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# **UPGRADING THE COLOMBIAN OIL WEATHERING (COW) MODEL- EXPERIMENTAL APPROACH**

**Cristian Yesit Celis Cataño**

Universidad Nacional de Colombia  
Facultad de Minas, Departamento de procesos y energía  
Medellín, Colombia  
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APPROACH**

**Cristian Yesit Celis Cataño**

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Director (Supervisor):  
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*To Mom and Dad,*

*Who always encouraged me to go ahead.*

*To Family Lamir Guzman,*

*Who taught me to believe in my abilities.*



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## Abstract

A sensitivity analysis was performed on the petroleum aging sub-models considered in the COW simulator designed by Ramírez et al. 2017. The sensitivity analysis determined the experimental parameters with the greatest impact on COW predictions, determining that the parameters associated with evaporation  $b = U(2)$ , emulsion  $U(5) = Y_{max}$ , and dispersion  $U(7) = b$ , showed greater sensitivity in predicting the aging model. In this way, the review and design of experimental setups was carried out to improve the predictions of Evaporation and emulsion. In this research, the dispersion model was not addressed by the scope of the project. Finally, a small-scale wind tunnel of 0.485 cm x 0.485 cm of cross-sectional areas and 87 cm long was designed to carry out oil evaporation experiments. The tunnel has the capacity to operate at speeds of 0.22ms<sup>-1</sup> - 7ms<sup>-1</sup> and temperatures of 27°C - 32°C. The tunnel will evaluate the effect of wind speed on the evaporated fraction of 4 types of Colombian crude. Regarding the emulsion, a linear shaker was used, which allowed to have an adjusted control of the temperature and the energy printed on the crude emulsion in water, in such a way that it simulated methoceanic conditions of the Colombian Caribbean Sea, to finally obtain parameters experimental tests for the emulsion model.

**Keywords:** *Wind tunnel, shaker, Colombian oil, weathering*

## Resumen

### ACTUALIZACIÓN DEL MODELO DE ENVEJECIMIENTO DE CRUDO COLOMBIANO(COW) – ENFOQUE EXPERIMENTAL

Se realizó un análisis de sensibilidad sobre los sub modelos de envejecimiento de petróleo considerados en el simulador COW diseñado por Ramírez et al. 2017. El análisis de sensibilidad determinó los parámetros experimentales de mayor impacto en las predicciones de COW, determinando que los parámetros asociados con la evaporación,  $b = U(2)$ , emulsión  $U(5) = Y_{max}$ , y dispersión  $U(7) = b$ , presentaban una mayor sensibilidad en la predicción del modelo de envejecimiento. De esta forma se procedió a realizar la revisión y diseño de montajes experimentales para mejorar las predicciones de Evaporación y emulsión. En esta investigación el modelo de dispersión no fue abordado por los alcances del proyecto. Finalmente se diseñó un túnel de viento de pequeña escala de 0.485 cm x 0.485 cm de área transversal y 87 cm de largo para realizar experimentos de evaporación de crudo. El túnel posee la capacidad de operar a velocidades de  $0.22\text{ms}^{-1} - 7\text{ms}^{-1}$  y temperaturas de  $27^{\circ}\text{C} - 32^{\circ}\text{C}$ . El túnel permitió evaluar el efecto de la velocidad del viento sobre la fracción evaporada de cuatro tipos de crudos Colombianos. Para evaluar el proceso de emulificación, se utilizó un agitador lineal, el cual permitía tener un control ajustado de la temperatura y de la energía impresa sobre la emulsión crudo en agua, de forma que simulara condiciones de metoceanicas del mar Caribe Colombiano, para finalmente se obtener parámetros experimentales para el modelo de emulsión.

**Palabras claves:** *Túnel de viento, shaker, crudo colombiano, envejecimiento*

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## **Introduction**

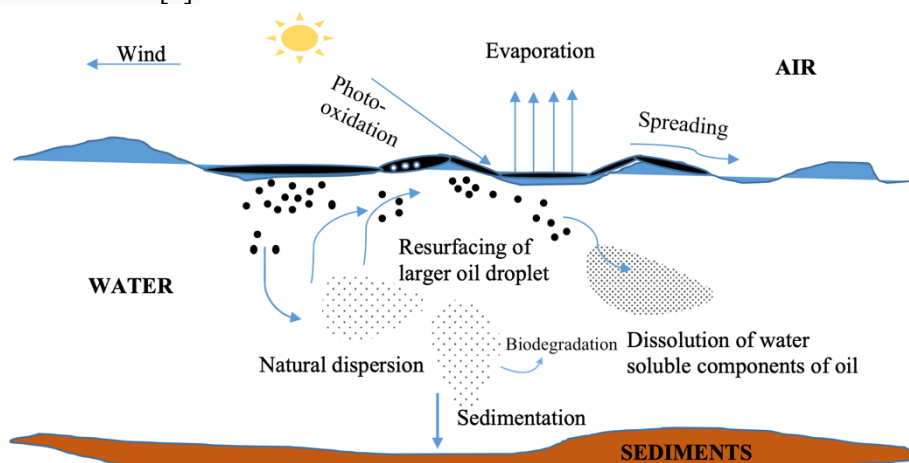
Colombian needs a good understanding of the oil weathering process in case of an oil spill accident. The Caribbean Sea has special conditions due to local oceanographic variables (wind stress, temperature, salinity, currents etc.), beside Colombian oils have innate properties as a result of compositions, these facts made arduous the predictions for commercial oil weathering software[1]. Ramirez et al., (2017) proposed a simulator for oil weathering in Caribbean Sea called COW, that takes into account the Colombian Caribbean Sea oceanographic conditions and Colombian oils properties (Ramírez et al., 2017). COW was a first approach to modeling Colombian oil weathering in sea surface, and as so is suitable for improvement. Particularly, Ramirez et al, (2017) approach was limited in the control of air temperature and velocity that was used in the evaporation experiments. According to the above, this research is focused in the improvement the predictions of the model COW in the weathering of a Colombian oil spill in the Colombian Caribbean Sea.

This dissertation has three chapters. Chapter 1 deals with Oil weathering fundamentals review and current laboratory-scale setups for the oil weathering experimental processes. Chapter 2, written as a manuscript, follow a format of a journal paper, it is focused in the sensitivity analysis of COW and the design of experimental laboratory setups for evaluated the evaporation, emulsification of Colombian oil weathering process. Chapter 3 presents conclusions and recommendations for future research.

# 1 Fundamentals of oil spill weathering – general view and review of laboratory-scale setups

## 1.1 Oil spill weathering

After oil is spilled on the sea surface, it is spread in a thin layer called oil slick. The oil slicks have an unpredictable behavior and it is affected by several chemical and physical processes known as oil weathering. These processes significantly change the slick properties; especially viscosity and density. Consequently it makes difficult the mitigation actions like pumps, burning and chemical treatments [2]. Oil weathering on the sea, it is composed of different phases, such as; spreading on the sea surface, evaporation, dissolution, emulsification, dispersion, photo-oxidation, biodegradation and sedimentation of oil. The study of the previously processes is complex, since they are self-competitive and linked [3].



**Figure 1** Representative weathering process after an oil spill in the sea (adapted from [4]).

Stages such as evaporation and dissolution are competitive and have been studied in an integrated experiment, presenting results consistent with real situations [5]. On the other hand, dispersion and emulsification is a challenge for their study due to the complexity of interfacial phenomena, the variables associated with wave turbulence and the composition of hydrocarbons [6], [7]. Beside the water-oil emulsion gradually diminish the evaporate rate as result of the water bubbles in oil, that proceed against the diffusion of low and medium hydrocarbons to the oil slick top [8]. The spread of oil is related to mechanical forces generated by gravity, surface tension and wind, these favor the distribution of the slick on the sea surface [9].

Evaporation is one of the most important phenomenon in weathering process, due to it is the primary mechanism of oil removal from sea surface, typical crudes oils can lose most of the volatile fractions within hours of spill, about 40-45% of their volume [10]. On the other hand, after the evaporation important changes are generated in properties such as density, viscosity and pour point, key elements in the processes of oil removal on the ocean. Evaporation is dependent on factors such as oil composition, solar radiation, wind, ambient temperature, thickness and surface area of oil [11]. Dissolution is the diffusion of low weight compounds to water phase. The chemicals in oil capable of dissolutions are also easy to evaporate. In view of evaporation is faster than dissolutions,

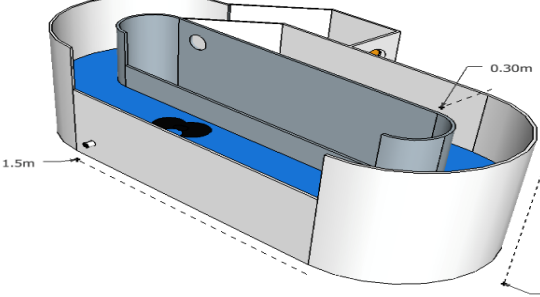
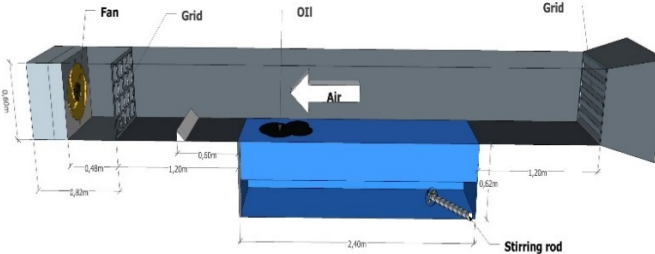
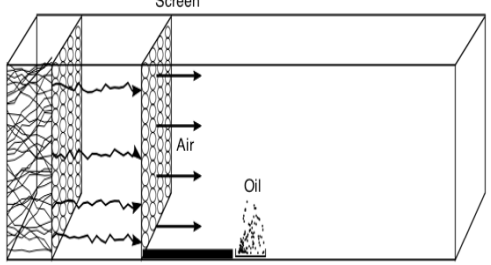
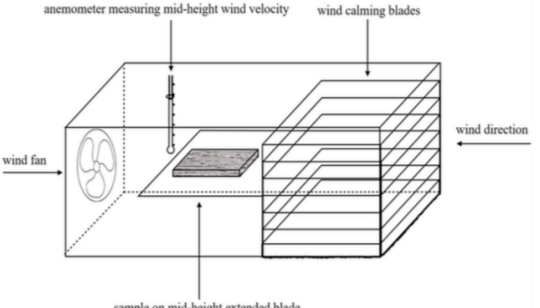
weathering models regularly disregard dissolution. The amount of oil lost by dissolution is minimum (ppm) contrast another process [12]. However, it has important effect in sea water toxicity and marine life, since majority of oil toxicity has been reported by polyromantic hydrocarbons (PAHs) and monoaromatics [13].

