. Introduction

Oil spills in marines are serious environmental disaster often leading to significant and long-term impacts on the sensitive aquatic systems. Having a detailed knowledge of oil slick behaviour on water can be important in making operational decision and taking appropriate action against pollution. When crude or refined oil products are spilt on the sea, they are spread to form an oil slick. The slick spreads over the water surface due to a balance between several forces. A number of natural processes take place, which disperse the oil and change its chemical and physical properties. These processes are made up of the complex physical, chemical and biological processes such as spreading, evaporation, water-in-oil emulsification, vertical dispersion, etc. A combination of these time dependent processes is called oil weathering. In this paper we focused on this subject to estimate the mass transfer rate and the changes of oil properties.

2. Oil Weathering Processes Modeling

Although oil spill models have improved significantly over the years, their capability for modelling of the chemical processes is considered to be the main disadvantage. The main important problem with the implementation of these models is primarily collecting the input data. Sometimes models require a series of data and parameters that are not routinely measured for oil and must be estimated using other techniques.

2.1. Spreading Process

The most effectiveness forces in oil spreading process can be categorized as surface flow, wind and turbulent forces due to wave breaking (API, 1999).

Equation of Fay (1971): He assumed that the initial and final form of slick is circular and introduced three major phases including inertial-gravity, gravity-viscous and viscous-surface tension phases as follows:

$$R_{IG} = K_{IG}\left(\Delta g V t^2\right)^{1/4} \quad ; \quad R_{GV} = K_{GV}\left(\Delta g V_{oil}{}^2 t^{3/2} \nu^{-1/2}\right)^{1/6} \quad ; \quad R_{VST} = K_{VST}\left(\sigma^2 t^3 \rho_w^{-2} \nu^{-1}\right)^{1/4} \quad (1)$$

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where R_i is the slick radius in each phases and K_i is their coefficients; $\Delta = 1-(\rho_o/\rho_w)$; ρ_o and ρ_w are oil and water density; V_{oil} is spilled oil volume; ν is the oil viscosity and σ is oil-water interfacial tension.

Equation of Mackay et al. (1984): Their proposed equation is based on the gravity-viscous formulation:

$$dA_s/dt = K_1 A_s^{1/3}(V_{oil}/A_s)^{4/3} \qquad (2)$$

where A_s is oil slick area; K_1 is constant with default value of 150 s^{-1} and t is time.

Equation of Lehr et al. (1984): They expressed that oil slick can expand as an ellipsoid form in which its larger diameter is in the wind direction. Their equation is presented as follows:

$$L_{\min} = 53.76(\Delta\rho/\rho_o)^{1/3} V_{oil}^{1/3} t^{1/4} \quad ; \quad L_{\max} = L_{\min} + 0.95 U_{wind}^{4/3} t^{3/4} \qquad (3)$$

L_{min} and L_{max} are ellipse slick diameter; U_{wind} is wind speed for 10 m over sea; $\Delta\rho = \rho_w - \rho_o$.

Mathematical Modelling of Oil Slick Dynamics: In pervious approaches, the spreading process has been analyzed by empirical formulations. Nowadays, with the computational science development, an oil slick dynamics model can afford to routinely use such accurate and physically relevant formulation like the Navier–Stokes equations (Warluzel and Benque, 1981) that expressed as following equation in x-y directions:

$$\partial h_s/\partial t + \partial(h_s v_j)/\partial x_j - \partial(D_s\, \partial h_s/\partial x_j)/\partial x_j = \pm Q_s \quad , \quad j = 1,2 \qquad (4)$$

h_s is the slick thickness; D_s is spreading function, Q_s is the disperse oil due to weathering processes. The effect of wind speed on the oil drifting velocity component v_i is assumed 0.03 (Tkalich et al., 2003).

2.2. Evaporation Process

The evaporation process causes the transfer of lighter components of the oil from the slick phase to the air. The highest contribution of oil mass loss during the first days after spilled is related to evaporation (Sebastiao and Soares, 1995). Below the frequently used schemes to determine the evaporation rate are listed.

Equation of Stiver and Mackay (1984): Their equation to estimate the evaporation rate (F_E) is:

$$F_E = \ln[1 + B(T_G/T_E)(K_E \cdot A_S \cdot t/V_0)\exp(A - B(T_B/T_E))][(T_E/(BT_G))] \qquad (5)$$

where $K_E = 2.5 * 10^{-3} * U_{wind}^{0.78}$; V_0 is initial volume of oil; T_B is initial boiling point; T_G is gradient of T_B and F_E line; T_E is environmental temperature; A and B are constants derived from distillation data.

