

Comparison of 5 oil- weathering models

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1 Introduction

Within the project CALPREA at RIKZ application of reliable oil spill models and oil data bases is an important issue.

An oil spill model contains in general a transport module, an oil weathering module, an oil data base, and possibly a user-friendly graphical user interface. Recently, de Jong (2004) has made a study of four particle models for transport of floating and dissolved substances (DemWaq, DREAM, GNOME and SIMPAR) within CALPREA. The present report gives a detailed comparison of five pre-selected oil-weathering models.

Oil weathering models were selected on the following criteria:

1. They can be coupled to the hydrodynamic programs WAQUA (2d) and TRIWAQ (3d) in SIMONA at RIKZ; or
2. They are at present available to RIKZ through the Internet or other through means and are user friendly.

The oil-weathering modules of category 1 for this study were:

- SIMPAR oil module: The SIMPAR knowledge module for oil weathering at RIKZ (2003) was designed to get insight in the complex oil weathering formulations and the sensitivity of results for various oil properties and model parameters. The module is not yet implemented in the mother version and tested without transport. The module has no oil database.
- MEMW-DREAM: Marine Environmental Modelling Workbench of the Dose-Related Exposure Assessment Model (2001). This module by SINTEF is a detailed oil-weathering module, has an extensive oil database and is coupled to 2D and 3D transport models. The oil data base is based on laboratory data by SINTEF. The model is further simply denoted as 'DREAM'.
- GNOME: General NOAA Oil modelling Environment (2002). This module is a 2-D transport oil spill module with limited oil weathering processes and a limited number of oil types. It is by NOAA. It's purpose is a 'quick and dirty' trajectory analysis calamitous oil spills.

The oil-weathering modules of category 2 for this study were:

- ADIOS: Automated Data Inquiry for Oil Spills ADIOS (2002). The ADIOS-2 module is a detailed oil-weathering module by NOAA and has an extensive oil database but no transport of oil is included. The database was compiled from a number of different sources from governmental organizations and industry.
- OWM: Oil Weathering Model (2004). This module by SINTEF is a detailed oil-weathering module, has an extensive oil database completely based on lab-experiments by SINTEF. As far as we know, the oil weathering models of MEMW-DREAM and OWM are identical.

The models ADIOS and GNOME by NOAA are freeware and can be downloaded from the Internet. The SIMPAR oil module is a beta-release. RIKZ has a license for SINTEF's models DREAM and OWM for governmental purposes only.

Findings with respect to the oil modules are reported. Test results for four selected oil types are given.

2 Oil processes and oil properties

2.1 Oil processes

The following processes were included in this study (these processes are included in the 5 models unless mentioned that they are absent):

1. *Initial spreading* of the oil instantaneously at release time. This process describes the spreading of oil the first few hours after the start of an oil spill.
2. *The oil-dispersion* is a function of wind speed and viscosity of the floating oil (Delvigne and Sweeney 1988). Here, we do not mean the diffusive transport of oil. Oil-dispersion describes the transformation of floating oil into oil droplets in the water column.
3. *The evaporation of floating oil* is a first order process. The first order decay rate can be fixed or a function of various parameters like vapour pressure, temperature, wind speed and molecular weight of the volatile fraction (MacKay and Matsugu, 1983), or is related to Temperature Boiling Point (TBP) curves (Stiver and MacKay, 1984) also known as distillation curves. The theory is semi-empirical since it is based on correlation between boiling points of an oil-fraction and its equilibrium vapour pressure..
4. *Emulsification* affects the water content, viscosity, evaporation, density and volume of the oil spill (emulsification increases the volume to be cleaned up significantly). Emulsification is not included in GNOME.
5. *The beaching of oil* (oil stickiness). This process is only relevant for oil weathering modules coupled to transport models and is not further discussed in this report.

An overview is given in Table 1 of these processes for 5 modules.

As far as we know from the User manuals the first 4 processes are identical in MEWM-DREAM and OWM. Therefore, in this report only OWM was tested.

In Table 2 a detailed overview is given for the dispersion process.

Additional oil processes that are not further discussed in this report are summarized in Table 3 (none of these processes is included in SIMPAR). These processes are:

- *(Bio)Degradation and photo-oxidation* of oil. This process is included in DREAM but it is not in OWM. It is not included in ADIOS since ADIOS is limited to a 5 days period and for such a time scale this process is not relevant (ADIOS-2, 2002).
- *Volatilization* of dissolved components from the water column. This process is included in DREAM but it is not in OWM. It is not included in ADIOS;

-
- *Adsorption of droplets to suspended sediments and sedimentation to the bed.* This process is included in ADIOS but it is not in OWM or DREAM;
 - *Dissolution from oil slicks and oil droplets.* Dissolution of chemical components in the oil in water (like aromatics) is not included in OWM and ADIOS, neither is the evaporation of dispersed oil. These processes are included in DREAM.
 - *Effects of icing on oil slicks:* is included in DREAM and OWM but not in other models.
 - *Cooling of heated oil:* Heavy oils like heating fuel oil are fluid in the ship (above their pour point due to heating), but get solidified when spilled in the water. Nowadays, large amounts of oil are transported this way and therefore the cooling and (possibly) solidification of these oils is important. Initially, these oils will be fluid some time before they are solidified. In ADIOS and SIMPAR this process can be modelled until the oil solidifies. After solidification of the spilled oil the models are not applicable. This process is not in OWM or DREAM.
 - *Surface spreading of sub sea blowouts:* due to water entrainment the oil will be carried to the surface as fine oil droplets. A radial surface slick will be formed. This process is included in OWM but it is not clear whether this is in DREAM. It is not included in ADIOS nor in SIMPAR.

Some limitations on the models

- As far as we know the physical processes in DREAM and OWM are very much alike and in many cases (initial oil spreading, oil-dispersion, evaporation and emulsification) identical. The DREAM model includes processes like adsorption to suspended matter or dissolution of chemicals in the water phase that are not in OWM.
- The ADIOS model is limited to time-scales of 0,5 hr - 5 days and does not include any processes on larger time-scales like photo-oxidation and biodegradation. This is also true for OWM, DREAM and SIMPAR.
- The GNOME model has a User's Manual (2002) and several papers about its purpose exist. However, no Technical documentation is available and therefore only information about oil processes is very limited. The weathering processes that affect the oil spill trajectories are included in GNOME but for only a limited number of oil types (gasoline, kerosene/jet fuels. Diesel, fuel oil No.4, medium crude, fuel oil No.6 and non-weathering oil) (Beegle-Krause, 2001). According to the author (CJ Beegle-Krause, pers.comm.) the oil-weathering module of GNOME is a 'simple 3 phase approach only suited for educational purposes'.
- The SIMPAR model does not include any chemical processes neither adsorption processes.

More details about the processes can be found in Chapter 3.

Table 1. Most important oil processes (input data are not discussed)

Process	SIMPAR knowledge module	ADIOS-2	DREAM and OWM	GNOME	Comments (author's best current knowledge)
Initial Oil spreading	Stationary formulation, Fay & Hoult	Stationary formulation, Fay & Hoult	Dynamic formulation	?	All similar although the dynamic form is more sophisticated
Dispersion	Stationary formulation Delvigne & Sweeney (1988), no droplet spectrum but integrated mass	Stationary formulation Delvigne & Sweeney (1988), no droplet spectrum but integr. mass	Dynamic formulation Delvigne & Sweeney (1988), droplet spectrum in floating and water phase	Included	DREAM/OWM seems physically not correct (discussion is ongoing). Results of models differ due to dispersion parameter C_0 .
Evaporation	MacKay & Matsugu, 2 components of which one does not evaporate or a 9-fraction multi-component model with vapour pressure fitted to TBP-curves	Semi-empirical distillation theory by Stiver & MacKay, vapour pressure fitted to TBP-curves	MacKay & Matsugu, multi-component, vapour pressures of components correlated to TBP-curves. Evaporation limited by terminal thickness	Simplification of ADIOS-2	Correlation of TBP-curves to vapour pressures and molecular weight is not documented (except SIMPAR). DREAM/OWM has been verified against <i>field</i> trials for some oils (Daling et al., 1990 and 1997). This is not reported for ADIOS-2 and GNOME and not done for SIMPAR. Only DREAM/OWM includes a terminal thickness. This study shows similar results for all models consistent with good agreement of TBP-curves.
Emulsification (water uptake in floating oil)	Eley (1988) with simple time delay for onset of emulsification Wind effect according to MacKay (1980) and Reed (1989)	Eley (1988) time delay included Wind effect related to wave energy but not documented	SINTEF formulation close to MacKay et al. (1980) Wind effect by MacKay (1980), regressed with data by Cormack (1983)	Seems not to be included?	All very similar and very depending on quality of input data on maximum water fraction and emulsification rate. ADIOS includes a time delay related to the asphaltene fraction but the quality of input data is questionable.

Table 2. Overview of choices for parameters in the dispersion formulation by Delvigne&Sweeney (1988) (? = not reported)

Dispersion parameters	SIMPAR knowledge module	ADIOS-2	DREAM and OWM	GNOME
Dispersion constant C_0	Function of viscosity by Delvigne & Hulsen (1994)	?	SINTEF fit as function of viscosity	?
Dissipation energy D_{ba}	Delvigne 1988	?	Delvigne 1988	?
'Fraction of sea surface hit by breaking waves': F_{wc}	Holthuijsen and Herbers (1986)	?	Monahan & O' Muircheataigh (1980)	?
Droplet spectrum	Integrated over the droplet spectrum with fixed distribution	Integrated over the droplet spectrum with unknown distribution	Droplet spectrum modelled	?

Table 3. Additional oil processes not further discussed in this report. Are these included? (Yes/No/don't know=?).

Process	SIMPAR knowledge module	ADIOS-2	DREAM	OWM	GNOME
(Bio)degradation and photo-oxidation	No	No	Yes	No	No
Volatilization	No	No	Yes	No	No
Adsorption to suspended sediments	No	Yes	?	No	No
Dissolution from oil slicks	No	No	Yes	No	No
Icing	No	No	Yes	Yes	No
Cooling of heated oil	Yes	Yes	No	No	No
Surface spreading of sub sea blowouts	No	No	Yes	Yes	No

2.2 Oil properties

The modelling of the following oil properties was studied:

1. *The viscosity of the oil* is a function of the water fraction due to emulsification (Mooney, 1951). The water content of the oil is often a function of the oil-water interfacial area and the maximum capacity of water uptake (Eley, 1988). The temperature dependence of the viscosity is (sometimes) also modelled. Details for this property are given in Table 4.
2. *Water content of floating oil (due to emulsification)*. Water content is due to emulsification, which is shortly described in Table 1.
3. *The oil density* is also modelled. It is a function of fresh oil density, the *water content of the oil*, oil temperature and the fraction of the fresh oil that has already evaporated (ADIOS2, 2002). In SIMPAR and DREAM oil density only depends on water content and not on temperature and evaporation fraction.
4. *Temperature of the oil* affects many oil properties.
5. *Fraction of the oil that evaporated*. This parameter is very important for many oil processes and oil properties and must be included in any oil-weathering module.
6. *Terminal thickness of the evaporating oil surface*. Due to emulsification and/or increasing viscosity of the oil slick, the surface area cannot expand after some time. The thickness of the oil is then limited to a critical value (Reijnhart and Rose, 1982). Only DREAM and OWM include this effect.