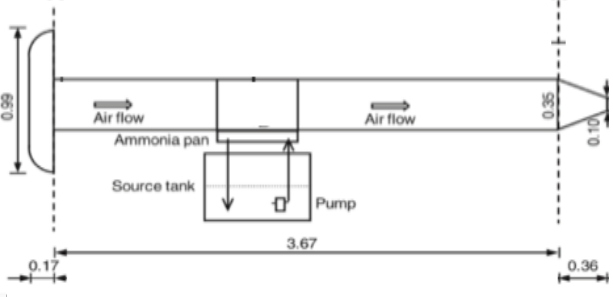
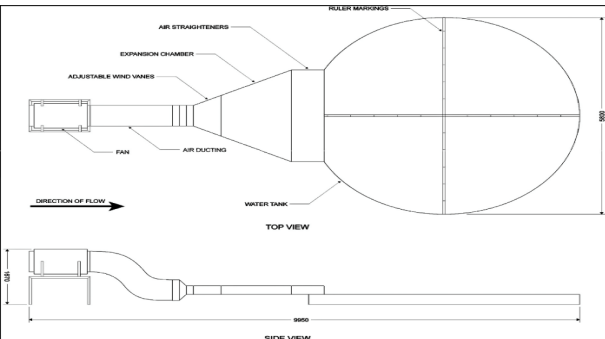
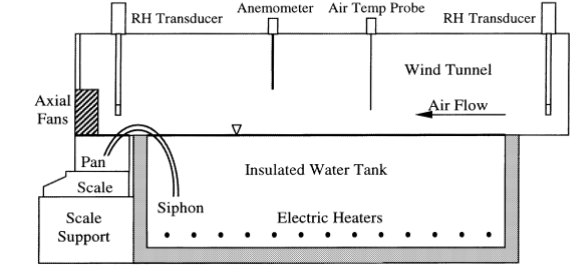
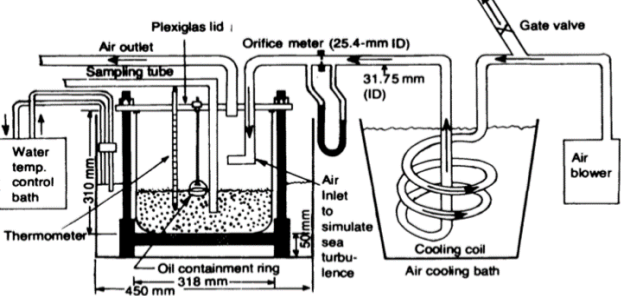
Emulsification and dispersion are processes that occur in reverse; in the first, water droplets migrate towards the oil slick forming a water-oil emulsion, whereas the dispersion occurs when crude droplets migrate towards the water column [14]. It is important to note that both processes are dependent on the composition of the spilled hydrocarbon [15]. Fingas et al. (1999) report that the water content for the emulsion can be 80-90%, and is associated with the fractions of asphaltenes, resins and waxes in the hydrocarbon. Also, the water content defines the stability of the emulsion, presenting a non-Newtonian behavior and an increase between 2 or 3 orders of magnitude in the viscosity, this may limit the effectiveness in the mitigation strategies; as the use of dispersants or pumping [16].

## **1.2 Review of laboratory – scale stups for the analysis of oil weathering after spills**

Experimental procedures have been indispensable in the oil weathering studies and models' formulation. Different approaches have been employed; setups that test from one to all phenomena involved have been proposed [17]. Evaporation has been one of the most studied phenomena, testing the influence of oil composition and wind stress [18]. Yang and Wang (1977) studied the effect of wind velocity on evaporation, through an elliptical wind tunnel, finding a proportional relationship between wind speed and evaporated weight percentage of oil (Table 2a) [19]. In turn, Cohen et al. (1980) analyzed the competitiveness between evaporation and dissolution, using a square cross-section tunnel with a pool in the middle, where the oil slick was located, it interacted with the air and energy provided by agitators, in order to improve the evaporation and dissolution respectively, checking that the evaporation affects the spill in greater proportion and speed than dissolution (Table 2b) [5]. Drozd et al., (2015) carried out evaporation studies with a synthetic mixture of hydrocarbons. they were categorized by number of carbons and their evaporations rates were estimated with a tracer (table1c) [20]. Also, Kotzakoulakis et al.,(2018) investigated the different between air boundary layer and diffusion limited evaporations models, the studies were conducted in an incubator (table1d), they found that limited models by diffusion had better coupling with the hydrocarbons evaporation [21]. In the way to search good experiment setups for oil evaporation, table 2 include setups that were used for ammonia (table 2e) and water evaporation (table 2f-g). Theses setups share good technical conditions for evaporations studies and they require small modifications to be used in oil evaporation.

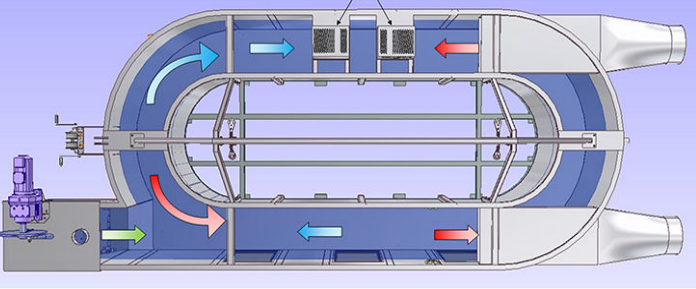
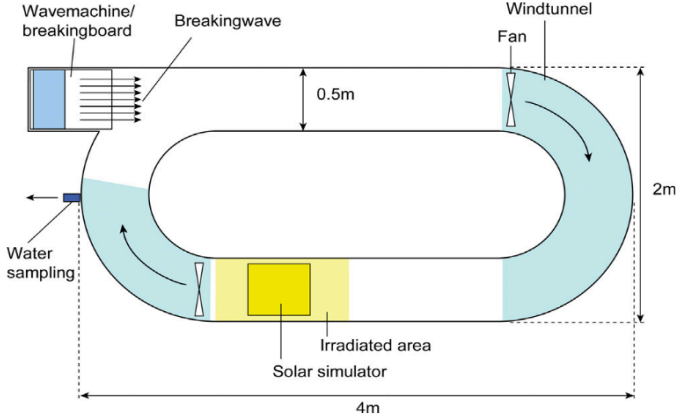
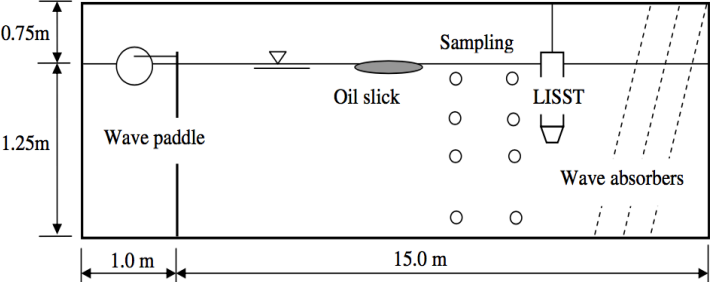
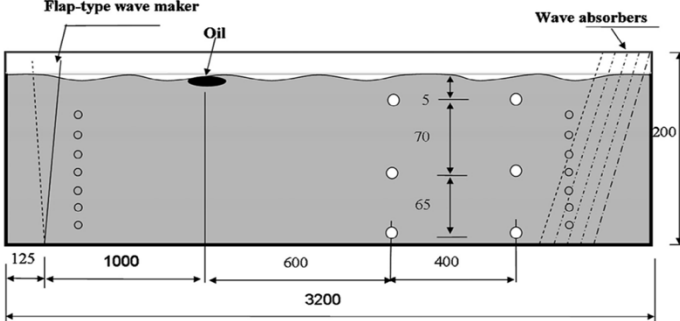
**Table 1** laboratory scale setups for oil weathering