Equation of Reed et al (1989): By their equation the evaporation rate is computed as:

$$F_E = K_E P_v A_s M_w / RT \qquad (6)$$

where, P_v is the vapour pressure; M_w is the molecular weight and R is the universal constant of gases.

Equation of Shen and Yapa (1988): The basis for their study is a combination of the previous models.

$$F_E = [\ln P_0 + \ln(CK_E t + 1/P_0)]/C \qquad (7)$$

Where ν is the molar volume; C is an evaporation constant; M_W is the oil molecular weight; T_0 is the reference temperature and API is API gravity. They proposed some equations to determination of the required parameters including, $K_E = (0.0025 U_{wind}^{0.7} A \nu)/(RT_E V)$; $\nu = (M_W)/(\rho_o \times 10^6)$; $C = 1158.9 API^{-1.1435}$.

Equation of Riazi and Edalat (1996): By their equation, the evaporation rate is defined as follows:

$$F_E = 1 - \exp(-(K^{vap} Z_{liq}^{sat}/y) \cdot t) \qquad (8)$$

that y is the slick thickness; K_{vap} is the mass transfer coefficient and Z_{liq}^{sat} is the oil dimensionless factor.

2.3. Vertical Dispersion Process

The water turbulence causes the entering of oil droplets into the water column and forming an oil-in-water emulsion. The formulation of Mackay et al. (1980) to compute the dispersion rate (D) is expressed as:

$$D = 0.11(U_{wind} + 1)^2 / (1 + 50\mu^{1/2} h_s s_t) \qquad (9)$$

where μ is the dynamic viscosity of oil and s_t is the interface tension of oil-water.

2.4. Water in Oil Emulsification Process

As the emulsion process develops, the movement of the oil in the waves causes the droplets of water which have been taken up in the oil to become smaller and smaller, making the emulsion progressively more viscous and stable. The equation of Mackay et al. (1980) to compute the water content changes, F_{wc}, is:

$$dF_{wc}/dt = K_{wc}(U_{wind}+1)^2(1-F_{wc})/OC \qquad (10)$$

2.5. Dissolution Process

The rate of oil dissolution is very smaller than other processes and depends on its composition, water temperature and degree of other processes. The equation of Riazi and Edalat (1996) is represented as:

$$F_V = 1-\exp\left(-\left(K^{dis}/y\right)\cdot\left(C_s/\rho_m\right)\cdot t\right) \quad ; \quad K^{dis} = 0.035(uL/\nu)^{0.8}(u/D_v)^{0.33}(D_v/L) \qquad (11)$$

where ν is the kinematics viscosity of seawater, D_v, is the diffusion coefficient of oil in water.

2.6. The Change of Oil Properties

Due to weathering processes, the physical and chemical properties of spilled oil will be changed. The most important of these properties are viscosity and the density that can have effect on the oil slick. The modification of these parameters is determined by following equations (Mooney, 1951; Mackay et al., 1980):

$$\mu = \mu_{ref}\exp\left(C_{E1}F_E + (C_{wc1}F_{wc})/(1-C_{wc2}F_{wc})\right) \quad ; \quad \rho_o = F_{wc}\rho_w + (1-F_{wc})(\rho_{ref}+C_{E2}F_E) \qquad (12)$$

3. Model Implementation and Evaluation

Spreading Process: To model this process, a simplified two-dimensional channel, $20\times0.5km^2$ is considered that is covered by a rectangular grid. The wind speed is 4.17*m/s*; the surface current velocity is assumed zero; the temperature is 288°*K* and 100*tone* of Statfjord oil is released in a single grid point. The characteristics of the Statfjord crude oil are presented in Table 1. Figure 1 shows the comparison of our model computed results with other empirical formulation. As shown, mathematical model's results have good agreement with Fay's model. Also Stiver and Mackey's equation computes this rate with a high estimation and needs to calibrate the empirical constant.