In computer codes also the oil mass and compartment (floating, dissolved or 'sticking to land') are important. These are not further discussed. Oil properties are either required for each oil fraction (e.g. evaporation with light fractions like benzene and heavy fractions) in the models or are averaged properties for the total oil mixture. For a non-weathering fraction only the oil mass and oil density are required.

Wind speed (m/s) and water temperature (deg. C) are available in the models as forcing functions, but are not particle properties. Salinity is included in ADIOS, DREAM and OWM and used to calculate the density of water and affects adsorption of oil to suspended sediments. In SIMPAR the water density is fixed and adsorption to sediments is not included.

Properties not further studied in this report are:

- *Pour point* (°C);
- *Flash point* (°C);
- *Solubility in water*;

The models coupled to databases (DREAM, OWM and ADIOS-2) give these properties.

Table 4. Overview of description of viscosity oil processes in 4 oil modules.

	SIMPAR knowledge module	ADIOS-2	DREAM and OWM	GNOME
Effect of emulsification	Mooney (1951)	Mooney (1951)	Mooney (1951)	No
Effect of evaporation	Mackay (1983)	Mackay (1983)	Exponential like Mackay (1983), but with 2 regression factors	Is included but formulation not given.
Effect of temperature	Perry's Handbook	Perry' Handbook	Not included	?
Other	Parameters are fixed	Parameters depend on oil-type	Parameters depend on oil-type	GNOME includes parameters for 6 oil types

3 Detailed description of the oil processes

3.1 Overview

Evaporation

The ADIOS2 manual even does not describe the evaporation process in detail. The evaporation process in ADIOS-1 has been given by Fingas (1995) and Lehr (1992) and it is based on an approach suggested by Stiver and MacKay (1984). It is not clear whether ADIOS-2 still uses this formulation but we assumed here that it does. ADIOS does not use a model with fractions but the fractions are lumped in a semi-empirical fit of the Henry constant (or likewise vapour pressure) depending on the degree of evaporation.

For evaporation in SIMPAR different formulations were tested since the ADIOS evaporation approach is semi-empirical and depends on non-physical constants of which only few examples are open to the public. The default choice in SIMPAR is the evaporation process based on the well-known evaporation formulae of MacKay and Matsugu (1980) with only 2 fractions of which one does not evaporate. An additional model is based on 9 fractions and given in Appendix A.2.

The evaporation formulae of MacKay and Matsugu (1980) is also used in the Norwegian models DREAM (2001) and OWM (2004) by SINTEF. DREAM and OWM correlate the vapour pressures of the components to the TBP-curves like in Stiver-MacKay but in a different manner. This is a true multi-component approach with oil fractions from the distillation curve. The molecular weight is depending on the evaporation (see Oistein, 2004), which is also different from Stiver-MacKay. Another important difference between ADIOS (Stiver-MacKay) and DREAM is that DREAM/OWM uses a terminal thickness of the oil slick due to increased viscosity of the slick. This limits the evaporation rate. A common value suggested by Rose and Reinhart (1982) is a terminal thickness of 3 mm. In DREAM and OWM the user can vary this terminal thickness and often 1mm is suggested as default.

An overview of evaporation is given by Fingas (1995). For basic theory of multi-component evaporation see Reinhart and Rose (1982) and Jones (1997).

Oil-Dispersion

The definition of dispersion in SIMPAR is slightly different from ADIOS2 and follows closely the original paper by Delvigne and Sweeney (1988). DREAM and OWM use a more sophisticated approach: the droplet spectrum is not integrated but each droplet is modelled using a distribution over discrete size-classes.

Emulsification

The formula by SIMPAR and ADIOS used for emulsification is according to Eley (1988) but with an emulsification rate that has been made dependent of wind speed according to MacKay et al. (1980). For times larger the half saturation time for maximum water uptake (emulsification) one can show that the wind-adapted formulation of Eley and the formulation by MacKay become identical. For shorter times the formulas are different.

The formulation by DREAM and OWM for emulsification is according to MacKay.

Also the maximum water uptake and the rate of water uptake by emulsification are of importance since these parameters affect the volume to be cleaned up.

3.2 Release of oil

Release of oil in the SIMPAR knowledge module and ADIOS is according to Fay and Hoult (1971). The process accounts for spreading due to gravity, momentum and viscous forces. The Fay and Hoult model spreads oil in a circle with radius R given by:

$$R = \frac{k_2^2}{k_1} \left(\frac{V_{oil}^5 g \left(\frac{\rho_w - \rho_{oil}}{\rho_w} \right)}{v_w^2} \right)^{1/12} \quad (3.1)$$

With:

- R = radius of the oil spill (m³);
- k₁ = 1.15;
- k₂ = 1.45;
- V_{oil} = Initial volume of the oil spill (m³);
- ρ_w = density of water (kg m⁻³);
- ρ_{oil} = density of oil (kg m⁻³);
- v_w = kinematic viscosity of water (m² s⁻¹);

Input parameters are:

- Density of the oil;
- Total mass of the oil spill or the volume of the oil spill;

The formula only applies to oils lighter than water. It is not valid for oil emulsion with a specific density slightly larger than seawater.

DREAM uses a different approach: within DREAM (2001) the process is dynamic and related to the type of spreading (instantaneous, continuous, circular, bounded etc.). For all types of spills a unique length scale 'X' is used which follows from the following ordinary differential equation:

$$\frac{d}{dt} X^{4/3} = 1.75 \left(h^2 \rho_{oil} g \frac{(\rho_w - \rho_{oil})}{\rho_w} \right)^{2/3} (\rho_w^2 v_w)^{-1/3} \quad (3.2)$$

with: X = length scale of the oil slick (m);
h = film thickness of the oil slick (m).

For circular spreading 'X' is the radius of the patch and volume is:

$$V = \pi h X^2 \quad (3.3)$$

with: V = volume of the oil slick¹;

For bounded volumes in channels different relations are used in DREAM but these are not available in OWM. Also a combination with elongation due to wind and tidal currents is possible.

The gravity spreading process in Eq. (3.2) is quickly overtaken by turbulent diffusion. The time until this moment can be defined as the *initial spreading period*. Eq. (3.1) describes only the integrated effect of this initial period whereas Eq.(3.2) gives the complete dynamics.

This initial spreading process is important for the fate of oil since at the start of an oil spill the oil dispersion process and oil evaporation process are both fully active (after some time they stop due to emulsification), and depend on the surface area of the slick. *So, the initial area is of importance for the competition between the oil processes.* This also makes that the relative contribution of oil processes in an oil slick changes when the amount of oil spilled increases. In principle, the relative importance of oil-dispersion increases for larger surface area's (larger spills).

After a few hours for many oils (but not always) the viscosity increased exponentially (due to evaporation and emulsification) and dispersion stopped. Thus, the oil-dispersion process is important for the total oil budget in case the oil does not emulsify, when not all the light oil fractions quickly evaporate or when the natural dispersion is very intense. An example of such a case was the *Braer* incident in 1993 near the Shetland Islands where *Norwegian Gullfaks* crude oil with low viscosity was quickly dispersed due to high wave energy (Harris, 1995).

3.3 Oil dispersion or entrainment of oil

Oil dispersion is modelled in SIMPAR, ADIOS, OWM and DREAM according to Delvigne and Sweeney (1988). The basic formulae is the gradient of the entrainment rate Q per square meter with oil droplet diameter d:

¹ The volume is related to spilled mass and oil density. The mass for a continuous release is related to the release rate. An approximation in this model (and that in Eq. 3.1) is the uniform thickness 'h' of the oil slick. According to Reijnhart and Rose (1982) in practice this thickness is non-uniform.

$$\left(\frac{\partial Q}{\partial d}\right)_{d_0} = C_0 D_{ba}^{0.57} S_{cov} F_{wc} d_0^{0.7} \quad (3.4)$$

with:

- Q = entrainment rate of oil droplets per unit surface area (kg m⁻²sec⁻¹);
 S_{cov} = sea coverage factor of oil (1.0 for closed patches)²;
 d₀ = oil droplet diameter (m);
 C₀ = oil dispersion parameter related to oil viscosity;

The fraction of the sea surface hit by breaking waves (per unit time) F_{wc}, is according to Holthuijsen and Herbers (1986):

$$F_{wc} = \frac{0.032 \max(U_w - 5.0; 0.0)}{T_w} \quad (3.5)$$

with:

- F_{wc} = fraction of the sea surface hit by breaking waves per unit time (-);
 U_w = wind speed (m s⁻¹);
 T_w = wave period (s⁻¹);

Below a wind of ~ 5 m/s there is no white capping and therefore oil dispersion then does not occur. DREAM and OWM follow a different approach by Monahan & O' Muircheataigh (1980):

$$F_{wc} = 3.10^{-6} U_w^{3.5} \quad (3.6)$$

The dissipation energy D_{ba} of a wave is given by:

$$D_{ba} = 0.0034 \rho_w g \left(\frac{H_0}{\sqrt{2}}\right)^2 \quad (3.7)$$

$$H_0 = \frac{0.243 U_w^2}{g}$$

with:

- D_{ba} = dissipation energy of a wave per unit surface area (J m⁻²);
 H₀ = significant wave height (m);
 g = gravity (m s⁻²);

(in DREAM the wind dependency of H₀ on wind is not specified in the Technical Documentation).

Both F_{wc} and D_{ba} are a function of wind speed only. In Eq. (3.4) the following particle size distribution for oil droplets is used:

² Note: Normally S_{cov} equals 1.0. In case the oil patch does not cover completely the enclosed surface (due to breaking of the oil patch), the coverage factor must be decreased.

$$N_d = N_0 d_0^{-2.3} \quad (3.8)$$

with:

N_0 = normalization factor;
 N_d = number of droplets per diameter d_0 ;

(Note: for different size distributions formulae (3.4) must be adapted).

Dynamic approach of droplets in DREAM

In DREAM the droplet spectrum is explicitly modelled starting from a given discrete size distribution. Droplets are migrated from the floating layer into the water column with a rate per discrete size class given in equation (3.4) of this section. The employed size distribution is a generalization of 2 empirical relations given in Delvigne and Sweeney (1988), for mean and maximum droplet size:

$$d_0 = \frac{Cv^{0.34}}{\sqrt{e}} \quad (3.9)$$

with: C = parameter varying from 500-3400;
 v = viscosity
 e = energy dissipation rate ($1000 \text{ J m}^{-3} \text{ s}$)

The energy dissipation rate is fixed and high which is not correct in a non-turbulent environment. It is not clear whether the size distribution in Eq. (3.8) was correctly applied.

Integration over the droplet spectrum (ADIOS and SIMPAR)

Droplets larger than a certain size d_{\max} will immediately resurface to the slick and therefore not contribute to dispersion of oil. Integrating the gradient of dispersion rate over all droplet classes from the minimal (d_{\min}) till maximal oil droplet diameter (d_{\max}) gives that the total entrainment rate Q of the oil per square meter is:

$$Q = \int_0^{d_{\max}} \left. \frac{\partial Q}{\partial d} \right)_{d_0} dd_0 = \frac{d_{\max}^{1.7}}{1.7} C_0 D_{ba}^{0.57} F_{wc} S_{cov} \quad (3.10)$$

Both ADIOS-2 and SIMPAR use $d_{\min} = 0\mu$ and $d_{\max} = 70\mu$.