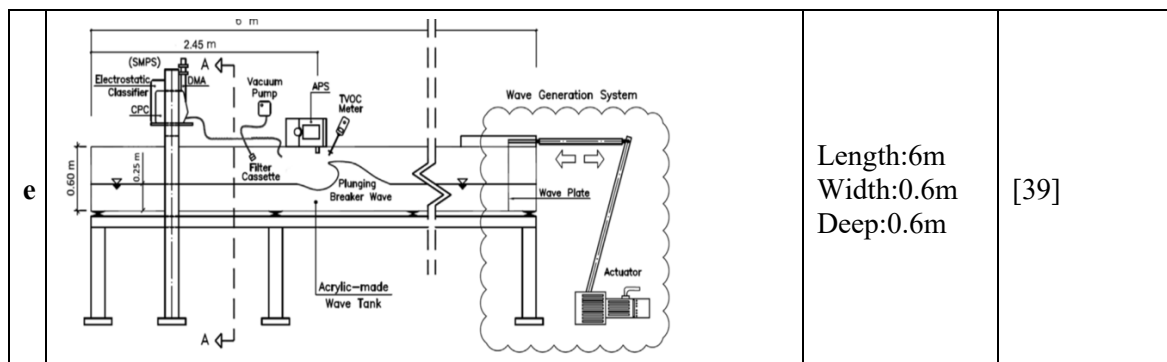
Setup	Process	Reference
<p><b>a</b></p> 	Evaporation	[19]
<p><b>b</b></p> 	Evaporation-Dissolution Length:5.62m Width:0.6m Height:0.6m	[5]
<p><b>c</b></p> 	Evaporation Length:3m Width:0.3m Height:0.3m	[20]
<p><b>d</b></p> 	Evaporation	[21]

e	 <p>Ammonia evaporation Length:3.67m Width:0.35m Height:0.35m</p>	Ammonia evaporation Length:3.67m Width:0.35m Height:0.35m	[22]
f	 <p>Water evaporation tank</p>	Water evaporation tank	[23]
g	 <p>Water Evaporation tunnel</p>	Water Evaporation tunnel	[24]
h	 <p>Dispersion</p>	Dispersion	[25]

i		Dispersion	[26]
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On the other hand, the analysis of dispersion and emulsification processes has been a key to the evaluation of the effectiveness of dispersant substances, those are used in field to treat spills [26], [27]. Both processes represent a great challenge for the experimental evaluation, due to the complexity of the scaling of the hydrodynamic variables; salinity, significant wave height, period, wavelength, temperature etc. [14], [28]. Different studies have been carried out at laboratory scale, beaker and wave channels, where turbulence conditions have been simulated by agitators or hydraulic shovels [29], [30]. Daling et al., (2003) and Ramirez et al., (2017) studied the effect of evaporation over emulsion, through a modify version of rotating cylinder suggested by Bocard et al., (1984). It was found that evaporation rise the concentration of heavy oil compounds, fact that improve the emulsion formation. Mackay and Szeto, (1981) developed a small-scale dispersant measurement technique (Table 1g), where they used a cylindrical tank in which pressure and temperature were controlled. The turbulence was applied to the environment through a current of air, which increased the complexity in its control but provided better results than turbulence generation by agitators and pumps, however the authors recommend to evaluate in detail the physical interaction between the waves and crude oil [25]. Daling et al., (1990), determined the effectiveness of dispersants and the distribution of drops in the dispersion of 3 types of crude oil, using the turbulent dissipation energy rate criterion, finding variable results for 3 types of small-scale experimental assemblies ( Table 1h), they suggested addressing in more detail the type of physical interaction between drop-water, and the way energy was applied to the system. [29], [31]. Other similar assemblies have been used by Blondina (1997), Bocard (1984), Sullivan (1993), which have allowed to evaluate the mechanisms of formation of the emulsion and dispersion, including the development of dispersants, but they have not adequately represented the data Experiments obtained in the field, this due to the difficulty of evaluating and controlling the hydrodynamic variables that influence these processes (Blondina et al., 1997; Bocard et al., 1984; Sullivan et al., 2005). Venosa and Holder (2013) studied the effectiveness of 9 dispersants on South Louisiana crude in a flask with baffles (table 1h), the results obtained by this method allowed to evaluate the effectiveness of the dispersants, but did not take into account factors such as advection, dilution and currents present in the field, which can reduce their efficiency [26], [35, pp. 63–66].

Wave flumes	Dimensions	Reference
<p><b>a</b></p> 	<p>Height:1.4m Width:0.6m</p>	<p>[36]</p>
<p><b>b</b></p> 	<p>Height:1.4m Width:0.6m</p>	<p>SINTEF</p>
<p><b>c</b></p> 	<p>Length:16m Width:0.6m Deep:2m</p>	<p>Oceanography Bedford institute. [37]</p>
<p><b>d</b></p> 	<p>Length:32m Width:0.6m Deep:2m</p>	<p>Oceanography Bedford institute. [38]</p>



Wave tanks have also been used to simulate the conditions that affect the emulsion and dispersion of crude oil. In Table 2a-b you can see the elliptical tanks used by CEDRE and SINTEF for weathering studies, these are equipped with a wave and current generator, ventilation equipment, temperature conditioning (water-air), and the SINTEF case has a solar simulator for photo-oxidation. Brakstad et al., (2014) studied the biodegradation of the Macondo 252 hydrocarbon in a dispersion and emulsion state, the SINTEF tank operated under the condition of breaking waves; created by the wave generator and fans [40]. Daling et al. (2003) evaluated the influence of the oil type on the water-oil emulsion, using air velocities between 5-10m / s [41]. Although these tanks allow the control of most of the processes involved in weathering, they present reflection problems and do not have the capacity to generate controlled waves that simulate hydrodynamic variables in sea, such as the height, period and wavelength in breaking waves conditions [42].

As for the straight wave tanks (table 2 c-e), great attention has been paid to their versatility in the control of hydrodynamic variables [42], [43]. Delvigne (1985) evaluated the natural and chemical dispersion of hydrocarbons in the field and laboratory, finding that it is possible to simulate and obtain good results in laboratory for the conditions of breaking waves, otherwise for non-breaking conditions where technical difficulties were encountered when introducing water and air currents [44]. Li et al. (2007) studied the effect of breaking waves on the dispersion of oil and the formation of mineral aggregates in the ocean. The wave tank of the Institute of oceanography of Bedford was implemented, the waves were created with a shovel generator; located 1 meter from the initial edge of the tank (Table 2b). The experiments were carried out in 2 cycles; the first of high frequency, immediately followed by another of low frequency, each with a duration of 20 seconds, generating waves with a significant height of 0.05m and a wavelength of 9.75m. These conditions allowed them to obtain a mixing zone at 7m from the generator, where the Corexit 9500 crude sample was located [37][45]. Studies over dispersion effect in evaporation process were done in a close wave tank (table2e). The tank operates with a vacuum pump to remove volatile compounds and a wave maker to produce braking waves with an energy dissipation from  $0.1m^2s^3$  to  $10m^2s^3$ . They found that dispersion reduce the evaporation amount of volatile compounds because it advantage the oil dissolution [39].

In accordance with review literature, an oil weathering setup will be selected, modified and built to carried out oil weathering studies that improve COW model's accuracy. Moreover, the effect of dissolution and emulsion over the evaporation will be studied. It has especial attention since COW models not enclose these effects. Beside it is supposed by researches that increases of viscosity due to emulsion formation may further affect volatile compounds diffusion and decreases the evaporation rate [8].

## 2 WEATHERING OF COLOMBIAN OIL IN THE COLOMBIAN CARIBBEAN SEA – EXPERIMENTAL ANALYSIS

### Abstract

A sensitivity analysis (SA) was made over Colombia oil weathering simulator (COW) to establish what elements of their weathering sub models could be improved. The SA shows that the evaporation and emulsification sub-model were sensitive to type of oil and empirical parameter associates to experimental conditions as temperature and wind velocity. A small wind tunnel was developed to tested four different Colombian oils, the wind tunnel has the capabilities to operate in a wind velocity range of 0.22 m s<sup>-1</sup> -7 m s<sup>-1</sup> and at temperature of 27°C -32°C ( $27.76 \pm 0.04$  °C,  $30.10 \pm 0.09$ °C,  $31.89 \pm 0.07$ °C), both metocean conditions typical from the Caribbean Sea. Beside for emulsification experiment, a linear shaker with bath temperature control was employed to made the water in oil emulsion.

**Keywords:** *weathering, wind tunnel, emulsion, Colombian oil*

### 2.1 Introduction

Accidental releases of offshore hydrocarbon extraction and crude oil transportation over years have resulted in significant damage to aquatic ecosystems and negative impacts to seaside communities. Knowledge to tracking the spill and design proper mitigations strategies, such as; chemical treatment (dispersants), burning or mechanical recovery, requires a good understanding of the chemical and physical changes spilled oil undergoes [46]. After an oil spill take place, the oil suffers a weathering process due to the oil interactions with the atmosphere and ocean, that drastically alter the oil composition and rheological attributes[47].

The weathering processes begin immediately the oil is released, it is integrated for different phenomena such as; evaporation, emulsification, dispersion, spreading, photo-oxidation, biodegradation and sedimentation. As is seen in several reviews of the state of the art ([2], [4], [48]–[51]), the predominant phenomena in crude oil weathering modeling are: evaporation, emulsification, dispersion and spreading. Ramirez et al., 2017, developed weathering model called COW that was calibrated with specific parameters to predict the weathering of Colombian oil in

metocean conditions relevant to the Caribbean Sea. This paper has the goal determine the elements of COW that have the highest influence on the prediction of weathering with a sensitivity analysis.

## 2.1 Materials and methods

### 2.1.1 Crude oils

#### 2.1.1.1 Oil selection and characterization

Two oils that characterize exports from Colombia, i.e. Vasconia and Cusiana, and two surrogate oils that were selected to represent two other major exports, (Caño Limón and Castilla) were selected for the oil weathering experiments [52]. **Error! Reference source not found.** presents the most relevant properties of the oils and oils surrogates. It also compares the reported value of Caño Limón and Castilla oils with those of the surrogates. The need to use surrogates was justified in the difficulty to obtain samples of these two last oils. Appendix A1 explains in detail the reasoning behind surrogate's preparation that basically tried to emulate the SARA composition of the original oils by mixing a light (Cusiana), an intermediate (Vasconia) and a heavy oil (Chichimene). Test methods for viscosity, SARA analysis and TBP were respectively ASTM D445, ASTM D4124-09 , ASTM D86-12. As Table 2 shows Cusiana and Caño Limon are light crude oil, while Vasconia and Castilla Blend are heavy crude oil, this allows to observe a variety of behavior while the oil are put under the effect of the physicochemical processes present in oil weathering.

