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A model for the weathering of Colombian crude oils in the Colombian Caribbean Sea

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ABSTRACT

A model that describes the weathering of crude in an oil spill caused by interaction with the atmosphere and the ocean was developed. This model was adapted to the Colombian crudes Cusiana (°API 43.2) and Vasconia (°API 20.7). To calibrate the model, evaporation and emulsification experiments were carried out at conditions similar to those of an oil spill in the Colombian Caribbean Sea. The dependence of evaporation with wind velocity, not predicted by the state-of-the-art models, was captured by a correlation for the mass transfer coefficient calculated from the experimental data. Emulsification rate, maximum water content and required evaporation to form an emulsion were determined and their values explained considering the effect of wax precipitation for Cusiana crude oil. When compared to well-established weathering software, such as ADIOS, the proposed model predicts the weathering of Colombian oils in a way that better agrees with the experiments conducted in the laboratory.

1. Introduction

Given the environmental and economical hazards associated to offshore hydrocarbon extraction and crude oil transportation, it is of paramount importance to understand the behavior of crude oil after the unfortunate event of an oil spill. The first step towards this understanding involves simulations that predict the relative motion of the oil slick. Knowledge of the path of the spill, obtained regularly in the oil spill community with a lagrangian approach, allows prediction of possible affected areas and helps in the design of proper mitigation strategies and alarm protocols. As crude oil is not an inert substance, but it changes properties once exposed to the atmosphere, in addition to the complex metocean models required to predict the final fate of an oil spill, it is mandatory to model oil weathering, or the physicochemical changes that the oil slick undergoes because of its interactions with atmosphere and ocean. A definitive representation of an oil spill is obtained by the combination of the spill-tracking and weathering models.

Weathering modeling is important in short- (days to weeks) and long-time scales (months to years). In the short-time scales the change in physicochemical properties, particularly an increase in viscosity, has a great influence in the feasibility of various oil-spill countermeasure techniques such as chemical treatment (dispersants), burning or mechanical recovery (Daling et al., 2003). Oil-weathering modeling also estimates, from the very first moment to even years after the spill, the amount of oil remaining on surface and the partition of unaccounted oil between air and water column.

As described in several reviews of the state of the art (ASCE, 1996; Fingas, 1995; Reed et al., 1999; Sebastião and Guedes Soares, 1995; Spaulding, 1988), a crude oil weathering model integrates different submodels that represent the predominant phenomena that take place after an oil spill: evaporation, emulsification, dispersion and spreading. In addition, when having low oil concentration, fugacity-based models estimate pollutant concentration in the surroundings of the oil spill (water, air, sediments, biota, among others) (Afenyo et al., 2016; Mackay, 2001; Nazir et al., 2008). Regardless of the approach, each submodel has a different number of empirical constants that depend on oil and weather conditions.

Although it is a common practice for oil-spill models to predict trajectories with weathering models that do not consider the particularities of the oil (Berry et al., 2012; Chao et al., 2001; Deqi et al., 2010; Guo and Wang, 2009; Korotenko et al., 2004; Lončar et al., 2012; Mariano et al., 2011; Nagheeby and Kolahdoozan, 2010; Nazir et al., 2008; Wang et al., 2005), several authors (Daling et al., 1997, 1990; Stiver and Mackay, 1984) have determined that the empirical character of most weathering submodels demands calibration of parameters to

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Table 1
Relevant physicochemical properties of the Colombian crude oils selected for this study.

Property	Value	
	Cusiana	Vasconia
°API	43.2	20.3
Viscosity (cP at shear rate 100 s^{-1}, 25 °C)	1.96	64
Wax content (wt%)	10.0	4.5
Asphaltene content (wt%)	0.3	6.4
Pour point (°C), ASTM D97-12 (ASTM International, 2012b)	0	6
Distillation, ASTM D86-12 (ASTM International, 2012a)		
5 vol% recovered (°C)	22.6	93.5
10 vol% recovered (°C)	36.6	136.9
20 vol% recovered (°C)	89.1	217.6
40 vol% recovered (°C)	168.4	320.5
60 vol% recovered (°C)	269.6	422.8
80 vol% recovered (°C)	372.4	552.1

the oil and the environmental conditions of a particular oil spill. This calibration normally takes place in benchscale experiments. This paper corrects this deficiency by developing, for the first time in the refereed literature, a weathering model that particularly targets two Colombian oils at metocean conditions relevant to the Caribbean Sea.

2. Materials and methods

2.1. Crude oils

Colombian crude oils Cusiana and Vasconia were selected for developing the model because of their importance in the exports of the Colombian oil company and the significant difference in physicochemical properties which challenge the predictive ability of the weathering model. Table 1 shows the main physicochemical characteristics of both crudes. According to the API gravities, Cusiana represents a light crude oil while Vasconia is closer to the range of heavy crude oils (8–20 °API). This is also evident in the distillation data in Table 1. Both crudes also exhibit a significant difference in the content of waxes and asphaltenes, compounds that have a strong effect on the formation of water-in-oil emulsions, and in the pour point.