The relation between C_0 and viscosity v is after Delvigne and Hulsen (1994):

$$\begin{aligned} \text{For } v < 125 : C_0 &= 1827.0v^{-0.0658} \\ \text{For } v > 125 : C_0 &= 436516.0v^{-1.1951} \end{aligned} \quad (3.11)$$

with:

v = oil viscosity (cSt);

The relation in DREAM is:

$$C_0 = 4450 v^{-0.4} \quad (3.12)$$

In Figure 3.1 these relations are compared. The figure shows that differences are large. This can lead to large differences in oil-dispersion for the models.

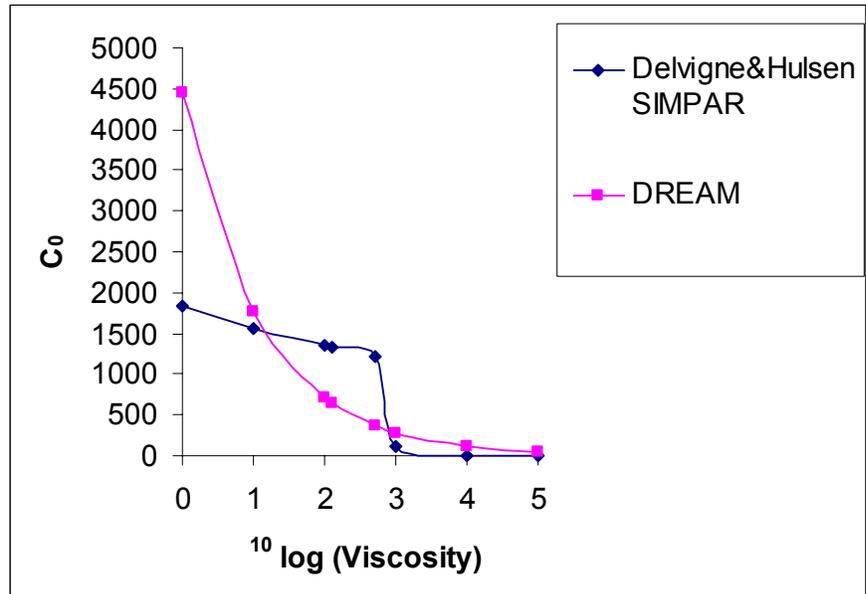


Figure 3.1 Delvigne&Hulsen (1994) against DREAM formulation for dispersion parameter C_0 . Delvigne and Hulsen is used in SIMPAR.

3.4 Evaporation of floating oil

3.4.1 Overview of evaporation

Evaporation of oil is commonly implemented in three ways:

- I. As a first order decay process with fixed constant K_{evap} (day^{-1}).
- II. Following a one-fraction model with either the formulation by MacKay and Matsugu (1983) or the semi-empirical distillation theory by Stiver and MacKay (1984).
- III. Following a multi-component model for evaporation based on theories by Reinhart and Rose (1982) or Jones (1997).

Models II and III also use a first order decay process and thus are extensions of I. Model III again is an extension of model II. The mass-transfer coefficient by MacKay and Matsugu is commonly used in all models of level 2 and 3.

Model III requires also a specific parameterization of the relation between vapour pressure (or Henry constant) to TBP-curves. Details of models of level III are further discussed in the Appendix.

3.4.2 First order evaporation

This model is a simplification of the other models and does not include effects of varying temperature, vapour pressure, molecular weight or wind speed in the environment. As input only the first order decay process with fixed decay constant k_{evap} (day^{-1}), and the dimensionless vaporizable fraction $f_{\text{evap}}(0)$ must be given. The model was used in the SIMPAR knowledge module for comparison but in practice its use is limited since evaporation rate is not a constant.

The relation between first order rate and mass flux is:

$$\frac{dm}{dt} = m(t) f_{\text{evap}} \exp(-K_{\text{evap}} t) \quad (3.13)$$

with:

$m(t)$ = total floating oil mass at t (kg);
 f_{evap} = volatile fraction of the floating oil;
 k_{evap} = evaporation rate (sec^{-1});

3.4.3 Evaporation according to Mackay and Matsugu

This formulation relates the first order decay rate to vapour pressure, temperature and molecular weight of the volatile fraction. Also this formulae works only for the volatile, non-emulsified fraction of the remaining floating oil. MacKay and Matsugu (1983) have derived the following mass rate of evaporation:

$$\frac{dm_s}{dt} = -K \frac{P_{\text{vp}} A}{RT} f_{\text{evap}} M_w \quad (3.14)$$

$$K = 0.029 (3600 U_w)^{0.78} D^{-0.11} S_c^{0.67} \sqrt{\frac{M_w + 29}{M_w}} \quad (3.15)$$

with:

K = mass transfer coefficient under prevailing wind conditions;
 m_s = oil mass of the slick in grams (g);
 t = time in *hours*;
 A = surface area of the slick (m^2);
 D = Oil slick diameter (m);
 P_{vp} = vapour pressure of the oil (atm) ;
 M_w = molecular weight (g mol^{-1});
 R = ideal gas constant ($8.206\text{E-}5 \text{ atm m}^3 \text{ mol}^{-1} \text{ K}$);
 T = temperature (K);
 S_c = Schmidt number of cumene (2.7);

Here Eq. (3.14) is general theory for ideal liquids and gases (see Appendix 1). Eq. (3.15) defines the mass transfer coefficient according to MacKay and Matsugu. The model in Eq. (3.14) uses only 1 fraction but can also be extended for many fractions (see Appendix A.1).

3.4.4 Semi-empirical distillation theory

In the ADIOS-1 model (Lehr et al., 1992) the evaporation is given according to the semi-empirical distillation theory derived by Stiver and MacKay (1984, eq.12) for multi-component liquids:

$$\frac{df_{evap}}{dt} = \exp \left[A - \frac{B}{T_{oil}} (T_0 + T_g f_{evap}) \right] \frac{d\theta}{dt} \quad (3.16)$$

with: T_{oil} = liquid oil temperature (°K);
 T_0 = parameter related to initial boiling point (°K);
 T_g = parameter related to gradient of the distillation curve (°K);
 θ = evaporative exposure (see Appendix A.1);
A, B = fitting parameters;

T_0 and T_g are derived from fractional distillation data, where T_0 is the initial boiling point ($f_{evap}=0$) and T_g is the gradient of the modified distillation curve. Running ADIOS-2 and looking for distillation curves under 'oil properties' gives the relevant data.

The ADIOS-1 model by Lehr et al. (1992) used (3.16) with:

$$A = 6.3$$

$$B = 10.3$$

A similar approach has been followed by Bobra (1992). Values for parameters for 8 different oils were derived from lab experiments and have been reported by Fingas (Fingas, 1995; Table 1). Those results show that A and B differ widely over the different oils suggesting that the ADIOS-1 model may be inaccurate. According to Fingas in 3 cases good results were achieved and in 2 cases the results were poor. We found for Troll crude oil and Ekofisk blend (see next section) that the values A,B from Lehr do not apply.

The model (3.17) can be transferred in a mass-flux equation by multiplication of (3.16) with the initial mass of the spill:

$$\frac{dm}{dt} = \frac{M_w}{v} HKA$$

$$H = \exp \left[A - \frac{B}{T_{oil}} (T_0 + T_g f_{evap}) \right] \quad (3.17)$$

This shows that the Henry constant is in fact not a constant but depends on the evaporation fraction (likewise the mole fraction x) of the oil. One can also define an effective vapour pressure for comparison with the model by MacKay and Matsugu:

$$P_{vp} = \left[\frac{RT}{v} \right] \exp \left[A - \frac{B}{T_{oil}} (T_0 + T_g f_{evap}) \right] \quad (3.18)$$

Thus, vapour pressure depends on the degree of evaporation whereas in the (original) model by MacKay and Matsugu it was constant. The molecular weight and molar volume of the oil are not dependent on the oil fraction but averages for the total oil mixture.

3.4.5 The evaporation models in SIMPAR, DREAM/OWM and ADIOS-2

SIMPAR

In SIMPAR the model uses the mass transfer coefficient according to MacKay and Matsugu and either:

- 1 vaporizable fraction and 1 fraction with zero evaporation constant (level II model).
- 9 vaporizable fractions with vapour pressures fitted to TBP-curves (level III, see Appendix A.2). This model is according to Reijnhart and Rose (1992).

DREAM and OWM

In DREAM and OWM many fractions (oil components) are used, each evaporates according to (3.14) (level III model). The set of differential equations involved is according to Reijnhart and Rose (1982) and given in Appendix A.2.

For each component DREAM requires input of:

- Vapour pressure $P_{vp,i}$;
- Molecular Weight M_i ;
- Evaporizable fraction f_{evap} (in DREAM a weight fraction is used)

In DREAM and OWM the vapour pressure and molecular weight data are obtained from laboratory data (DREAM, 2001). In OWM a correlation is made with TBP-curves (OWM, 2004; Oistein, 2004, see Appendix). Such an approach makes that the model gets close to the ADIOS model (see next section) although still different correlation equations are used in both the models and still OWM is a true multi-component approach based on a discrete sum of oil fractions. In case of DREAM the correlation procedure is not described but probably equivalent to that of OWM.

In DREAM different formulae for the wind dependent mass transfer coefficient is used as in (3.15):

$$K = C_d U(t) \quad (3.19)$$

Here the wind drag coefficient uses a staircase profile (see DREAM 2001, p. 14).

ADIOS-2

The set of differential equation in ADIOS-2 is not given. Most probably it is according to Jones (1997). The vapour pressure is probably according to Stiver and MacKay as in ADIOS-1.

Comparison of the models

A comparison of OWM, ADIOS-2 and the 2 SIMPAR models was made. Results are given in Figure 3.2 for Ekofisk Exxon (for OWM we used Ekofisk Blend).

Results of OWM and ADIOS-2 are very much alike. We also found that the TBP-curves for Ekofisk Blend and Ekofisk Exxon in these models are almost identical.

The MacKay approach in SIMPAR starts initially too slow since it has only one fraction. But after some time (here 1 day) it crosses with the other curves by OWM and ADIOS-2 and then overestimates evaporation (vapour pressure in the SIMPAR-1-fraction model was calibrated to give identical results after 1 day). These results show the need of a good multi-component evaporation model. However, for simulations with lots of particles the 1 component model is much more efficient and therefore may still be a good alternative.

The 9 fraction model in SIMPAR overestimates evaporation for Ekofisk (and Troll) for $A=6.3$ and $B=10.3$ (values from Stiver and MacKay). After calibration ($A=4.8$ and $B=10.3$) SIMPAR is in good agreement with OWM and ADIOS-2.

In Figure 3.3 it is shown that also for Troll the parameter values $A=4.8$ and $B=10.3$ give a good agreement between SIMPAR and OWM.