**Table 2** Physicochemical properties of the Colombian oils and surrogates used in the experiments

Property	Value					
	Cusiana	Vasconia	Caño Limon	Caño Limon (S)	Castilla Blend	Castilla Blend (S)
°API	43.2	20.3	29.1		18.8	
Viscosity (cP) 25°C	1.96	64				
SARA						
Saturated (S)	74.3	40.7	60	49.62	43.2	41.62
Aromatics (A)	23.0	38.2	24	20.60	33.9	24.31
Resin (R)	2.3	14.7	8	25.58	12.8	27.15
Asphaltenes (A)	0.3	6.4	8	4.20	10.1	6.90
Waxes	10.0	4.5	-	-	-	-
Distillation, ASTM D86-12						
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				

\*(S) indicates surrogate

### 2.1.1 Sensitivity analysis

As a first step towards improving the estimates obtained with COW, a sensitivity analysis (SA) was applied to assess the importance of the different parameters present in the evaporation, emulsification and dispersion submodels in COW. A SA determines the relative rate of change of the model output as function of variation in an input parameter. The SA applied in this dissertation followed the method outlined by [53] that makes use of a relative sensitivity coefficient that is given by Eq. 1.

$$S_l^{(i)} = \frac{\partial y_i}{\partial \varphi_l}(t, \varphi_l) \left( \frac{\varphi_l}{y_i} \right) \quad (1)$$

where  $S_l^{(i)}$  is the relative sensitivity coefficient for variable  $i$ ,  $y_i$  is the dependent variable (model output),  $\varphi_l$  refers to parameter  $l$ , and  $t$  is the independent variable. The first term in Eq. 1 represents the change of the dependent variable with the parameter, while the second normalizes the sensitivity coefficient. The relative sensitivity for each input parameter was calculated using Eq. 1 for specified ranges while keeping the other parameters that were not being tested constant at their reference's values. Appendix A2 presents details of the SA. In the following sections the vector  $U$  groups all the different parameters ( $\varphi_l$ ) that were studied in the SA.

The SA considered the oil slick volume as output variable because of its high impact on recover and mitigation actions [3]. The oil slick volume can be approximated as the sum (Eq. 2) of the volume of the sea water present in the slick, which changes due to emulsification, and that of oil in the slick, which constantly varies due to evaporation and dispersion.

$$V_{OS} = V_{oil} + V_w \quad (2)$$

$$V_{oil} = V_0 - V_{eva} - V_{dis} \quad (3)$$

where  $V_{OS}$  represents the total volume of the slick;  $V_w$  and  $V_{oil}$  are the volumes of water and oil in the slick, respectively;  $V_0$  is the initial oil volume; and  $V_{eva}$  and  $V_{dis}$  are the volumes of oil lost due to evaporation and dispersion, respectively.

The sections below briefly describe the evaporation, emulsification, and dispersion submodels present in COW in order to clearly identify the different parameters involved in the SA. For a more detailed explanation the reader is referred to **Ramírez et al, 2017**.

**2.1.1.1** Evaporation: in this submodel that follows the procedure described by Payne et al. [40] and modified by Ramirez et al. [49] a mass transfer coefficient,  $k_w$ , represents the evaporation of multiple pseudocomponents.  $k_w$ , as described by Mackay y Matsugu [55], has an exponential dependence on wind velocity ( $U_w$ ), a power law dependence for the oil density (API) and for the form factor ( $X$ ) that represents the equivalent diameter of the oil spill. The expression for estimating the mass transfer coefficient is given by Eq. (4).

$$k_w = a * (API)^b e^{cU_w} X^{-0.11} \quad (4)$$

where  $U_w$  is the wind velocity,  $X$  is a scale factor that represents the equivalent diameter of the oil spill. Variations in  $X$  are normally not addressed in laboratory-scale experiments as the experimental setups have sizes that are order of magnitude smaller than those encountered in a real-life spills. **a**, **b**, and **c** are empiric parameters. Ramirez et al. [49] reported the following values of **a**=3.04x10<sup>-9</sup>, **b**=3.06 and **c**=0.5 for Cusiana and Vasconia.

The SE of evaporation considered parameters a, b and c.  $\mathbf{a} = U(1)$  is a multiplication factor on  $k_w$ ,  $\mathbf{b} = U(2)$  is the exponent for the API gravity that is related to the type of crude, and  $\mathbf{c} = U(3)$  is a factor associated with the wind speed acting on the slick.

- 2.1.1.2 Emulsification:** this sub model predicts the variation of the amount of water emulsified in the slick with time as well as changes on viscosity and density changes due to emulsification [49]. The emulsification rate is given by Eq.5 [56].

$$\frac{dY_{emu}}{dt} = k_{emu}(U_w + 1)^2 \left(1 - \frac{Y_{emu}}{Y_{max}}\right) \quad (5)$$

where  $Y_{emu}$  is the weight fraction of water in the emulsions,  $k_{emu}$  is the emulsion formation constant, and  $Y_{max}$  is the maximum possible value of  $Y_{emu}$ . The parameters analyzed for this model were  $U(4) = k_{emu}$  and  $U(5) = Y_{max}$ , which are experimental constants that are specific for each type of crude oil. Ramirez et al. [49] reported values for Cusiana and Vasconia that changed with the evaporated fraction and temperature.

- 2.1.1.3 Dispersion:** this sub model predicts the amount of oil that migrates to the water column due to the surface sea turbulence[29]. The rate of volume of oil dispersed in time is denoted by the empirical model in Eq. 6.

$$\frac{dV_D}{dt} = - \frac{C_{ent} D_a^{U(6)} S F_w d_0^{U(7)} \Delta dA}{\rho} \quad (6)$$

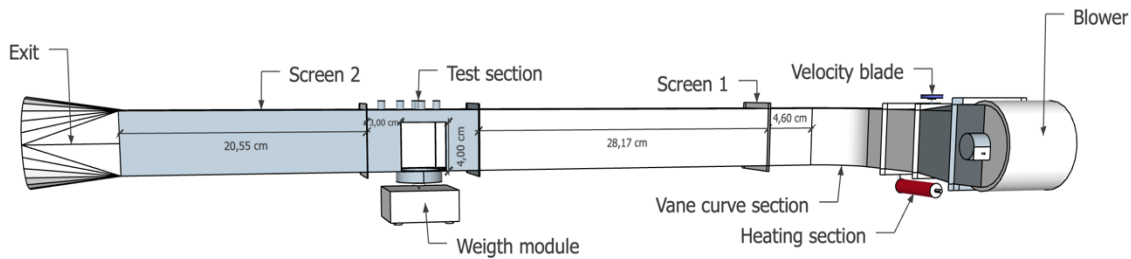
where  $V_D$  is the dispersed volume of oil,  $C_{ent}$  is an experimental drag constant,  $D_a$  is the energy dissipated by a breaking wave,  $S$  is the area of the slick,  $d_0$  is the diameter of the dispersed crude particle in water,  $\Delta dA$  is the interval of particle diameter.

The parameters associated with the emulsion are  $U(6) = a$ , an exponent associated with the energy dissipation of a breaking wave, and  $U(7) = b$ , the exponent related to the dispersed crude particle diameter. For the Colombian oils tested by Ramirez et al. [49],  $U(6) = 0.57$  and  $U(7) = 0.7$ .

## 2.1.2 Wind tunnel – evaporation experiments

As discussed below, evaporation is one of the processes with the most significant effect on weathering prediction, therefore the experiments considered the construction of a wind tunnel to evaluate and improve the evaporation model. While various authors [5], [20], [57], [58] [22], [53] have used wind tunnels with cross-sectional areas of the order of  $0.3 \times 0.3 \text{ m}^2$  and lengths of the order of 5 m, this type of experimental setup was discarded because of its relatively large dimension that would require a large amount of oil sample, something sometimes difficult to obtain, to conduct

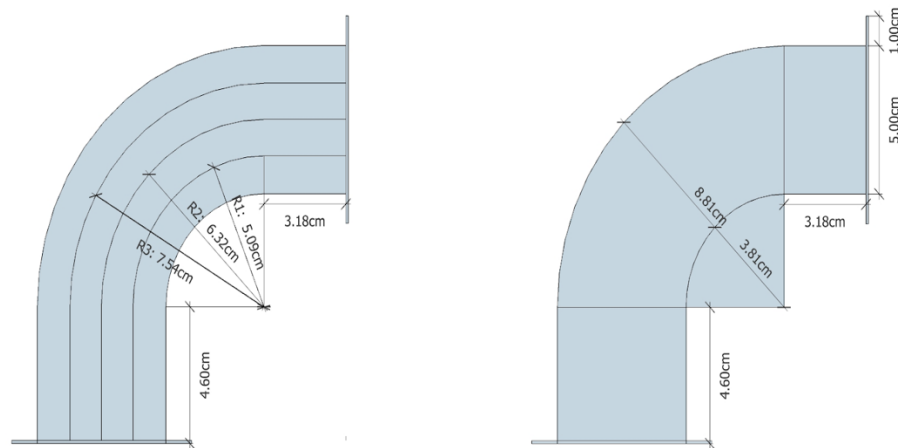
experiments. As an alternative, a smaller wind tunnel based on that previously used to study the evaporation of war agents [59] was selected.



**Figure 2** Sketch of the wind tunnel selected for the evaporation experiments. Dimensions are discussed in the text

**Error! Reference source not found.** presents a sketch of the tunnel that is 87 cm long and has a cross-sectional area of  $4.85 \times 4.855 \text{ cm}^2$ . It is made of seven pieces that make up five sections: (1) Heating, (2) Turning Vane, (3) Stabilization, (4) Weighting and (5) Exit. In the Heating section, which is 10-cm long, a flow (between 62.2 slpm and 121.0 slpm, (standard conditions are 298 K and 101325 Pa)) of hot air mixes with a flow of ambient air. The flow of ambient air is regulated between 189 slpm and 782 slpm with a damper to achieve the nominal speed wind speed of the experiments. The hot air is supplied from a heating element (XX-cm long, YY-cm I.D.) that responds to a PID that manipulates the power of the heating element as it controls the air temperature in the weighting zone.