Although the difference in pour point when both crudes are fresh is of only 6 °C, this value increases as both crudes undergo evaporation. Fig. 1 presents the pour point curve, i.e. the variation of the pour point with evaporated fraction. To construct the plot the pour point test was carried out with crude oil samples with different evaporated fraction obtained with the wind tunnel explained below in Section 2.2. According to Fig. 1 once Cusiana reaches 35% of evaporated fraction the pour point is about 25 °C, which is in the range of temperatures registered for the Colombian Caribbean Sea. Contrary, the pour point for Vasconia does not exceed 21 °C.

2.2. Wind tunnel: evaporation experiments

A wind tunnel was adapted to evaluate the evaporation rate of Colombian crude oils. Fig. 2 shows a schematic description of the experimental setup. The total length of the tunnel is 3.0 m with a circular cross section of 30 cm of diameter. Two blockages were included at the interior of the tunnel to mitigate the effect of wind on the scale measurements. Crude oil was poured into a stainless steel tray with a $40 \times 20\ cm^2$ rectangular cross section and a height of 1.5 cm. An OHAUS scale measured the weight loss due to evaporation with 1 g of sensibility and 5 s of temporal resolution. An interface connected the scale to a computer allowing an online evaluation of the evaporation rate. To isolate the evaporation from the effect of temperature, given that the experimental setup does not control temperature, only the experiments carried out when temperature varied between 21 and 25 °C were considered. A type "J" thermocouple measured the air temperature that was recorded every 5 s. The wind velocity was measured with a conventional pitot tube coupled to an electronic manometer which displays the wind velocity with a sensibility of 0.01 m/s. Fig. 2 shows the location of the pitot tube and the thermocouple in the wind tunnel with respect to the evaporation tray. The tunnel has a radial blower, coupled with a variable-speed drive that guarantees different wind velocities at the nominal value ± 0.2 m/s.

Experimental profiles of wind velocity, horizontal and vertical (HH′ and FF′ lines, respectively, in Fig. 2) are presented in panels a and b in Fig. 3, respectively, at different rotational speeds of the wind tunnel blower (150, 250 and 400 rpm). In panels a and b in Fig. 3 the horizontal profiles are more uniform than those vertical. In addition, a CFD simulation, explained in detail in Ramírez (2014), suggested that the distance between Blockage 1 and the evaporation tray, 86 cm in Fig. 2, is long enough to guarantee a developed velocity profile above the tray.

Crude oil evaporation models consider the wind velocity measured at a reference height of 10 m over the ocean surface away from the most significant velocity gradients. For this reason the "effective" wind velocity for the 150, 250 and 400 rpm cases were taken as 4.0, 6.5 and 10.5 m/s as they represent regions where the velocity gradients are minimal as represented with the dotted lines in Fig. 3b. The range 4.0 m/s to 10 m/s covers the typical wind velocity values found in the Colombian Caribbean Sea (Ruiz and Bernal, 2009).

To evaluate experimental uncertainties, the standard deviation of two experiments for each wind velocity was evaluated. Therefore a total of 12 wind tunnel experiments (two crude oils, three wind velocities and two replicates for each condition) were conducted.

The variation of density due to evaporation was determined by pycnometer. Changes in viscosity were measured with a rheometer AR 1500EX for low viscosity values (0.5 cP–1000 cP) and a viscometer Haake VT5500 for higher viscosities.

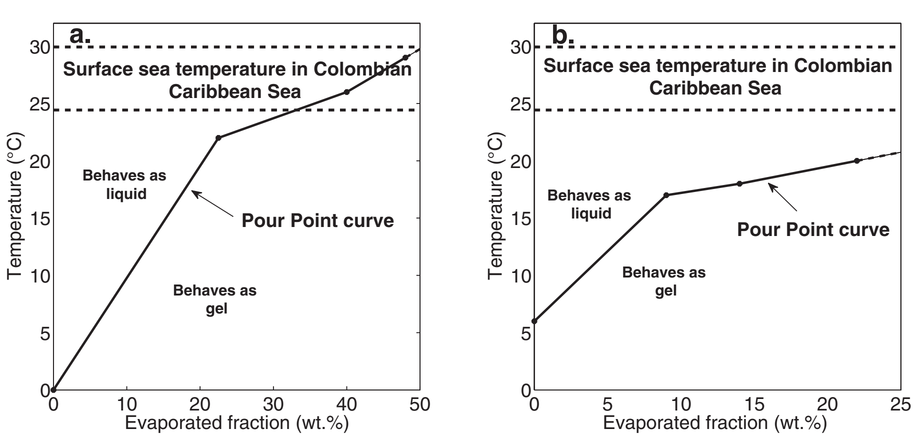

Fig. 1. Pour point variation with evaporated fraction for Colombian crude oils. a. Cusiana (measured in this research). b. Vasconia (taken from reference Environment Canada (2001)). The range of temperatures in the Colombian Caribbean Sea was taken from reference Bernal et al. (2006). Note the differences in the extreme values for the x axis in both plots.