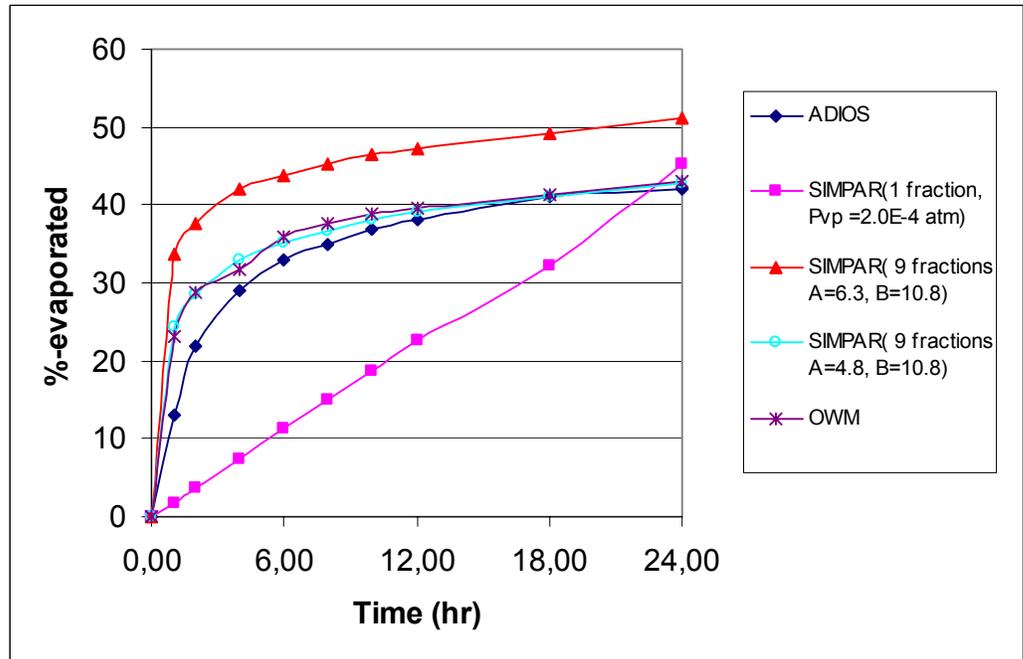


Figure 3.2. Evaporation curves for Ekofisk-Exxon for 5 models (ADIOS, 3 SIMPAR variants and OWM). Vapour pressure in SIMPAR for 1 fraction ('MacKay model') is $2.0E-4$ atm.

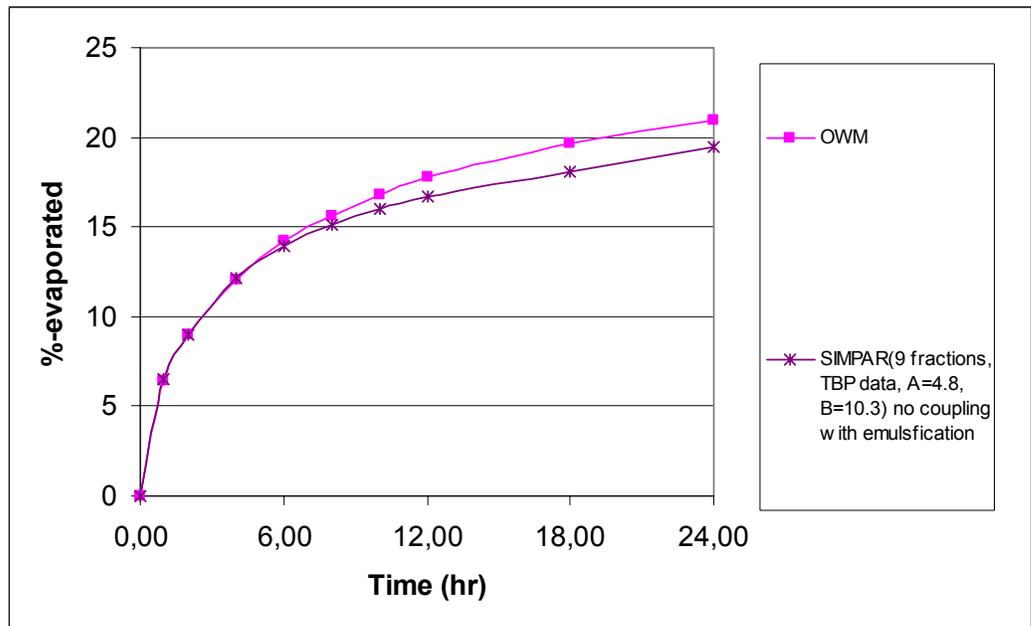


Figure 3.3. Evaporation curves for Troll (IKU) for OWM and the calibrated SIMPAR model ($A=4.8, B=10.3$) with 9 oil fractions.

3.5 Density of oil

Density of oil is modelled in ADIOS-2 (2002) by:

$$\rho_{oil}(y, T) = y\rho_w + (1-y)\rho_0(0, T_0) \left[1 - c_1(T - T_0)(1 + c_2 f_{evap}) \right] \quad (3.20)$$

with:

T	=	temperature (°C or Kelvin);
T ₀	=	reference temperature (°C or Kelvin);
c ₁	=	oil dependent constant;
c ₂	=	oil dependent constant;

Parameter values for c₁ and c₂ used by ADIOS-2 are unknown.

SIMPAR, OWM and DREAM use this model but (by lack of any data) with c₁ = 0.0, c₂ = 0.0 (T₀ = 20.0 °C), i.e. any temperature dependence is neglected. The water density in SIMPAR is fixed at 1030 kg m⁻³ and the reference oil density is the one specified in the input file. The ADIOS-2 fresh water density depends on the specified water temperature and salinity. It is not specified how DREAM models density of seawater but it seems to be fixed 1025 kg m⁻³.

3.6 Oil viscosity

Oil viscosity is a function of:

- water fraction (y);
- evaporation fraction (f_{evap});
- temperature.

The dependency on water fraction is according to Mooney (1951) for all models, but with different coefficients. The dependency on evaporated fraction is according to MacKay et al. (1983) in ADIOS-2 and SIMPAR and different from DREAM and OWM. The temperature dependency is according to Perry 's Chemical Engineers Handbook in ADIOS and SIMPAR and not implemented in DREAM and OWM.

3.6.1 Effect of emulsification on oil viscosity

The dependency on water fraction is according to Mooney (1951), but with coefficients for oils:

$$\ln \left(\frac{\nu(y)}{\nu(0)} \right) = \frac{2.5y}{(1 - c_v y)} \quad (3.21)$$

with: c_v = coefficient for polydispersity;

In SIMPAR and DREAM a coefficient for crude oils is used: c_v = 0.654. In ADIOS-2 this coefficient is varied but values are not specified.

Mooney's relation is fundamentally derived for emulsions of rigid spheres. The coefficient c_v in the Mooney equation mimics the degree of polydispersity of the spheres and is substantially lower for

(bidisperse) mixtures of small and large spheres than for monodisperse spheres. In the bidisperse case the small spheres will fill up the gap between the large spheres leading to only a minor increase of viscosity. The coefficient 2.5 in the nominator is required to comply with Einstein's theory for the viscosity of diluted mixtures of rigid spheres in a viscous fluid. This coefficients holds in practice also for water in oil emulsions and need not be adapted.

The equation has been used successfully by ADIOS to fit viscosity dependence on water fraction for water in crude oils (eg non-rigid spheres), and the coefficient $c_v = 0.65$. This coefficient closely resembles those for a mixture of polydisperse rigid spheres with $c_v = 0.75$ (Eilers, 1941). Data by Eilers show that Mooney's equations holds when $y < 0.6$ but underestimates viscosity for $y > 0.7$ (see Mooney, Fig. 2).

3.6.2 Effect of evaporation on oil viscosity

The dependency on evaporated fraction in SIMPAR and ADIOS is according to MacKay et al. (1983):

$$\ln\left(\frac{\nu(f_{evap})}{\nu(f_{evap0})}\right) = c_b (f_{evap0} - f_{evap}) \quad (3.22)$$

with: c_b = coefficient (-);
 f_{evap0} = the total oil fraction that may evaporate (-);

For SIMPAR a fixed value of $c_b = 5$ is applied whereas ADIOS uses values depending on the kind of oil. In SIMPAR, when 50% of all oil has evaporated, viscosity will increase with a factor $\exp(2.5) = 12$. We found that this coefficient gives good results for heavy oils. However, for lighter oils a value $c_b = 5$ overestimates the viscosity in comparison predicted viscosity by ADIOS2 (see test for Gasoline in Chapter 4).

In DREAM (2001) and OWM (2004) a somewhat different relation is used:

$$\ln\left(\frac{\nu}{\nu_0}\right) = a_v + b_v f_{evap} \quad (3.23)$$

where a_v and b_v are regression factors. The models are identical in case $a_v = c_b f_{evap0}$ and $b_v = -c_b$.

3.6.3 Effect of temperature on oil viscosity

In the SIMPAR knowledge module and in ADIOS-2, the temperature dependency is according to Perry's Chemical Engineers Handbook (1973).

$$\ln\left(\frac{\nu(T)}{\nu(T_0)}\right) = c_T \left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (3.24)$$

with: c_T = coefficient in Kelvin;
 T = temperature in Kelvin;
 T_0 = reference temperature in Kelvin;

In SIMPAR a fixed value $c_T = 5000$ K is used whereas in ADIOS this value is varied. In DREAM (2001) this effect has not been implemented.

3.7 Emulsification of floating oil

3.7.1 Eley formulation used in ADIOS and SIMPAR

In ADIOS and SIMPAR emulsification of oil is incorporated according to Eley (1980). Eley describes the water content 'y' to be a function of the ratio of interfacial surface area to volume S ($\text{m}^2 \text{cm}^{-3}$) and the water droplet diameter (d_w). For S a differential equation is used whereas the droplet diameter is assumed to be fixed.

$$y = \frac{sd_w}{6 + sd_w} \quad (3.25)$$

$$s = s_{\max} (1 - \exp(-k_s t))$$

with: s = ratio of interfacial surface area to volume ($\text{m}^2 \text{cm}^{-3}$);
 d_w = water droplet diameter (m);
 k_s = emulsification rate (sec^{-1});
 s_{\max} = maximal ratio s ;

In SIMPAR, for simplicity a transformed set of equations is used that does not require s or d_w :

$$x = sd_w = \frac{6y}{(1-y)}$$

$$x = x_{\max} (1 - \exp(-k_s t)) \quad (3.26)$$

$$x_{\max} = \frac{6y_{\max}}{(1-y_{\max})}$$

where y_{\max} is the maximum water content given by substitution of s_{\max} in (3.25). Note that $y = 0$ at $t = 0$ and $y = y_{\max}$ at $t = \infty$.

Wind dependency of emulsification

Emulsification rate must be a function of wind speed since with high winds oils emulsify much faster. Unfortunately, ADIOS2 does not specify such a wind dependency but only remarks that the emulsification rate is a function of (wind-induced) wave energy.

In SIMPAR, the wind dependency is analogue to a study by MacKay et al. (1980). However, the MacKay model for emulsification is different and is:

$$y = y_{\max} (1 - \exp(-k_y t))$$

$$k_y = \frac{k_0}{y_{\max}} (U_w + 1)^2 \quad (3.27)$$

with: k_y = emulsification rate (sec⁻¹);
 k_0 = emulsification rate for $y_{\max}=1$ and zero wind (sec⁻¹);

Reed (1989) specifies a value of $k_0 = 2.0 \text{ E-}6 \text{ sec}^{-1}$ and $y_{\max} = 0.7$ for crude oils and heavy fuel oil (and much lower for home heating oil). Comparison of MacKay's model and Eley's model reveals that they are *identical* for large times (with respect to half saturation times of the emulsification process) when the emulsification rate of Eley is:

$$k_s = \frac{k_0}{y_{\max}} (U_w + 1)^2 \quad (3.28)$$

Identity (3.28) is used in the SIMPAR oil module for the Eley method in order to specify the wind dependency.