The Turning Vane section has a length of 38 cm, an angle of  $90^\circ$  and a radius of curve of 12.62 cm. The curve favors air mixing and helps to generate a uniform profile of speed and temperature in the air. The Turning Vane section includes 4 veins parallel to the flow and they have a free distance of 1.23 cm. **Error! Reference source not found.** shows in detail the cross-section of the Turning Vane section.



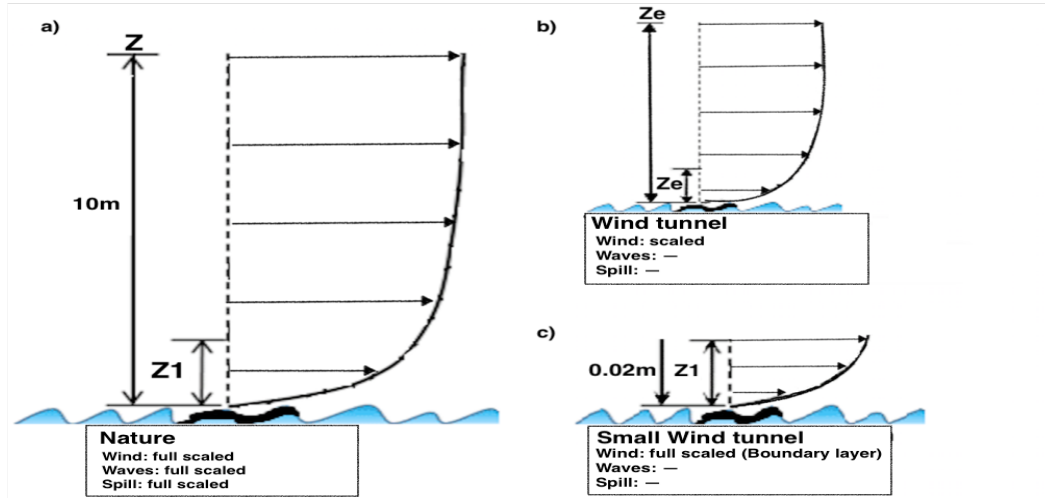
**Figure 3** Detail of the Turning Vane section

In the Stabilization section the flow passes through a 3-mesh arrangement (20, 18, 10 mesh) that orders the flow before reaching the Weighting section. The Weighting section has a length of 10.16 cm; in the upper zone it has seven ports used for speed and temperature measurements. In the bottom it includes a stainless steel deposit of 3.6 cm in diameter and 1 cm deep that holds the crude oil sample. The upper part of this deposit is aligned to the bottom of the tunnel to minimize the effect that the surface may have on the evaporation process. The deposit is supported on a weighting module (Radwag MAS 220) that measures the change in weight over time of the sample and feeds a custom-made-Labview data acquisition interface. Finally, the Exit Section has a length of 30.55 cm, and includes a 2-mesh arrangement (20, 18 mesh) in order to reduce the effect of the outlet on the flow in the Weighting section.

One of the most critical elements of the wind tunnel is that in the scale of cm it simulates the effect of wind velocity on the evaporation process that occurs at a much larger scale (of the order of ms). For meteorocenic applications the wind velocity is commonly evaluated at 10 m over the surface[60], where it is steady and characterized by a horizontal velocity that decreases with altitude. Figure 4a, adapted from reference [61], represents this decay in wind velocity from a constant value at  $Z = 10$  m, down to a lower value at  $Z = Z1$ .

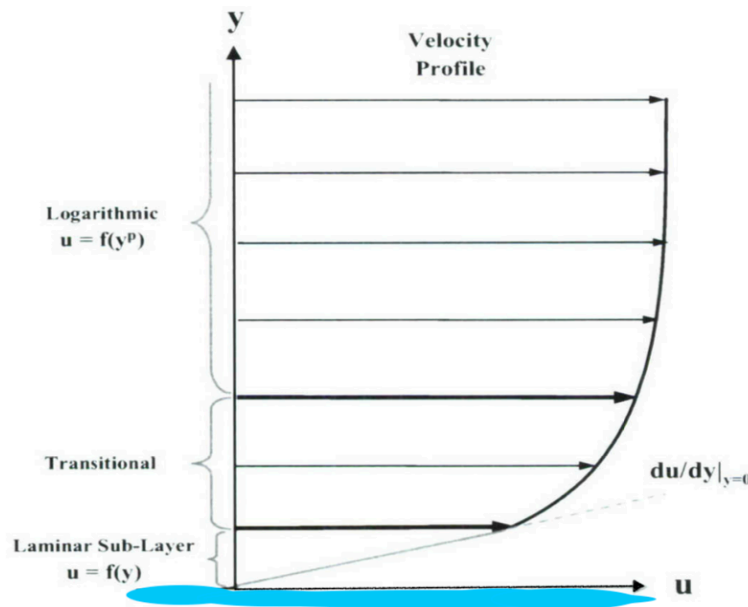
One approach to scaling down the environmental phenomena at ocean scale to lab scale is to scaled down the velocity profile as Figure 4b illustrates. In this case the velocity in the wind tunnel is reduced so that  $Re$  is the same as that in the ocean. This approach, while it does scale the hydrodynamics, does not scale the size of the waves or the size of the oil spill [3] [11] [46] [47]. Furthermore, this approximation is not accurate for an evaporation process that takes place near the surface where surface phenomena are important [59]. Although, in real oceanic applications the wind profile near the surface is intermittent, unsteady, and of swirling motion, the processes near the sea surface are the main area of interest for an oil spill evaporation. It seems, therefore, very important to capture the real velocity at the spill surface as is this what boost the mass transfer coefficient. Figure 4c illustrates an alternative approach for scaling down the phenomena from the ocean to a wind tunnel. In this case the velocity just above the oil is taken as that of the ocean (full scaled). This

approach, although does not scale the waves or the size of the oil spill, is deemed as more accurate as it includes the actual velocity above the spill.



**Figure 4** Wind tunnel boundary layer profile, a) Nature scale of boundary layer, b) Wind tunnel with boundary layer scaled, c) Small wind tunnel with boundary layer at full scale.

As the small wind tunnel will work a full scaled, it is required a turbulent boundary layer (TBL) description. The figure 7 shows the main three regions in the TBL; the laminar sub-layer, transitional and logarithmic. In the laminar region the velocity is proportional to the height and the velocity has a linear profile with the height about the surface. The transitional or buffer is the region between the transitions from laminar to logarithmic occurs. Finally, the logarithmic region is the turbulent zone where the velocity profile is proportional to the height raised to a power.



**Figure 5** Boundary layer velocity profile nomenclature

In the turbulent region, the vertical profile is a logarithm function of the height above at smooth surface and is expressed in equation 2. It is known as the law of the wall, and is frequently used to model the turbulent velocity profile for transport in the air-sea interface for deep sea conditions [62], [63].

$$\frac{u}{U_\tau} = \left(\frac{1}{k}\right) \ln\left(\frac{U_\tau y}{\nu}\right) + C \quad (2)$$

Summary expression

$$u = a \ln(y) + b \quad (3)$$

where  $u$  is the velocity,  $U_\tau$  is the friction velocity,  $k$  is the Von-Karman constant (0.4),  $y$  is the height from the surface,  $\nu$  is the kinematic viscosity of the air and  $a$ ,  $b$ ,  $c$  are constants.

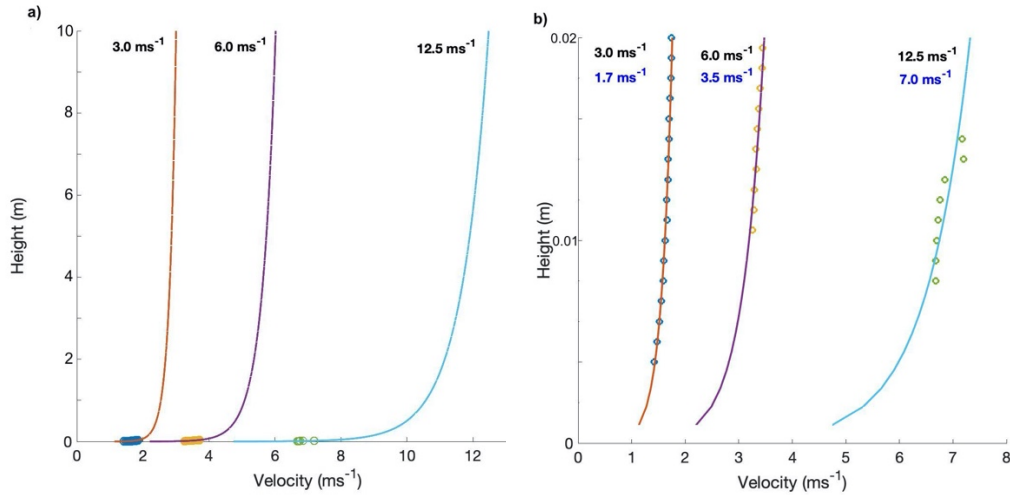
According to the above, the speed in the wind tunnel must correspond to the speed in the lower part of the boundary layer corresponding to typical speeds of the Caribbean Sea measured at a height of 10m above the sea surface. That is, the speed in the tunnel must be the one that would be at 2 cm above the sea when the wind speed at 10 m above sea level has typical values, such as for example  $3 \text{ m s}^{-1}$ ,  $4 \text{ m s}^{-1}$  and  $12.5 \text{ m s}^{-1}$  [49]. To achieve the above, a theoretical profile was calculated by using the least squares method, where equation 3 was fitting with the wind velocity profile in the Weighting section. Table 3 presents the constants for the law of the wall in the small wind tunnel for three wind velocity conditions, this allowed to approximated the wind tunnel profile to a theoretical wind velocity profile on the ocean surface. As can be seen in table 3, the approximations for the low and medium conditions has a less standard error, contrary to high condition that has a bigger error because the high turbulent condition at high velocities made difficult to measure the velocity inside the wind tunnel.

