# Predicting the weathering of fuel and oil spills: A diffusion-limited evaporation model

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## HIGHLIGHTS

- Incorporates molecular diffusion and predicts the oil composition gradient.
- Highly accurate on all types of fluid tested, including oils, fuels and synthetic mixtures.
- Applicable in different region as it takes into account the environmental conditions.
- Model inputs can be limited to oil composition or distillation data.
- A multitude of oil properties are predicted, in addition to the weathered oil composition.

## ARTICLE INFO

## ABSTRACT

The majority of the evaporation models currently available in the literature for the prediction of oil spill weathering do not take into account diffusion-limited mass transport and the formation of a concentration gradient in the oil phase. The altered surface concentration of the spill caused by diffusion-limited transport leads to a slower evaporation rate compared to the predictions of diffusion-agnostic evaporation models. The model presented in this study incorporates a diffusive layer in the oil phase and predicts the diffusion-limited evaporation rate. The information required is the composition of the fluid from gas chromatography or alternatively the distillation data. If the density or a single viscosity measurement is available the accuracy of the predictions is higher. Environmental conditions such as water temperature, air pressure and wind velocity are taken into account. The model was tested with synthetic mixtures, petroleum fuels and crude oils with initial viscosities ranging from 2 to 13,000 cSt. The tested temperatures varied from 0 °C to 23.4 °C and wind velocities from 0.3 to 3.8 m/s. The average absolute deviation (AAD) of the diffusion-limited model ranged between 1.62% and 24.87%. In comparison, the AAD of a diffusion-agnostic model ranged between 2.34% and 136.62% against the same tested fluids.

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## 1. Introduction

Hydrocarbon mixtures such as crude oils and petroleum products are complex fluids containing hundreds to thousands of individual compounds (Neumann et al., 1981). Their composition can vary significantly, and they can contain high amounts of toxic and carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs) that are dangerous to humans and other organisms once they are released in the environment (National Research Council, 2003; Echols et al., 2015). Weathering is a general descriptive term for several processes occurring in the environment that alter the composition of crude oils and petroleum products both physically and chemically (Fingas, 2010). These processes include evaporation, photooxidation, and biodegradation, as well as dispersion, dissolution and emulsification if the spill has occurred on a water surface. Of the aforementioned processes evaporation is the most important process in the case of crude oils and petroleum fuels (Fingas, 2010), since it is responsible for the largest loss of mass, including toxic aromatic components during the initial stages of weathering. In order to estimate the exposure of biota to these chemicals we need to know the fate of the oil and its individual components once they are accidentally released in the environment (Engraff et al., 2011). Direct measurement of the changes occurring in an oil or fuel spill in the marine environment can be impractical due to the time required for the mobilization of analytical equipment and specialised personnel to the location of

the spill, often under unfavourable weather conditions. In this case modelling is an effective tool that we can use in our effort to assess the environmental risk and prepare a remediation strategy.

Modelling the evaporation of a complex mixture such as a crude oil is a challenging task, and requires an understanding of the controlling mechanism(s) of the process. Past efforts to model evaporation can be divided into two main categories: theoretical models, and empirical correlations. Most of the theoretical models developed in the past have borrowed mathematical formulations from the existing theory of water evaporation by adapting the concept of a gas boundary layer between the liquid and gas phase (Fingas, 2010). Due to the complex nature of crude oils and the continuous alteration of their properties as evaporation progresses, modellers need to make some assumptions and simplifications in order to arrive at an implementable model that preferably requires a small number of usually known properties. Inevitably, simplifications have the potential to introduce errors that can be revealed when the predictions are compared with experimental results. One oversimplification is that crude oils can be treated as one pseudo-component having a single evaporation rate (Blokker, 1964; Mackay and Matsugu, 1973; Stiver and Mackay, 1984; Brighton, 1985). Other researchers followed a more detailed approach by assigning multiple evaporation rates to a number of pseudo-components, but made the assumption that a boundary layer in the gas phase is the sole controlling mechanism of the evaporation process and that the liquid phase stays homogenous over the evaporation period (Leinonen and Mackay, 1975; Yang and Wang, 1977; Payne et al., 1987). One exception to this assumption is the modification made to the Mackay and Matsugu (1973) model by Brown and Nicholson (1991) where they introduced a simple correction to the mass-transfer constant for the "thick skin" that develops on the oil surface as evaporation progresses. The most commonly used evaporation model today is that of Mackay and Matsugu (1973), including variants implemented by several researchers (Leinonen and Mackay, 1975; Yang and Wang, 1977), including those of Stiver and Mackay (1984) who suggested that the gas phase boundary layer is the sole controlling mechanism. One process that has not been implemented by the previously mentioned models is molecular diffusion in the liquid phase (the inner body of the oil) and its effect on the evaporation rate of an oil spill. As we shall demonstrate in this study with experimental and simulation results, the diffusion transfer rate can limit the evaporation rate, depending on the oil composition, the physical properties of the fluid, and the environmental conditions.