For shorter times the MacKay formulae emulsifies the oil slower. The half saturation time $t_{1/2}$ for emulsification of the MacKay model is about 2/3 of that in the Eley model. Conversion of half saturation times in rate constants can be done by:

$$k = \frac{\ln 2}{t_{1/2}} \quad (3.29)$$

Therefore, it is advised to use a somewhat smaller value than MacKay for k_0 in (1.19), eg. 0.67 times the MacKay evaporation rate.

Daling et al. (1997) clearly show for Troll crude oil the dramatic effect of wind speed and values for the half saturation of oil. In that study $y_{\max} = 0.75$, $t_{1/2} \sim 1.25$ hour for $U_w \sim 7.5$ m/s and $t_{1/2} \sim 12$ hour for $U_w \sim 4$ m/s (the wind effect is even more than quadratic but wind varied during those field experiments).

For the SIMPAR oil module, at $U_w \sim 7.5$ m/s we reproduce $t_{1/2} = 1.25$ hour when we set $k_0 = 1.0\text{E-}6$ in the Eley model (1.19), and $k_0 = 1.5\text{E-}6$ in the MacKay model (1.18). This is only 25% below the emulsification rate $k_0 = 2.0\text{E-}6$ used in Reed et al. (1989).

The short half saturation times for emulsification compared to values for evaporation, shows that emulsification of crude oils is important. It makes these oils persistent against oil-in-water-dispersion after a few hours. It also gives a large increase of volumes to be cleaned up. The volume to be cleaned up at t is:

$$V(t) = V_0 m_s(t) \frac{1}{(1-y(t))} \frac{\rho_0}{\rho(t)} \quad (3.30)$$

with: V_0 = initial volume spilled;
 ρ_0 = initial density of the oil;
 m_s is the mass of *floating* oil at t ;

The coupling of evaporation with emulsification is discussed in section 3.8.

The weathering model may give important information whether actions can be undertaken to add dispersants (hereto in general viscosity must be low enough). Also can it simulate the spreading of dispersed oil and give indications on mass of possibly toxic evaporated oil fractions.

Delay in the onset of emulsification

In ADIOS emulsification is for some oil types delayed depending on a experimental fit between experimental data for water uptake and the asphaltene fraction. For crude oils without experiments interpolation is done. For other crude oils an estimate is made depending on oil density, or more precisely on API Gravity ($API = 141.5/\rho_{oil} - 131.5$).

In ADIOS-2 onset of emulsification can be specified simply also as a time in hours. This option is also implemented in SIMPAR but not in DREAM.

3.7.2 Emulsification in DREAM and OWM

In DREAM (2001) a different approach is used that directly focuses on water content y (and not on s):

$$y(t + \Delta t) = y_{\max}(t) - [y_{\max}(t) - y(t)] 0.5^{\frac{\Delta t}{t_{1/2}}} \quad (3.31)$$

The constant $t_{1/2}$ is a wind dependent half time for emulsification. The value for y_{\max} has now a profile depending on time. The function y_{\max} is time-dependent since it is considered to depend on fraction evaporated. The wind dependency for DREAM is expressed for a reference wind speed $U_{ref} = 10$ m/s. The reference wind speed is related to a true wind speed according to Cormack (1983):

$$t_{1/2} = \left[\frac{1 + U_{ref}}{1 + U_w} \right]^2 t_{ref} \quad (3.32)$$

Both t_{ref} and y_{\max} have been derived from laboratory experiments by SINTEF.

The approach in (3.30) is a numerical implementation of MacKay et al. (1980) given in Eq. (3.27). The relation (3.31) specifies the rate constant in MacKay according to Eq (3.29).

OWM specifies the maximum water uptake y_{\max} for fractions of the oil.

At present, it is not clear how OWM uses y_{\max} data for the various fractions (150+, 200+ and 250+) given in its data base. It seems that OWM varies y_{\max} as a function of the non-evaporated fraction (see also Daling et al., 1990). Also, the emulsification rate seems to vary with non-evaporated fraction but is not clear from the technical documentation.

3.7.3 Comparison of emulsification modules

In Figure 3.4 the approach followed in SIMPAR (Eley, wind according to MacKay) is compared to DREAM (MacKay) for zero wind and a wind speed of 10 m/s. Parameters were $y_{\max} = 0.7$ and $k_0 = 2.0E-6 \text{ s}^{-1}$ ($t_{1/2} = 2.43E+5 \text{ s}$ at $w = 0.0 \text{ m/s}$). ADIOS follows SIMPAR but wind effect in ADIOS is not documented.

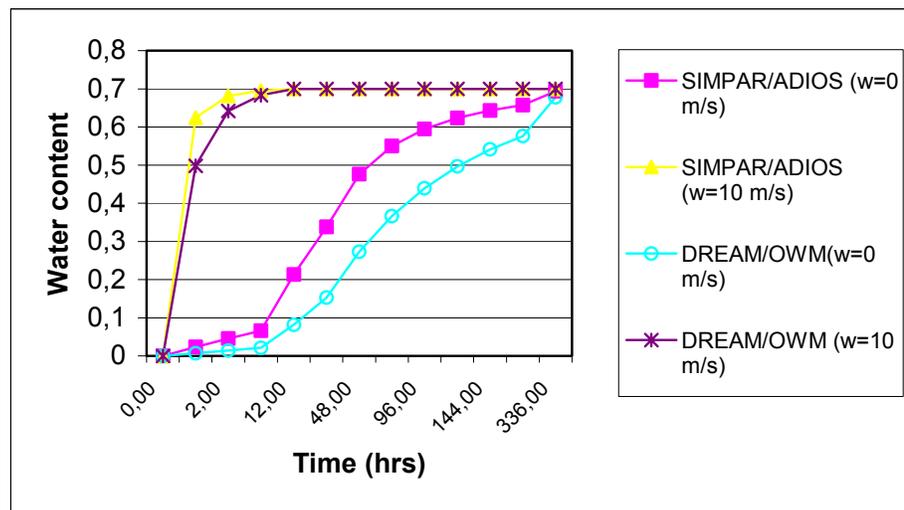


Figure 3.4 SIMPAR and ADIOS (Eley, wind according to MacKay) compared to DREAM and OWM (MacKay) for zero wind and a wind speed of 10 m/s. Parameters were $y_{\max} = 0.7$ and $k_0 = 2.0E-6 \text{ s}^{-1}$ ($t_{1/2} = 2.43E+5 \text{ s}$ at $w = 0.0 \text{ m/s}$).

3.8 Coupling of emulsification and evaporation of oil

It seems obvious that a coupling between emulsification and evaporation is required since emulsification leads to enormous oil viscosities and thus to limited evaporation. However, in none of the models a coupling mechanism seems to be included. Nevertheless, the OWM model has been extensively tested against field data and so the effect must in some way be modelled. At present we have no information about this subject.

In SIMPAR the following approach was tested: it was assumed that an amount of mass equivalent to the water fraction is not able to evaporate:

$$m_{evap} = (1 - y)m_s \quad (3.33)$$

with: m_{evap} = oil mass that can evaporate;
 m_s = total oil mass;

The model (3.33) gives a flat evaporation curve after about 24 hours when a crude oil is completely emulsified. Given the fact that this is not observed in OWM it seems that this mechanism is not correct in SIMPAR.

We repeated the simulations for Ekofisk-Exxon with SIMPAR but now with a coupling according to Eq. (3.33) included. The result is given in Figure 3.5 (compare with Figure 3.2).

For the 1 component model the calibrated vapour pressure was now much higher ($1.5E-3$ atm) than without coupling. The calibration is done to get agreement with ADIOS-2 after 24 hrs and since less mass is now available for evaporation a higher vapour pressure is required.

The multi-component approach in SIMPAR was with the parameters $A=6.3$, $B=10.8$. It starts fast but levels off to a flat curve. The flattening of the curve is due to the coupling in model (3.33) which is therefore too strong. Given the good agreement with OWM and ADIOS-2 (which have been verified against field data) we further omitted any coupling.

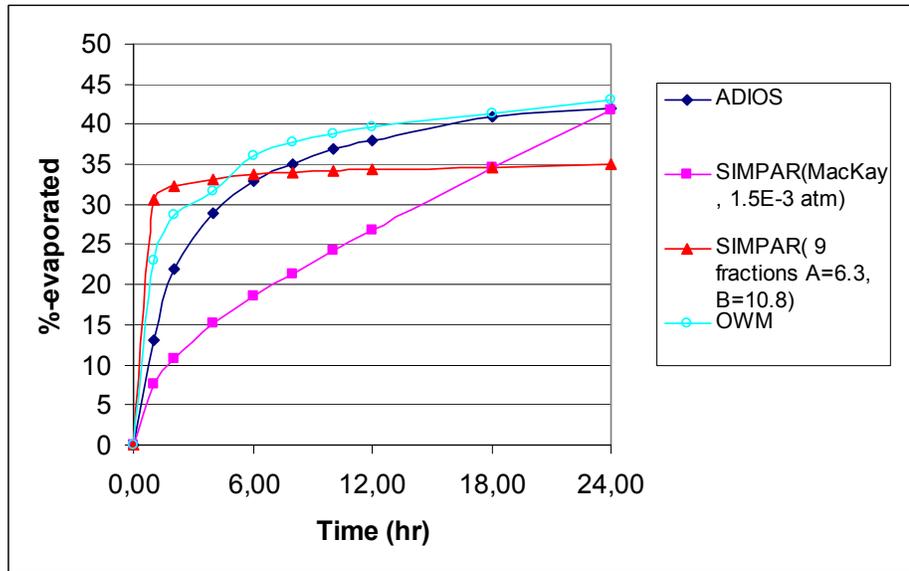


Figure 3.5. Evaporation curves for Ekofisk-Exxon for 4 models. Vapour pressure in SIMPAR for 1 fraction is $1.5E-3$ atm. The SIMPAR models now include coupling between emulsification and evaporation according to Eq. (3.33).

4 Test results

4.1 Test simulations

4.1.1 Introduction

The following oil-weathering models (all without transport) were tested:

- ADIOS-2;
- OWM;
- SIMPAR but only the option with 9 fractions (see section 3.4.5 and Appendix A.3). The SIMPAR module used is the version without transport.

The following oils³ were tested:

- Troll Crude Oil (Troll (IKU) in OWM, not in ADIOS-2);
- Ekofisk Exxon (Ekofisk Blend in OWM);
- Automotive Gasoline Exxon (Not in OWM);
- Arabian Heavy (IKU in OWM and Exxon in ADIOS-2).

DREAM was not tested since it is assumed to behave like OWM. GNOME does not include information on specific oils and was therefore not tested.