**Table 3** Law of the wall (equation 3) constants for the wind profile over the sample in the wind tunnel.

Velocity Conditions	<b>a</b>	<b>b</b>
<b>Low</b>	$0.2001 \pm 0.006$	$1.1573 \pm 0.015$
<b>Medium</b>	$0.4097 \pm 0.011$	$2.2487 \pm 0.034$
<b>High</b>	$0.8291 \pm 0.219$	$4.8379 \pm 0.534$

**Error! Reference source not found.** illustrates the coupling of the theoretical wind profile on the ocean surface with the profile obtained in the wind tunnel. **Error! Reference source not found.**a shows the logarithmic extrapolation using the wall law (Equation 1), on the wind profile obtained in the tunnel, for speeds at 10 m of  $3 \text{ m s}^{-1}$ ,  $6 \text{ m s}^{-1}$  and  $12.5 \text{ m s}^{-1}$ . It can be seen that the extrapolated profile agrees with the speed observed in the ocean at a height of 10 m. **Error! Reference source not found.**b presents in greater detail the adjustment of the experimental profile with the theoretical

extrapolated. In **Error! Reference source not found.b** we can determine the wind speeds inside the tunnel, which we will call as nominal, as  $1.7 \text{ m s}^{-1}$ ,  $3.5 \text{ m s}^{-1}$ ,  $7 \text{ m s}^{-1}$  which correspond to  $3 \text{ m s}^{-1}$ ,  $4 \text{ m s}^{-1}$  and  $12.5 \text{ m s}^{-1}$  respectively at conditions of 10 m above the sea.

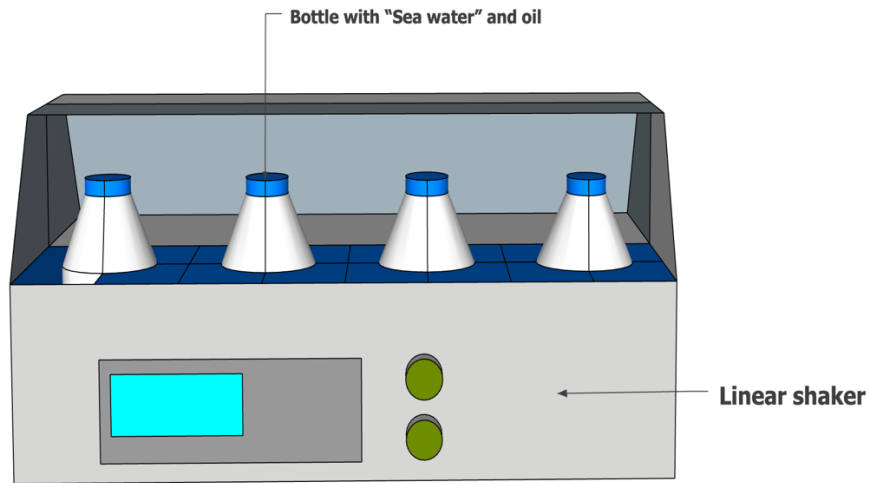


**Figure 6** Variation of wind speed with height above sea level (7a) or above the surface of the wind tunnel (7b). a) Theoretical wind profile on the ocean surface according to the speed law. The legend indicates the characteristic value at 10 m above sea level b) Theoretical wind profile (lines) according to the wall law and experimental (points) in the wind tunnel. The legend indicates the nominal speed at the center of the wind tunnel (blue) and the nominal value at 10 m above sea level (black).

On the other hand, the temperature conditions were fixed for three temperatures; 27, 30 and  $32^{\circ}\text{C}$ , in agreement with the Caribbean sea range of temperature [1].

### 2.1.1 Linear shaker - emulsification

The emulsification experiment methodology used a linear shaker with temperature and agitation control. For the experiment, 200 ml of salty water, with the typical salinity of the Caribbean sea ( $35\text{g/l}$ ), and 20 ml of oil were put inside of 500 ml boro laboratory bottles. Then they were introduced in a linear shaker (Jubalo sw22) equipped with a water bath temperature control, the temperature was fixed in  $30^{\circ}\text{C}$ , that is a common Caribbean Sea temperature ( $27^{\circ}\text{C} - 32^{\circ}\text{C}$ ). The linear shaker works a 180 RPM, which be in agreement with the power given by the waves over the spill in deep sea and surface near to shore, more details in appendix C. Then, they were agitated for 24 hours with registration of the water uptake at 5, 10, 15 and 30 minutes and 1, 2, 4, 6, 8, 12 and 24 hours.



**Figure 7** Experimental setup for water in oil emulsion

**Error! Reference source not found.** illustrated a sketch of the emulsification setup. The bottles had the same diameter, because of this, the change of water in the crude oil phase is proportional to the change of height of the crude phase in the tube, then the water uptake percent in the crude oils was measured with equation 4.

$$Y(t) = \frac{h(t) - h_0}{h(t)} 100\% \quad (4)$$

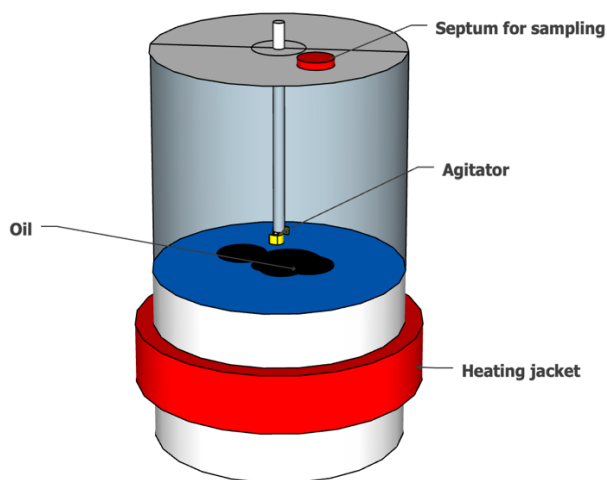
where,  $Y(t)$  is the percent of water up taken by the oil,  $h_0$  is the initial height of the oil phase in the settling tube,  $h(t)$  is the height of the oil phase in time. The measure of the water uptake variations in time can provide a kinetic index related with the emulsification rate, for this research is valuable to get the half-time index ( $t_{1/2}$ ), defined as the mixing time passed when the water content is half of its maximum value.

Besides it is important to know the stability of the water in oil emulsion, that is evaluated follow the equation 5, where a value of  $R_{2/1}$  equal or close to 1 is for stable emulsions and  $R_{2/1}$  close to 0 for unstable emulsions

$$R_{2/1} = \frac{R_2}{R_1} = \frac{\text{Water to oil ratio after settling period}}{\text{Water to oil ratio before settling period}} \quad (5)$$

### 2.1.1 Agitated container - Dissolution

The experimental setup to study the dissolution of oil in water was adapted from [64]. An agitated tank of 360 ml was filled with 300 ml of salty water (35g/l) and 30 ml of crude oil. The oil-water relation was 1:100 in agreement with previous dissolution studies, this relation showed good results for oil dissolution [65]. The container was kept a temperature of between 27°C to 32°C with a heating jacket. The stirred tank operate a 80 rpm, this revolution was related with the wave dissipation energy in the sea for deep sea (1-10 W/kg) and surface layer near shore ( $10^{-5}$ - $10^{-2}$  W/kg) wave conditions[66] , using the methodology in [67]. Sampling was done with a spinal syringe in the bottom of the container, for times of 2h, 4h, 8h, 24h, 36h, 48h, 72h, 96h and 12h. Before sampling, the system is left at rest for 10-15 minutes to achieve reincorporation on the surface of the oil drops. In addition, the sample must be filtered ( $0.45\text{-}1\mu\text{m}$  filter) to reduce the effect of suspended droplets on the dissolved concentration [68]. **Error! Reference source not found.** illustrated a sketch of the dissolution setup.



**Figure 8** Agitated container with heating jacket for oil in water dissolution.

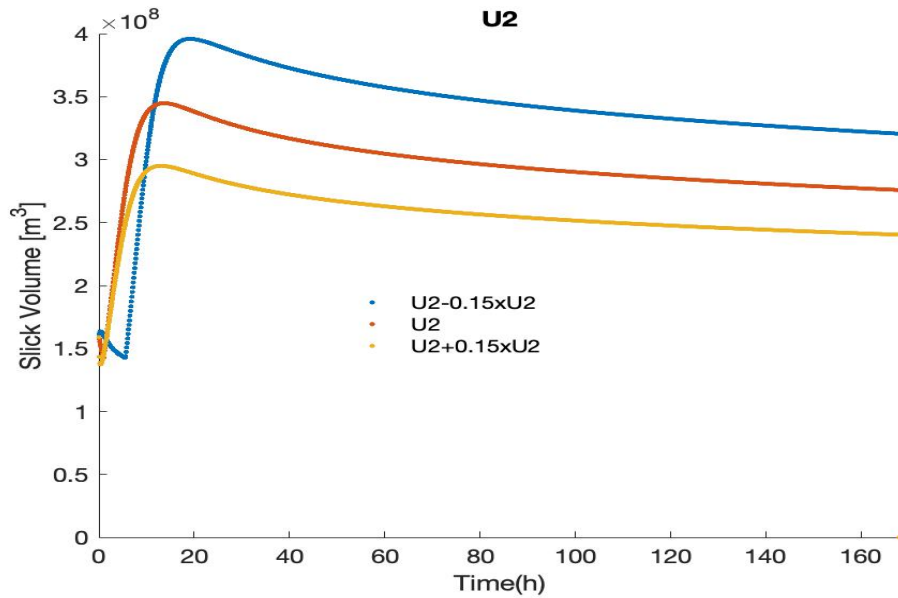
The samples obtained in the dissolution experiment were analyzed through a photo-colorimeter, following a methodology proposed by INVEMAR, see reference for more details [69].