Table 1: Statfjord crude oil characteristics used in the modeling of weathering processes (Nazir et al., 2008)

Density (*kg/m*^{3})	832	Molecular weight (*g/mol*)	128.2
Viscosity @ 40 °*C* (*cP*)	3.03	Solubility @ 25 °*C* (*g/m*^{3})	31.7
T_B (initial boiling point) (°*K*)	301	Vapour pressure @ 25 °*C* (*Pa*)	10.4
T_G (°*K*)	500	Oil–water interfacial tension (*dyne/m*)	2000

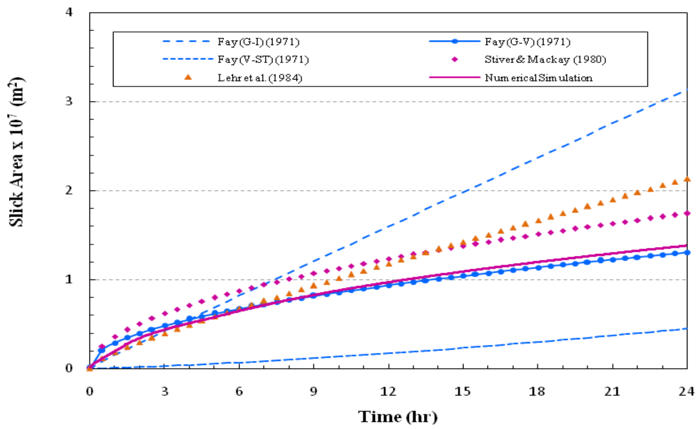

Fig. 1: Comparison between the dynamic model results and the empirical equations, test case 1

Evaporation Process: At this stage, Ahwaz crude oil with available experimental data is used. Its physical properties are given in Tables 2. The wind speed is 5*m/s*, water temperature is 25°*C* and 33.739*gr* of oil is released. Figure 4 presents the computed evaporation rates by our OWM model based on reintroduced equations. The results of model applying the first and third equations have a good agreement with measured data. The advantage of these equations is that the need for detailed information of petroleum products is not necessary. If the detailed distillation data of oil components is available, other model can be more applicable.

Table 2: Ahwaz crude oil characteristics used in the modelling of weathering processes

T_B (K)	776	API gravity	29
M_W (g/mol)	525	Density at $20^oC(g/cm^3)$	0.875

Dispersion and Dissolution Processes: The Statfjord oil is used for the other processes, but there isn't any experimental work to compare the results. Therefore, only the computed rates are presented in Figure 5.

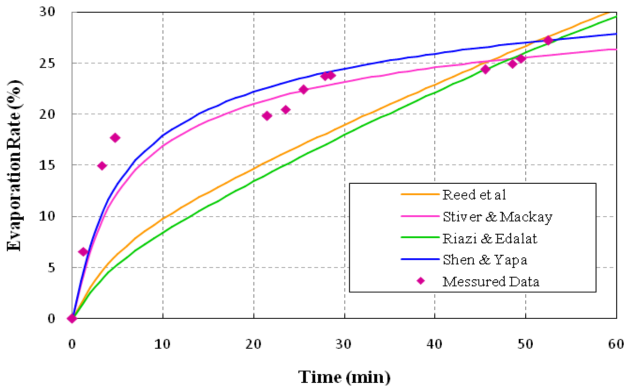

Fig. 3: Comparison of evaporation rates; wind speed = 5 m/s; temperature = 25 °C

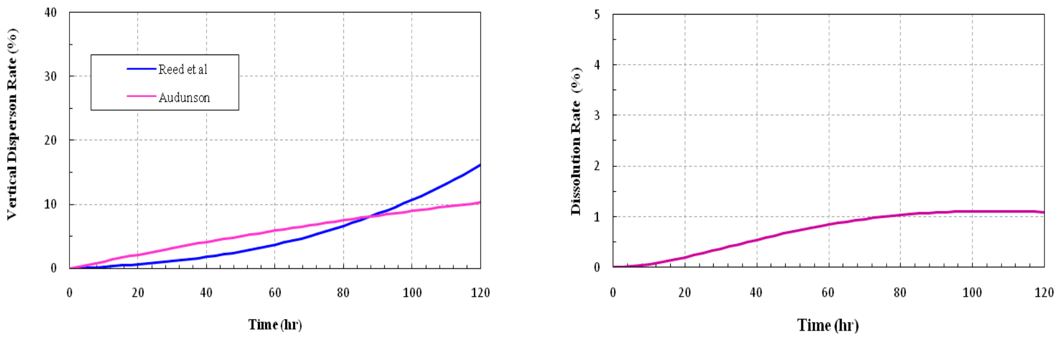

Fig. 4: Computed rates of vertical dispersion and dissolution

Emulsification Processes: As shown in Figure 6, the water content in fresh oil is equal to zero and it increases significantly in the first time to reach its maximum value (70%), then it preserves constant value.