Two simulations with SIMPAR were performed, namely:

- SIMPAR-O: SIMPAR with input parameters from OWM or a best guess based on OWM;
- SIMPAR-A: SIMPAR with input parameters from ADIOS-2 or a best guess based on ADIOS-2;

In all cases the wind speed was 8.0 m/s and water temperature was 15°C. Density of water was 1030 kg m⁻³ in SIMPAR and ADIOS-2, and 1025 kg m⁻³ in OWM. The release was instantaneous with a total mass of 1000 metric tonnes (10⁶ kg). The corresponding volume depends on the fresh oil density but is approximately 1100 m³. The simulations lasted 24 hours.

A comparison is made of the oil budget (% floating, dispersed and evaporated), and oil properties (viscosity, density, volume ratio and water uptake). Volume ratio is the ratio of the volume to be cleaned up to the spilled volume and is obtained from Eq. (3.30). Results are given after 6 hrs and 24 hrs except for gasoline where results are given after 2 hrs and 3 hrs.

³ Automotive Gasoline is classified here as an oil.

4.1.2 Oil parameters

OWM and ADIOS-2

OWM and ADIOS-2 parameters from the data base values were applied. For OWM a terminal thickness of 1mm was applied in all cases (for ADIOS-2 and SIMPAR this is not a model parameter).

Some of the oil parameters for OWM and ADIOS-2 are given in Tables 4 (only OWM), 5 and 6. Note that for Arabian Heavy the maximum water uptake of OWM and ADIOS-2 is very different.

OWM specifies the maximum water uptake y_{\max} for fractions of the oil. Data from the OWM data base are given in Table 4.

Table 4. Maximum water uptake y_{\max} for oil fractions in OWM.

Distillation fraction	Ekofisk Exxon	TROLL	Automotive Gasoline	Arabian Heavy
150+	0.91	0.75	-	0.78
200+	0.88	0.75	-	0.74
250+	0.72	0.75	-	0.55

The value for Arabian Heavy for all fractions topped above 250 °C (250+) is 0.55 (see also Daling,1990). The OWM data base shows a $y_{\max} = 0.78$ for the fraction 150+ which is more in line with ADIOS-2. However, OWM-model simulations give on average that $y_{\max} \sim 0.55$ in line with the 250+ data and this was used in further tests with SIMPAR-O (in SIMPAR and ADIOS y_{\max} does not vary with oil fraction). In OWM for Ekofisk y_{\max} (250+) = 0.72 and y_{\max} (150+) = 0.91, the latter value again in agreement with ADIOS-2. OWM-model simulations give on average that $y_{\max} \sim 0.8$ in line with the 200+ data and this was used in further tests with SIMPAR-O. For Troll the data do not vary with oil fraction.

The TBP-curves for OWM and ADIOS-2 for Ekofisk and Arabian Heavy are given in Figures 4.1 and 4.2. These curves are almost identical.

Table 5. Oil parameters in OWM.

Parameter	Ekofisk Exxon	TROLL	Automotive Gasoline	Arabian Heavy
Density in kg m ⁻³	825.6	893	-	888.5
Viscosity of the oil in cSt at 15°C	6.9	27.0	-	37
Maximum ¹ emulsification fraction (-)	0.8	0.75	-	0.55

1) estimated from model simulations, the data base specifies different values for 3 oil fractions (150+, 200+ and 250+).

Table 6. Oil parameters in ADIOS-2.

Parameter	Ekofisk Exxon	TROLL	Automotive Gasoline	Arabian Heavy
Density in kg m ⁻³	825	-	745	898
Viscosity of the oil in cSt at 15°C	11.9	-	3.6	73
Maximum ¹ emulsification fraction (-)	0.9	-	0.0	0.88

1) estimated from model simulations.

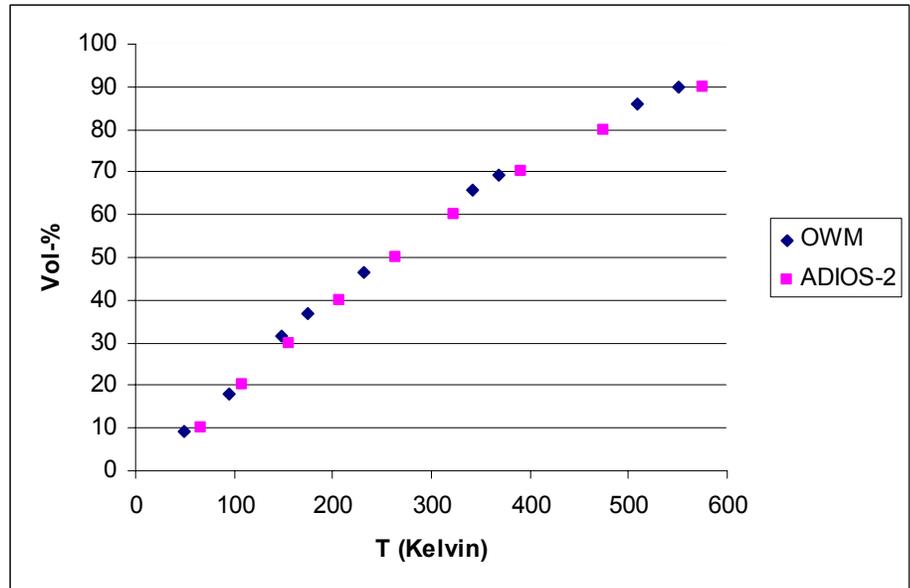


Figure 4.1 Temperature Boiling Point curve for Ekofisk Exxon for OWM and ADIOS-2.

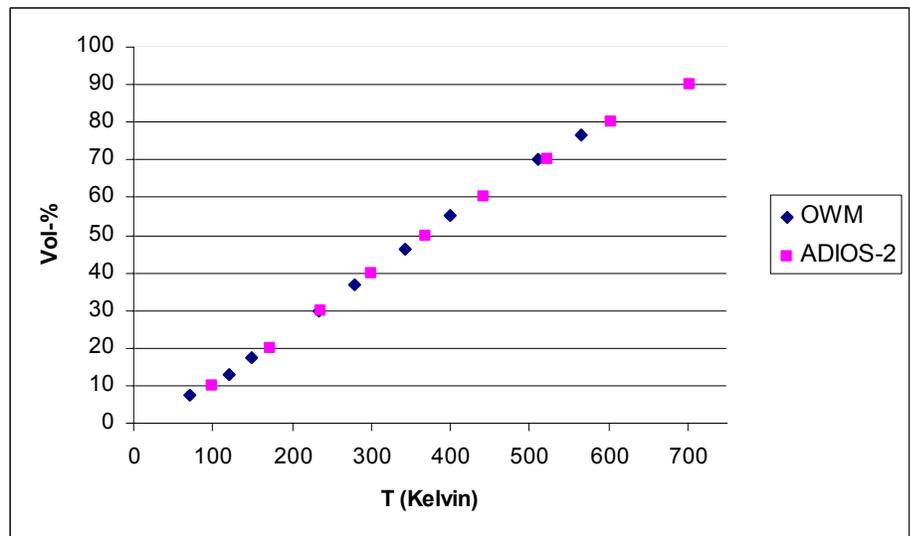


Figure 4.2 Temperature Boiling Point curve for Arabian Heavy for OWM and ADIOS-2.

SIMPAR

In SIMPAR for evaporation a calibrated 9 fraction evaporation model with parameters $A=4.8$ and $B=10.3$ was used with input from TBP-curves. TBP-curves were taken from ADIOS-2 (except for Troll). Since TBP-curves between OWM and ADIOS-2 are almost identical (see Figures 4.1 and 4.2) this does not affect the model results of SIMPAR-O.

Differences for initial viscosity and density between ADIOS-2 and OWM are small but not negligible.

The emulsification rate at zero wind and average molecular weight for SIMPAR are a 'guess' since these parameters were not specified by the models. The guess for emulsification rate is based on the half saturation time for water retrieved from simulations with ADIOS-2 and Troll at zero wind.

Maximum water fraction y_{\max} was either from OWM or from ADIOS-2. See Table 7 for these parameters.

Table 7. Input parameters for SIMPAR simulations for molecular weight and emulsification (other parameters from Table 4 and 5). First value is an estimate from ADIOS-2 model simulations and is used in SIMPAR-A, second one from OWM which is used for SIMPAR-O is also an estimate.

Parameter	Ekofisk Exxon		TROLL		Automotive Gasoline		Arabian Heavy	
	ADIOS	OWM	A	OWM	ADIOS	O	ADIOS	OWM
Average molecular weight in g mol ⁻¹	139	139	-	139	114	-	139	139
Maximum emulsification fraction (-)	0.9	0.8	-	0.75	0	-	0.8	0.55
Emulsification rate at zero wind ¹ in s ⁻¹	1.E-6	3.E-6	-	4.E-6	0	-	1.E-6	2.5E-7

4.2 Test results

4.2.1 Ekofisk Exxon

Table 8.1 Mass balance of Ekofisk after 6 hrs and 24 hrs (fl. = floating, disp. = dispersed and ev. = evaporated).

Ekofisk									
T= 6 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2	T= 24 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
% fl.	61,1	64,3	66,2	66,0	% fl.	48,0	56,4	56,6	58,0
% disp.	2,9	0,7	0,6	1,0	% disp.	9,7	0,9	0,6	1,0
% ev.	36,0	35,0	34,8	33,0	% ev.	42,3	42,7	42,8	41,0

Table 8.2 Oil properties of Ekofisk after 6hrs and 24 hrs (visc. = viscosity, dens. = density and vol. = volume).

T= 6 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2	T= 24 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
visc. (Cst)	7500.0	1711.0	8140.0	950.0	visc. (Cst)	12000.0	2662.0	16025.0	30000.0
dens. (kg m ⁻³)	997.6	989.0	1007.0	976.0	dens. (kg m ⁻³)	1000.0	989.0	1010.0	1000.0
Vol. ratio (-)	2.5	2.7	4.7	1.9	Vol. ratio (-)	2.0	2.4	4.7	4.8
water (%)	79.3	80.0	88.4	70.0	water (%)	79.7	80.0	90.0	90.0

- Evaporation is in good agreement;
- Oil-in-water dispersion in OWM is much higher than in SIMPAR and ADIOS-2. OWM is somewhat closer to SIMPAR-O but the difference between SIMPAR-A and SIMPAR-O is small. *After 24 hrs the mass dispersed in OWM is 9.7%, and after 48hours (not shown in Table 8.1) it is 16.7% and still is increasing.* In SIMPAR and ADIOS the dispersion process almost stopped completely at 24 hrs due to increased viscosity of the oil. Since also in OWM viscosity has increased ($v > 10.000$ Cst after 24 hrs) and thus the dispersion parameter C_0 is very small, we do not understand why the oil dispersion process still continues. This seems incorrect and needs further investigation.
- Viscosity is very different between the models. Also differences between SIMPAR-A and SIMPAR-O are large (detailed analysis shows that the difference follows from parameters y_{max} and initial viscosity).
- Density is in good agreement;
- Water uptake in SIMPAR-A is in good agreement with ADIOS-2 and for SIMPAR-O close to OWM due to a different value for maximum water uptake. This is strongly reflected in the volume-ratio.
- After 6 hrs water uptake in ADIOS is small compared to SIMPAR-A which is an indication that emulsification rate must be smaller than given in Table 7.