## 2.1 Results

### 2.1.1 Sensitivity analysis

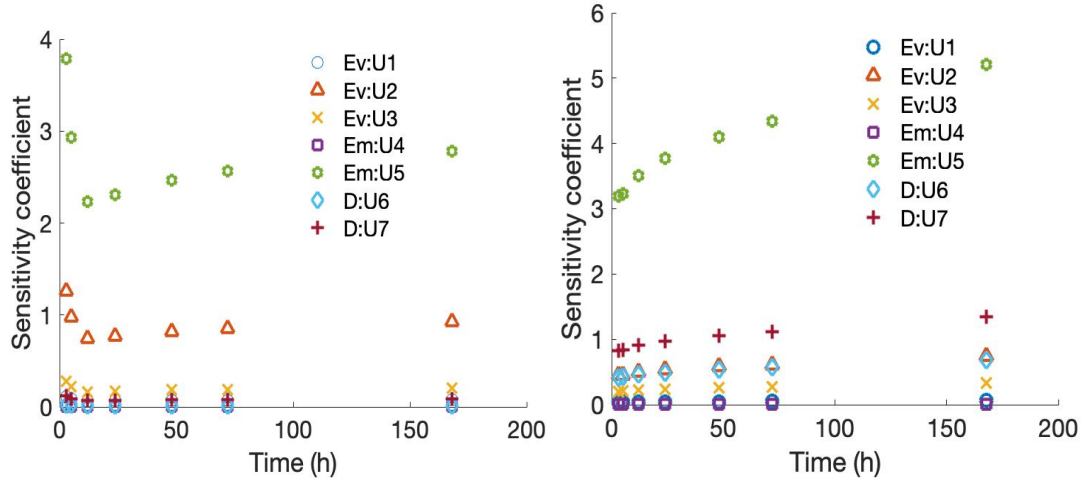
The SA was carried out for two Colombian oils that are frequently transported through the Caribbean Sea, Cusiana and Vasconia [52]. For both crudes, COW was run coupled with a relativity sensitivity routine. It was programed in Fortran and MATLAB, the appendix A1 presents the code. At time from 0 to 180 hours, equivalent to one week, was used to evaluated parameter sensitivity coefficient, since physicochemical properties changed in short time scales. As soon as meteorological conditions,

SA consider at temperature of 30°C and wind speeds of 5ms<sup>-1</sup> and 10.5ms<sup>-1</sup>, all typical Caribbean Sea environment.



**Figure 9** Evaporation parameter (U2) influence in COW. a) slick volume prediction

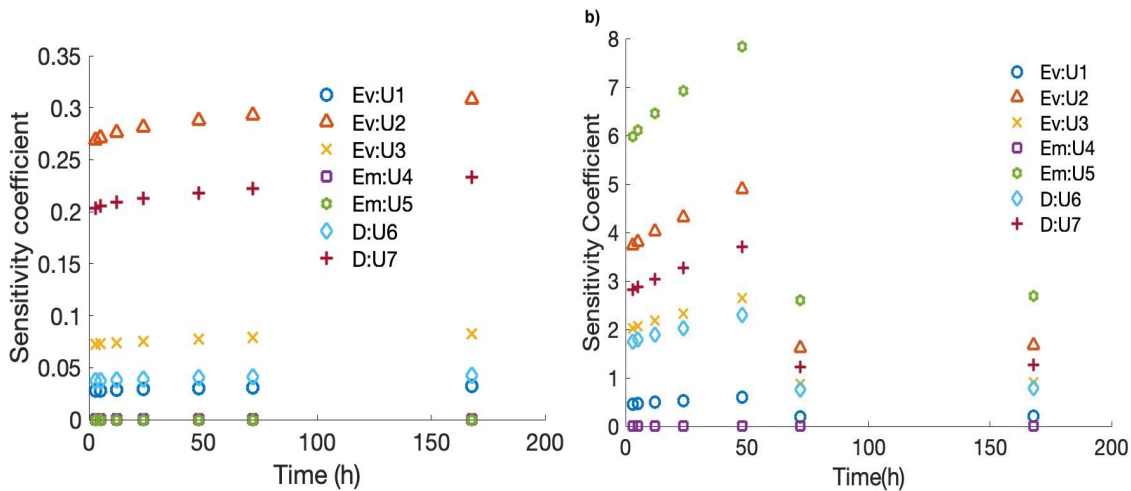
The **Error! Reference source not found.** shows the U2 parameter influence in COW oil slick volume (m<sup>3</sup>) prediction in time (h). It can be seen, that in the first 10 hours the mean value (red line) and upper value (yellow line) has a similar behavior, where the slick volume was reduced quickly, in contrast, the lower value (blue line) shows a slower decrease. That is because, at the beginning of the weathering process, evaporation is dominant over the other phenomena and highest values in U2 raise the mass transfer coefficient (equation 4), opposite happens with low values. Then the slick volume change to an upward trend, because the emulsion process, where the water percent in the slick is raised until its maximum value, at this point, lower values of U2 helps the increase of volume, due the reduction in the mass transfer coefficient. Then approximately after 20 hours the oil slick was reduced slowly cause the stationary state between evaporation, emulsification and dispersion process.



**Figure 10** Cusiana sensitivity coefficient. a) wind velocity 5m/s, b) wind velocity 10.5m/s

The Cusiana SA is shown in **Error! Reference source not found.**, It is shown the absolute value of the sensitivity coefficient (SC) in time for all parameters, where highest value of SC means a greatest level of influence in the model results. For the slow wind velocity conditions, as it is saw the parameters for evaporation (U1-U3) has a great influence (specially U2) over the slick volume in the test time, mostly at the beginning of the weathering, due to evaporation of oil volatile fractions happens in a high rate for lights oils [70]. As the same time the parameter U5, linked with the water uptake, for emulsion has an important impact over COW.

In the other hand, high wind speed conditions (figure1b) made sensitive COW mainly to emulsion (U5) and dispersion parameters (U6-U7). Dispersion is important because of the proportional relation of the wind velocity and the turbulence in the sea surface (waves). That is, high wind velocity make a wave conditions of high energy, and it is closely related to the dispersion process [44], [71], [72]. Evaporation parameters, though with less uncertainly, should be check for high velocity conditions.



**Figure 11** Vasconia sensitivity coefficient. a) wind velocity 5m/s, b) wind velocity 10.5m/s

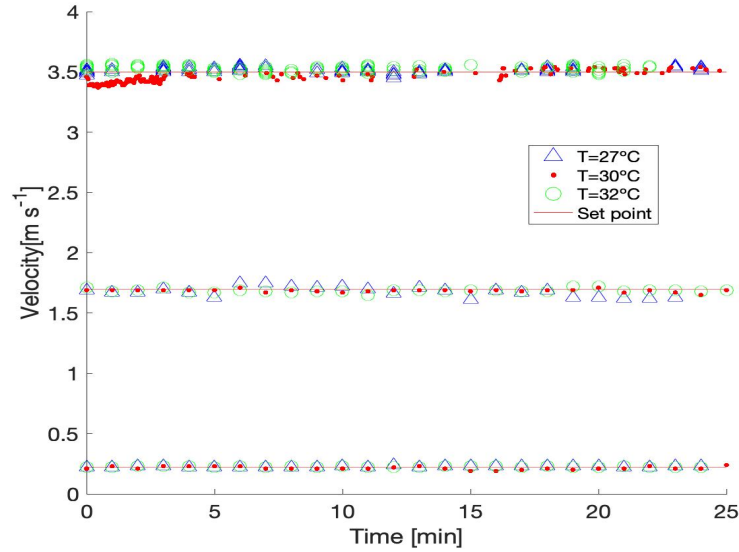
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The Vasconia SA is shown in **Error! Reference source not found.** To slow wind velocity, like Cusiana, evaporation parameters (U1-U3) has the greatest uncertainty (specially U2), but in this case it is small. That is because the slowly evaporation rate in heavy oils [70]. As the same than Cusiana the parameter U7, linked with the droplet diameter, for dispersion has an important impact over COW. Both parameters uncertainty look to tend to a constant value while time increase. Differently, in high speed wind, dispersion parameters (U6-U7) affects mainly the COW predictions. Uncertainty for evaporation parameters is present, but for the most part due to U2 parameter. It is important to note that around the 72 hours the influence parameter is abruptly decrease, because this time the rate of evaporation and dispersion is reduced.

In conclusion, COW required a parameter checking with experimental method to reduce the uncertainty in evaporation and dispersion predictions with both types of oils. The evaporation parameters (U1-U3) prescribed special attention under low wind velocities, on the contrary to dispersion parameters (U6-U7) needs a calibration in high speed wind velocities. Finally, in all cases analyzed in the SA, the parameter related with the type of oil (U2) suggest the development of an experimental methodology to let test a lot of kinds of oils.