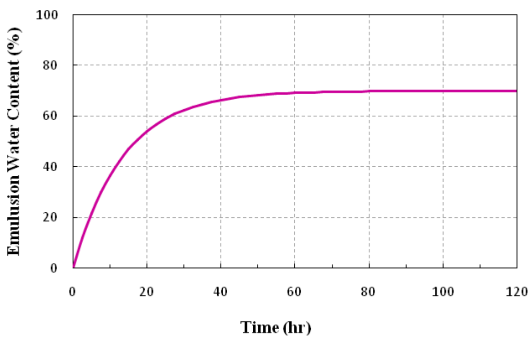

Fig. 5: The change of water content in water-in-oil emulsion

Changes of oil properties: As expected, a noticeable change is seen on the properties of oil (Figure 8). During the time, the viscosity increases and it causes the stability increasing of the reminder oil.

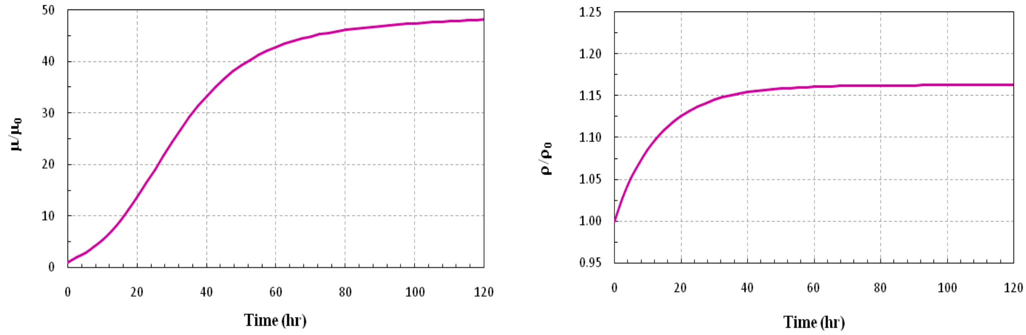

Fig. 7: The change of oil viscosity and density compared to their initial value

Composition of all processes: To compare the proportion of any processes in oil weathering, the oil mass balance was computed as a function of time (Figure 9). According to the simulation results, after 5 days about 35% of the total oil mass is lost by evaporation, 10% enters the water column by dissolution and vertical dispersion and 55% remains on the water surface. It's clear that, the mass balances on these phases depend on oil properties, environmental conditions and marine situations.

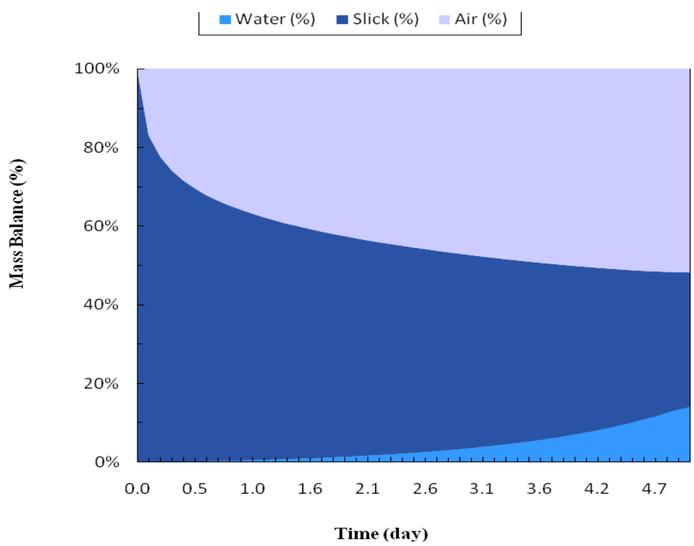

Fig 9: The portion of any processes in oil weathering

4. Results and Discussion

In this paper, a mathematical OWM is introduced to predict the oil slick behaviour on the sea and to compute the mass transfer rates due to most important weathering processes; evaporation, vertical dispersion, dissolution and emulsification. Also, it can calculate the change of oil properties during these processes. Because data deficiency is the most important problem in the preparation of OWMs, experimental measurements and semi-empirical equations results have been used to evaluate the mathematical model validation. As presented in results, the rates of oil mass losses significantly depend on the oil type (chemical and physical properties), the weather conditions (wind speed and direction, waves and temperature) and the properties of the seawater (salinity and temperature). In real incident, the OWM will applicable for calculation the rates of oil mass losses, evolution the stability of oil slick on water surface and complete view point on making discussion and evaluating the cleanup scenarios. In fact, the proposed model in this paper is part of the research done in the field of numerical simulation of oil slicks behaviour in marine environments.

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