Additional tests on differences in oil-in-dispersion

- Oil-in-water-dispersion depends on dispersion parameter C_0 . An additional simulation SIMPAR-O with C_0 from Eq. (3.12) gives 2.2 % dispersed oil after 24 hrs, closer to OWM but still a factor 4 smaller than OWM (9.7%).
- Oil-in-water-dispersion depends on viscosity. Viscosity is very different between SIMPAR-O and SIMPAR-A and sensitive to input parameters y_{max} and initial viscosity. However, this hardly affects oil-in-water dispersion. This is probably due to a fast emulsification of Ekofisk in SIMPAR. In SIMPAR (both -O and -A) after 1 hr the water-% is 70%. The water-% after 1 hr in OWM is 43% and in ADIOS-2 this is 30%.

4.2.2 Troll Crude Oil

Table 9.1 Mass balance for Troll after 6 hrs and 24 hrs (fl. = floating, disp. = dispersed and ev. = evaporated).

T= 6 hrs				T= 24 hrs					
	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2		OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
% fl.	83.4	85.2			% fl.	68.2	79.5		
% disp.	2.4	0.9			% disp.	10.9	1.0		
% ev.	14.2	13.9			% ev.	20.9	19.5		

Table 9.2 Oil properties for Troll after 6 hrs and 24 hrs (visc. = viscosity, dens. = density and vol. = volume).

T= 6 hrs				T= 24 hrs					
	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2		OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
visc. (Cst)	2700	1582.0			visc. (Cst)	5500	2596.0		
dens. (kg m ⁻³)	995.6	992.8			dens. (kg m ⁻³)	998	995.7		
Vol. ratio (-)	2.9	2.8			Vol. ratio (-)	2.4	2.4		
water (%)	74.4	73.0			water (%)	75	75.0		

Discussion:

- Evaporation is in good agreement;
- Oil-in-water dispersion in OWM is much higher than in SIMPAR (a factor 10 after 24 hrs). Similar to Ekofisk we note that after 24 hrs the mass dispersed in OWM is 10.9%, and after 48hours (not shown in Table 9.1) it is 19.9% and still is increasing.
- Water fraction is in good agreement between SIMPAR and OWM and with the North Sea field Trial experiment by Daling (1997). Half saturation of the emulsion for water is 1h5m in SIMPAR and 1h20m in OWM
- Viscosity is higher in OWM than in SIMPAR. From the field trials by Daling it is difficult to decide which model is best since the oil spill used there where much smaller and wind was somewhat larger and varying. Neglecting these factors OWM is closer to the 'Charlie field Trial' (Daling, 1997).
- Density is slightly higher in OWM than in SIMPAR.
- The volume-ratio is somewhat higher in SIMPAR.

4.2.3 Automotive Gasoline Exxon

Table 10.1 Mass balance for gasoline after 2hrs and 3hrs.

Gasoline									
T= 2 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2	T= 3 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
% fl.			16.0	33.0	% fl.			6.0	14.0
% disp.			0.0	1.0	% disp.			0.0	1.0
% ev.			84.0	66.0	% ev.			94.0	84.0

Table 10.2 Oil properties for gasoline after 2hrs and 3hrs.

T= 2 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2	T= 3 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
visc. (Cst)			182.0	25.0	visc. (Cst)			372.0	60.0
dens. (kg m ⁻³)			745.0	860.0	dens. (kg m ⁻³)			745.0	876.0
Vol. ratio (-)			0.16	0.29	Vol. ratio (-)			0.06	0.12
water (%)			0.00	0.00	water (%)			0.00	0.00

- Evaporation is somewhat faster in SIMPAR than ADIOS2 (since gasoline evaporates very fast, the difference can be due to the numerical implementation)
- Dispersion is zero and very small in ADIOS-2;
- Viscosity is substantially higher in SIMPAR than ADIOS-2. In ADIOS2 viscosity reaches an asymptotic value of 60 cST after 10 hours. The origin of this error has been discussed in section 3.6.2;
- Density is constant but it rises to a value of 878 in ADIOS-2;
- The final water is zero and this agrees with ADIOS-2.

4.2.4 Arabian heavy

Table 11.1 Mass balance for Arabian Heavy after 6 hrs and 24 hrs (fl. = floating, disp. = dispersed and ev. = evaporated).

T= 6 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2	T= 24 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
% fl.	78.8	81.0	82.6	79.9	% fl.	61.2	76.2	79.1	72.9
% disp.	2.3	2.2	0.6	0.1	% disp.	9.5	3.8	0.6	0.1
% ev.	18.9	16.7	16.8	20.0	% ev.	24.3	20.0	20.3	27.0

Table 11.2 Oil properties for Arabian Heavy after 6 hrs and 24 hrs (fl. = floating, disp. = dispersed and ev. = evaporated).

T= 6 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2	T= 24 hrs	OWM	SIMPAR-O	SIMPAR-A	ADIOS-2
visc. (Cst)	1163.0	257.0	3889.0	10000.0	visc. (Cst)	7397.0	658.0	5937.0	30000.0
dens. (kg m ⁻³)	950.0	945.0	998.2	984.0	dens. (kg m ⁻³)	981.6	965.0	1001.7	1012.0
Vol. ratio (-)	0.9	1.3	3.3	2.1	Vol. ratio (-)	1.0	1.5	3.5	4.9
water (%)	15.7	40.0	78.0	66.0	water (%)	41.8	54.0	80.0	87.0

- Evaporation is in good agreement between the models;
- Oil-in-water dispersion is much larger in OWM than in SIMPAR and ADIOS-2. Similar to Ekofisk we note that

after 24 hrs the mass dispersed in OWM is 9.5%, and after 48hours (not shown in Table 11.1) it is 16.1% and still is increasing.

- There is a large difference in oil-in-water dispersion between SIMPAR-O and SIMPAR-A. SIMPAR-O is closer to OWM but still much smaller.
- Viscosity in ADIOS-2 is much larger ($\nu \sim 3.0E+5$ Cst) than in SIMPAR and OWM;
- Density is different in the models;
- Water uptake in OWM goes much slower than in SIMPAR-A and ADIOS-2. Emulsification in SIMPAR-O is closer to OWM due to different input for emulsification but still faster. This is reflected in the volume-ratio's.
- In SIMPAR-A the water uptake is somewhat faster than in ADIOS-2.

Additional tests on differences in oil-in-water-dispersion

- Oil-in-water-dispersion depends on dispersion parameter C_0 . Contrary to the tests with Ekofisk, an additional simulation SIMPAR-O with C_0 from Eq. (3.12) gives somewhat lower%-dispersion. This is due to a higher initial viscosity of Arabian Heavy, which leads to a lower C_0 -value in SIMPAR-O than in SIMPAR-A.
- Oil-in-water-dispersion depends on viscosity. Viscosity is very different between SIMPAR-O and SIMPAR-A and sensitive to input parameters y_{\max} and initial viscosity. Contrary to the tests with Ekofisk, this affects oil-in-water dispersion with SIMPAR-O since the emulsification now is slower than for Ekofisk. In SIMPAR-O after 1 hr the water-% is 11% whereas in SIMPAR-A this is 51%. In OWM after 1 hr the water-% is 4%.

4.3 Conclusions with respect to test results

- Results with respect to mass budget and oil parameters like viscosity, density and water-fraction are very sensitive to the input parameters used in the models, see e.g. some of the differences between SIMPAR-A and SIMPAR-O simulations.
- The models are in good agreement for *evaporation*;
- *Oil-in-water dispersion* is very small in ADIOS-2 and SIMPAR-A and much larger in OWM (*often a factor 10 larger after 24 hrs*). Simulations with SIMPAR-O are closer to OWM but still a factor 4 smaller. Our analysis showed this is partially due to:
 - Viscosity is different;
 - C_0 is different (Eq. 3.12);
 - Emulsification is differently formulated and only OWM uses several fractions.

However, there may be still be other factors that cause the large difference between OWM and the other 2 models. In particular, we note that after 24 hrs the mass dispersed in OWM is still increasing and this seems to be incorrect given the large viscosities (and small values of C_0) of the oils after 24 hrs.

- *Viscosity* is different between the models. Differences in viscosity affect the oil-in-water-dispersion (eg for Arabian

Heavy) but not always. In case the emulsification of the oil goes very fast (Ekofisk) the viscosity differences are not reflected in the %-of oil dispersed.

- *Water uptake* is generally in good agreement except for Arabian Heavy. In that case the results for OWM differ much from ADIOS-2 and SIMPAR-A due to different input parameters for emulsification;
- Differences in *volume ratio* can be large since the volume ratio depends strongly on water fraction when the water fraction approaches 1.0. It also depends on evaporation rate and oil density. Large differences were found for Arabian Heavy and Ekofisk Exxon.
- The OWM and ADIOS-2 models show 3 important differences:
 - a) The oil-in-water dispersion for OWM is large compared to ADIOS and SIMPAR and keeps growing after 24 hrs. This seems to be incorrect in OWM.
 - b) Only the emulsification process in OWM depends on the oil fraction and this is physically more detailed. The effects on the results are not very large except for the volume ratio of the oil. Since this latter parameter has important practical consequences for the oil to be cleaned up, the OWM model might be preferable.
 - c) The viscosity is very different in the models but since we have very limited experimental information on this parameter we cannot decide what model is correct.
- We observed that there is a strong coupling between emulsification and oil-in-water dispersion in case there is moderate or strong wind (> 6 m/s). Therefore, experiments to calibrate the oil-in-water dispersion must not be solely based on an analysis of the dispersion process but must incorporate an analysis of the emulsification process for moderate and/or strong wind conditions as well.

5 Conclusions and recommendations

Considering documentation:

- Technical documentation of the oil-weathering models ADIOS-2 and DREAM/OWM is not very accurate. Especially, correlations between TBP-curves and vapour pressures (and molecular weights) for oil fractions cannot be found.
- For GNOME a technical document does not exist.
- For SIMPAR a first version of a technical document exists but it has not been accepted yet in SIMONA since the module is a beta-release.

Considering test results:

- Results are very sensitive to the input parameters used in the models (e.g. see differences between SIMPAR-O and SIMPAR-A results). Thus the existence of a reliable oil databases is a prerequisite for use of these oil-weathering modules.
- OWM seems to be most reliable since its oil database is fully based on lab experiments. For ADIOS-2 this is not known and for SIMPAR there is no oil data base, whereas for GNOME it is limited to 6 oils;
- However, the OWM model gives much larger oil-in-water dispersion than the other two models, nearly a factor 10 after 1 day of simulation. There is no good explanation for this difference and this needs further investigation.

Recommendations:

1. With respect to oil weathering modules:

- In general, more research is needed during real operational conditions during oil spill incidents. Especially, for strong wind conditions the models need to be validated.
- The present testing of the oil-weathering models should be extended with more oil types. Also the effect of oil fractions on emulsification must be investigated in more detail.
- Discussion with SINTEF is required, especially concerning the oil-in-water dispersion results obtained with OWM and DREAM.
- Discussion with NOAA is required concerning the quality and openness of the oil data base of ADIOS-2.