More recently, Arey et al. (2007) developed a two-layer model that takes into account the diffusion-limited transfer in both the oil phase and the gas phase boundary layer. The model assigns discrete vapour pressures to a number of pseudo-components. One limitation of this model is that the oil layer is assumed to be homogenous and there is no concentration gradient developed due to diffusion resistance. A more sophisticated model was developed by Lemkau (2012) where diffusion-limited transfer is taken into account in both the gas boundary layer and the oil layer that is described by a number of sub-layers. As evaporation from the top layer progresses, the concentration drop of a pseudo-component is propagated to the underlying layers according to Fick's second law, creating a layer-based concentration gradient. Both of the aforementioned models have only been tested by simulating already weathered oils of past oil spills, and they have not been verified with experiments in a controlled environment where the progression of evaporation over time can be recorded.

Some researchers followed a different approach by rejecting the gas phase boundary layer controlling mechanism and developed empirical equations based on the observation that all naturally occurring hydrocarbon mixtures such as crude oils and their petroleum products follow either a logarithmic or an exponential type evaporation curve (Butler, 1976; Fingas, 1998). Although such empirical correlations can provide an approximate prediction since the empirical factors include the contribution from other controlling mechanisms, they are applicable only to specific types of oil and they lack the accuracy and flexibility of a detailed model sensitive to different environmental conditions.

The aim of this study was to develop an evaporation model that accounts for the limitations set by the rate of diffusion in the body of the oil. The model would have to treat the oil body as a diffusive layer where each (pseudo) component can develop a concentration gradient and the overall transfer rate is a function of both the evaporation and diffusion rates. Such a model would be capable of predicting the evaporation rate of different types of oil or fuel, over a wide range of environmental conditions. Furthermore, evaporation experiments were to be conducted on different types of fuels and oils and under different conditions, in order to assess the performance of the developed model and possibly identify the types of fluids that diffusion in the liquid phase is a limiting factor on the evaporation rate.

## 2. Materials and experimental methodology

### 2.1. Fuels and synthetic mixtures

Two synthetic mixtures, three fuels and two crude oils were used for the validation of the developed model.

The fuels used were a Special Antarctic Blend (SAB) diesel, a Marine Gas Oil (MGO) and an Intermediate Fuel Oil 180 (IFO-180). The SAB is a very light diesel fuel and mainly consists of $C_9$–$C_{16}$ hydrocarbons (Snape et al., 2006). The MGO is a light marine fuel also known as Marine Diesel Oil (MDO) that conforms to the ISO 8217 Grade DMA specifications. Compared with the SAB, it has a broader $C_7$–$C_{26}$ hydrocarbon distribution (Wang et al., 2003; Snape et al., 2006; ETC, 2015). Lastly, IFO-180 is a heavy and viscous marine fuel used by large marine vessels. It is a blend, generally containing less than 10% distillate with the remaining 90% being a heavy residual fuel (Bunker C) and with a boiling range extending well over 700 °C (ETC, 2015). All three fuels are used in the Australian Antarctic Territory for station and marine operations.

Pure tert-butylbenzene and n-dodecane of analytical grade were used to prepare two synthetic mixtures. The first synthetic fluid (Fluid A) was a binary mixture of 5% by mass tert-butylbenzene dissolved in 95% n-dodecane. The second synthetic fluid (Fluid B) consists of 4% by mass tert-butylbenzene and 13% n-dodecane dissolved in 83% artificially weathered IFO-180 fuel. The artificially weathered IFO-180 has lost all of its volatile components and it was prepared according to the procedure described in the supplementary information. It was used in synthetic fluid B in order to increase the overall viscosity of the fluid.

Additionally, two crude oils were included in the validation experiments since they exhibit different evaporation behaviour and produce a "logarithmic" shape evaporation curve. These are the Kuwait crude oil (ETC, 2015) and the Alberta ASMB reference 4 crude oil (ETC, 2015). Both oils have a wide hydrocarbon distribution with large amounts of volatile components and a significant amount of non-volatile heavy residue. The ASMB evaporation experiment was conducted by Fingas (1998) and the experimental results are originating from this publication. The physical properties and distillation data for this crude oil were retrieved from the Environment Canada oil properties database (ETC, 2015). All the remaining experimental results are based on the experimental work conducted during this study.