2. With respect to coupling to particle tracking module of SIMONA:

It would be interesting to couple the SIMPAR algorithm of particle tracking to the DREAM (or OWM) oil weathering module and its data base. SIMPAR has the following advantages:

-
- a) SIMPAR has drying and flooding.
 - b) Particle tracks depend on water depth whereas this is neglected in DREAM. In shallow areas this leads to different results (see also de Jong, 2004).
 - c) SIMPAR was validated successfully by Directorate Zeeland with tracer experiments and it is therefore well accepted within Rijkswaterstaat.
 - d) End of 2005 SIMPAR will have a backtracking function.
 - e) In a beta-release of SIMPAR there is 3-dimensional transport including an accurate numerical scheme for vertical diffusion. For simulations of dissolved matter in stratified waters like the Dutch coastal zone this is an important issue.

A.1 Theoretical background of evaporation

Some fundamental properties of the evaporation process are the dimensionless evaporative exposure θ and the dimensionless Henry constant H (Stiver and MacKay, 1984; Fingas, 1995). The mass balance equation for evaporation can for one fraction ($f_{\text{evap}} = 1$) be written in various ways:

$$\frac{dm_s}{dt} = -M_w \frac{dN}{dt} = -M_w \left[\frac{KAP_{vp}}{RT} \right] = -M_w \left[\frac{P_{vp}}{RT} \right] [KA] = -M_w \left[\frac{H}{v} \right] \left[V_0 \frac{d\theta}{dt} \right] \quad (\text{A.1})$$

with:

- m_s = mass of the liquid (kg)
- dN / dt = molar flux (mol s^{-1});
- V_0 = initial volume of the oil spilled (m^3);
- v = liquids molar volume ($\text{m}^3 \text{mol}^{-1}$);
- θ = evaporative exposure (-);
- H = Henry constant (-);
- K = mass transfer coefficient (m s^{-1});
- A = surface (m^2);
- P_{vp} = Vapour pressure of the gas (Pa);
- M_w = molecular weight of the gas (kg mol^{-1})

MacKay and Matsugu (1973) have derived a well-known formula for the mass transfer coefficient K as given section 3.4.2.

The evaporative exposure is given by:

$$\theta = \frac{KA t}{V_0} \quad (\text{A.2})$$

The evaporative exposure θ can be seen as the volume of the exposed vapor volume at time t ($KA t$) versus the volume of the initial spill.

The Henry constant is given by:

$$H = \frac{P_{vp} v}{RT} \quad (\text{A.3})$$

The Henry constant is the ratio of the equilibrium concentration of the substance in the vapor phase (P/RT assuming an ideal gas) versus that in the liquid phase. This follows from the equilibrium concentration C_0 (kg m^{-3}) of the gas:

$$C_0 = \frac{M_w P_{vp}}{RT} \quad (\text{A.4})$$

and of the liquid phase ρ (kg m^{-3}):

$$\rho = \frac{M_w}{v} \quad (\text{A.5})$$

The ratio of C_0 and ρ gives:

$$H = \frac{C_0}{\rho} \quad (\text{A.6})$$

The Henry constant relates the vapor pressure of a dilute dissolved substance to its mole fraction x (or concentration) in the solvent according to Henry's Law:

$$P_{vp} = Hx \quad (\text{A.7})$$

For a large Henry constant, the vapor pressure is large and evaporation will be fast. For mixtures, the Henry constant will be dependent on the mole fraction x or likewise the fraction evaporated f_{evap} .

In case H is independent of t , the evaporation is complete when:

$$\theta = \frac{1}{H} \quad (\text{A.8})$$

Since the total mass of the oil spill M_{tot} can also be written as:

$$M_{\text{tot}} = \frac{M_w V_0}{\nu} \quad (\text{A.9})$$

Also a liquid-phase resistance can influence the evaporation process (Stiver and MacKay, 1984, Fingas 1995) and often this resistance is added to the Henry constant. This approach has not been further investigated yet.

From equation's (A.1) and (A.6) it follows that the mass balance equation can also be written as:

$$\frac{dm_s}{dt} = -[KA]C_0 = -Q_{\text{ev}}C_0 \quad (\text{A.10})$$

with: Q_{ev} = rate of evaporation (kg s^{-1}).

Formulae (A.10) is by Reinhart and Rose (1982) and simply follows from thermodynamics for surface evaporation.

A.2 Multi-component evaporation theory

First of all the mass-balance equation (A.10) is written in a sum of components. Hereto, we use for the molar fraction x_i of the n components in the liquids (based on Henry's law, eq.A.7):

$$P_{vp} = \sum_{i=1}^n p_i x_i \quad (\text{A.11})$$

and for the molecular weight of the gas M_w^g that:

$$M_w^g = \sum_{i=1}^n M_{wi} y_i \quad (\text{A.12})$$

where y_i is the molar fraction of the component in the gas and M_i the (average) molecular weight of the component.

Together with Raoult's law:

$$y_i P_{vp} = x_i p_i \quad (\text{A.13})$$

the mass balance equation (A.10) is written as:

$$\frac{dm_s}{dt} = -Q_{ev} C_0 = -Q_{ev} \sum_{i=1}^n \frac{x_i p_i M_i}{RT} \quad (\text{A.14})$$

In multi-component evaporation oil models it does not suffice the solve only a mass balance equation. In that case also n mol-balance equations must be solved for all n fractions in the liquid (Reinhart and Rose, 1982; Jones 1997). The mol-balance equation for one component is:

$$\frac{d}{dt} \left(x_i \frac{m_s}{M_w^l} \right) = -Q_{ev} \frac{y_i}{M_w^g} \quad (\text{A.15})$$

with the molecular weight of the liquid:

$$M_w^l = \sum_{i=1}^n M_{wi} x_i \quad (\text{A.16})$$

Equation (A.15) can be written in a more convenient form using (A.13) and the variable:

$$x_i^n = x_i \frac{m_s}{M_w^l} \quad (\text{A.17})$$

Then the mole balance equation reads:

$$\frac{d}{dt} x_i^m = - \left(\frac{Q_{ev}}{m_s} \frac{M_w^l}{M_w^g} \frac{p_i}{P_{vp}} \right) x_i^m \quad (\text{A.18})$$

The mole-fraction of a component with high partial pressure and high mol-fraction in the liquid will decrease very fast in time.

In SIMPAR small time-steps are used (smaller than in other oil-processes, e.g. we use time-splitting) and we first solve the mass balance equation (A.10) with a simple Euler method (A.10) and make up the molecular weight. Then (A.18) is solved by:

$$x_i^m(t + \Delta t) = x_i^m(t) \exp(-ct)$$

$$c = \frac{Q_{ev}}{m_s} \frac{M_w^l}{M_w^g} \frac{p_i}{P_{vp}} \quad (\text{A.19})$$

The set of equations (A.11)-(A.16) is also solved in DREAM and OWM (SINTEF, 2004; Oistein, 2004). The numerical solution method of OWM is not given.

It is not clear what set of equation's is used in ADIOS or GNOME. It is very likely that ADIOS follows the approach by Jones (1997) of NOAA. The differential equations in that model are analogous to those presented here.

The differences in the models are most probably in the expressions used for the partial vapor pressures p_i and the molecular weights M_i .

A.3 Determination of partial pressures from Temperature Boiling Points (TBP) and relations for molecular weights

A well known saying is '*the devil is in the detail*' and for evaporation models these details are :

- Determination of partial pressures of the fractions;
- Determination of molecular weights of the fractions.

In OWM, DREAM and ADIOS these relations are not documented. In SIMPAR the relations are given in this section.

OWM and ADIOS

Personal communication with SINTEF (Oistein, 2004) gives the expressions for hydrocarbons and these are simple semi-empirical correlations for vapor pressures and molecular weights. Oistein uses a approach for hydrocarbons based on the Clausius-Clapeyron equation which is very similar to relations for hydrocarbons given by Jones (1997) and Fingas (1995). Examples are given in the next section.

For the molar weights of the hydrocarbon fractions Oistein (2004) uses an empirical correlation.

Jones (NOAA, 1997) uses a relation between molar weights and boiling points for hydrocarbons.

We have no further information for other oils (crude oils etc.) for OWM, DREAM and ADIOS. A useful Table of vapour pressures is given in the DREAM Technical Documentation (2001, Table 2 on p.23) but it is not clear how this Table is used in DREAM.

SIMPAR

For partial pressures we use a correlation between the TBP-curve and the Henry constant suggested by Stiver and MacKay (1984, see also section 3.4.4):

$$\ln H = \left(A - B \frac{T_B}{T} \right) \quad (\text{A.20})$$

with:

A, B = constants;
 T_B = temperature boiling point of the oil fraction (°K);
T = oil temperature (°K)

We assume that this relation is valid for partial pressures of pure liquid components and use

$$p_i = \frac{RT h_i}{v_i} = \frac{RT M_i}{\rho} \exp \left[A - B \frac{T_{B,i}}{T} \right] \quad (\text{A.21})$$

It turns out in practice that this works good. For A and B one can use the suggested values by Stiver and MacKay for crude oils (A=6.3 and B=10.3). Re-calibration of A and B against OWM data give for evaporation of Ekofisk and Troll the values A=4.8 and B=10.3.

In SIMPAR it is simply neglected that the molar fractions have different weights. There is one average molecular weight for all fractions.

A.4 Estimation of the vapour pressure from Clausius Clapeyron equation

Vapor pressures are often not given in literature. ADIOS and OWM/DREAM report oil distillation temperatures for oil fractions evaporated and not vapor pressures. To estimate the average vapor pressure one may first try to the average Clausius-Clapeyron equation (American Society of Testing and Materials, Fingas 1995):

$$\frac{d \ln P}{dT} = \frac{Q}{RT^2} \quad (\text{A.22})$$

leading to:

$$^{10}\log P(\text{mmHg}) = 2.88 + C \left(\frac{T_{oil} - T_s}{273.16 + T_{oil}} \right) \quad (\text{A.23})$$

$$C = \frac{QM_w}{4.57}$$

with:

- P = vapor pressure in mmHg (1 atm = 760 mm Hg);
- T_{oil} = liquid oil temperature (°C);
- T_s = average distillation temperature of the oil fraction (°C);
- C = a constant;
- Q = heat of evaporation (cal⁻¹ g).

For hydrocarbons C=5.0±0.2 (Fingas, 1995) and (A.9) gives good results. For heavy fuels this is not so: C must be smaller and C also changes continuously during the evaporation process. We have found no references what values can be used then (e.g. note that with C=5.0 the equation gives indefinite results when T_s is large).

Oistein (2004) uses a similar relation:

$$^{10}\log P(\text{Pa}) = C_1 + C_2 \left(\frac{T_B - B_1}{T_B + B_2} \right) \left(\frac{T + B_2}{B_2 - T} \right) \quad (\text{A.24})$$

with C₁, C₂, B₁ and B₂ fitting parameters and T_B the boiling points fo the fraction.

For 'gasoline' we have for T_s=131 deg.C that P = 7.34 mmHg or 9.67 E-3 atm. This is consistent with the following equation that relates P to the number of carbon atoms (Fingas, 1995):

$$P(\text{mmHg}) = \exp(10.94 - 1.06N) \quad (\text{A.23})$$

with: N = number of Carbon atoms;

This is consistent with 1.19 for N=8.5 which is a reasonable estimate for gasoline. One must notice that in this equation the vapour pressure is a steep function of the carbon number N.

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