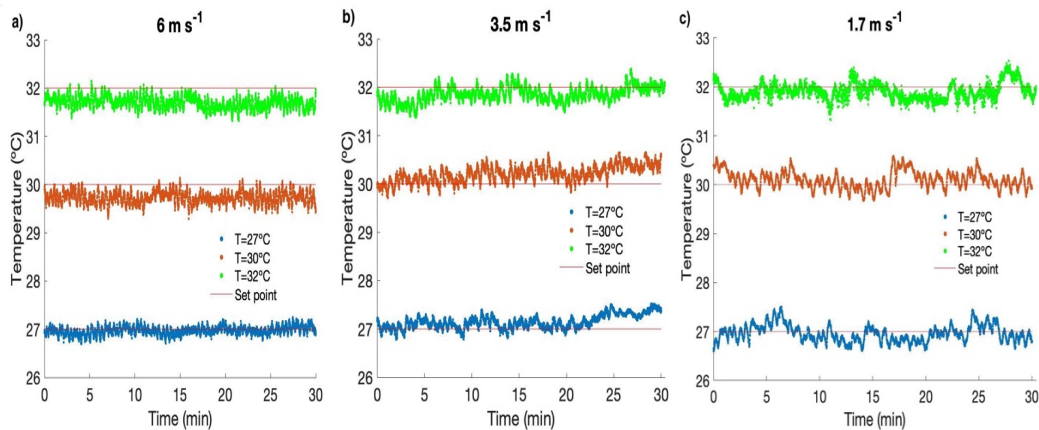
### 2.1.1 Wind tunnel performance and oil evaporation

The wind tunnel built to evaluated the evaporation fraction of crude oils, it is suitable to operate in the range of  $0.22 \text{ m s}^{-1} - 7 \text{ m s}^{-1}$  of wind velocity and control the air temperature in the range of  $27^{\circ}\text{C} - 32^{\circ}\text{C}$ , both in agreement with the conditions required to fulfill the Caribbean Sea conditions[1]. The tunnel was tested about its performance in the velocity and temperature stability. The velocity range was typified in three temperature conditions with the purpose to estimate the wind velocity stability. **Error! Reference source not found.** illustrated the wind velocity stability for different temperature conditions over the weighting section. It was found that for operating velocities of  $0.22 \text{ m s}^{-1}$ ,  $1.70 \text{ m s}^{-1}$  and  $3.50 \text{ m s}^{-1}$  the average velocity in the center of the tunnel was  $0.23 \pm 0.05 \text{ m s}^{-1}$ ,  $1.67 \pm 0.04 \text{ m s}^{-1}$  and  $3.52 \pm 0.03 \text{ m s}^{-1}$  respectively.



**Figure 12** Velocity stability in the weighting section

Moreover, the temperature stability was tested over in the range of 27°C – 32°C for the range of wind velocity (0.22, 1.7, 3.5 m s<sup>-1</sup>). The **Error! Reference source not found.** presents the temperature behavior in the wind tunnel for the three velocity conditions. The temperature was stable and show a little oscillation near the set point stablish for each velocity specification. The temperature in the wind tunnel had an average value of 27.76 ± 0.04 °C, 30.10 ± 0.09°C and 31.89 ± 0.07°C.



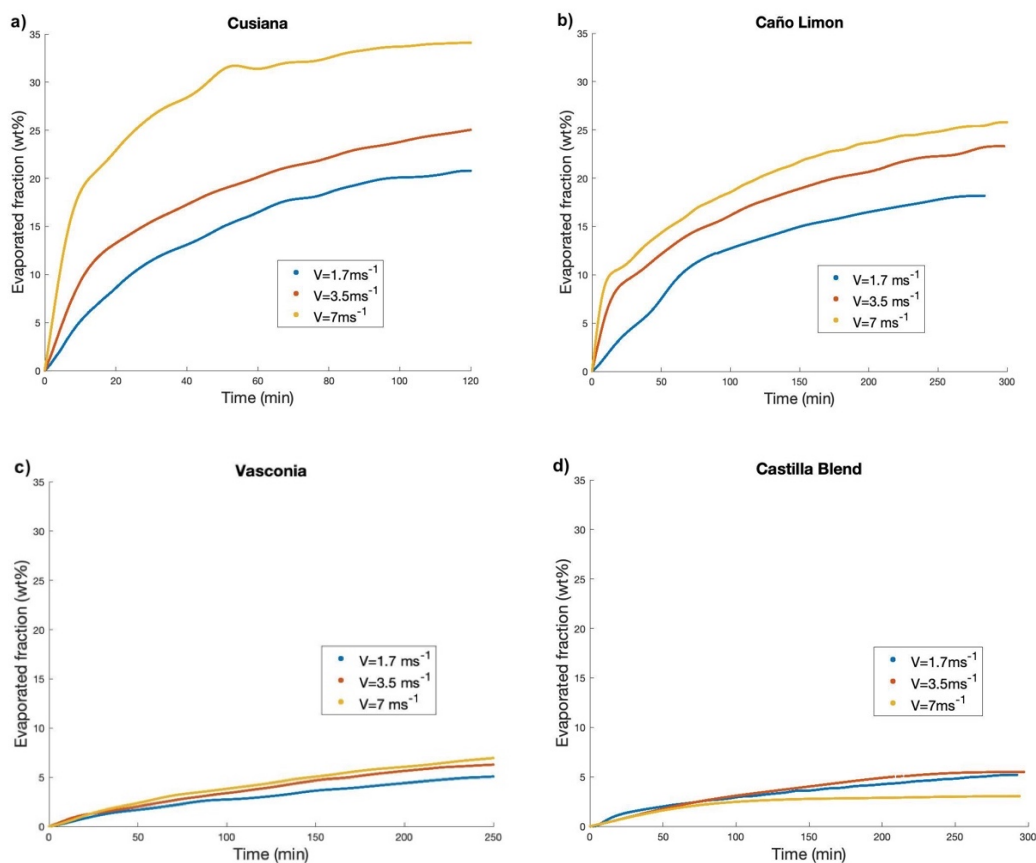
**Figure 13** Wind tunnel temperature stability for 27°C, 30°C and 32°C. a) temperature stability for a nominal velocity of 6.0 m s<sup>-1</sup>. b) temperature stability for a nominal velocity of 3.5 m s<sup>-1</sup>. c) temperature stability for a nominal velocity of 1.7 m s<sup>-1</sup>.

As seen previously the wind tunnel operations deal with the requirement in velocity and temperature to simulate an oil evaporation stage in the Caribbean Sea conditions fixed in this research. Ones the wind tunnel shows a good performance, the evaporation of crude oil was carry out with the purpose

of get the evaporation fraction in time. Equation 6 was employed to calculate the evaporation fraction for the Colombian oils.

$$F_{eva} = \frac{m_i - m(t)}{m_i} \times 100 \quad (6)$$

where,  $m_i$  is the initial mass,  $m(t)$  is the mass in time and  $F_{eva}$  is evaporated fraction.

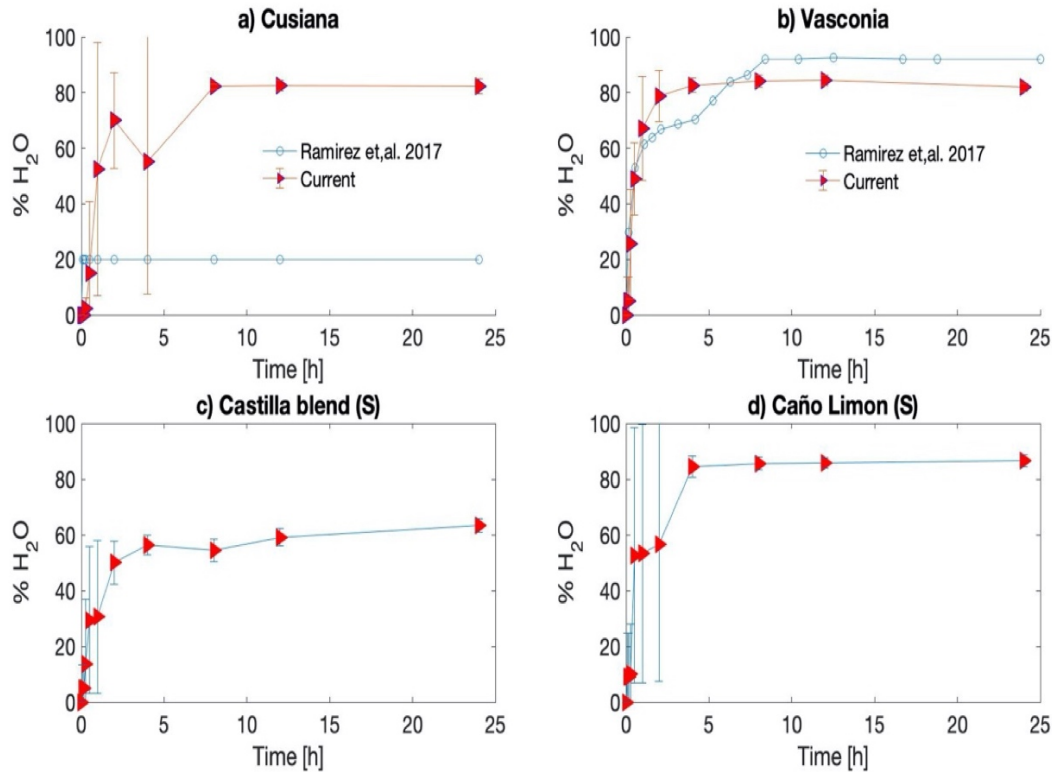


**Figure 14** Oil evaporation fraction at 30°C and three nominal wind tunnel velocities; 1.7 ms<sup>-1</sup>, 3.5 ms<sup>-1</sup> and 7 ms<sup>-1</sup>. a) Cusiana, b) Caño Limon, c) Vasconia, d) Castilla Blend.

The **Error! Reference source not found.** show the behavior of the evaporation fraction for Cusiana, Vasconia, Caño Limon and Castilla Blend at 30°C and different wind velocities. For any of the three velocity conditions, the evaporated fraction of Cusiana and Caño Limon (S) is higher than Vasconia and Castilla Blend (S) for the same time, this is because the physicochemical properties of the oils, as it is seen in **Error! Reference source not found.**, Cusiana and Caño Limon (S) has a higher volatility of oil low fractions, it let them rise evaporate fraction values over the 15% and made them more sensible to the wind velocity, which has a proportional behavior with the evaporated fraction [73]. On the other hand, heavy crude oils such as Vasconia and Castilla Blend (S) has a less evaporate fraction value, lower than 5%, they also showed to be less affected by the wind velocity[58].

### 2.1.1 Emulsification

This session evaluates the emulsion formation rate and the effect of evaporation in the emulsion stability and finally shows the parameter found to calibrate COW emulsion model.



**Figure 15** Water uptake percent in emulsification process of Colombians oils, Cusiana, Vasconia, Caño Limon(s) and Castilla Blend(s).

In the **Error! Reference source not found**, shows the percent of water uptake in time for Cusiana, Vasconia, Caño limon (s) and Castilla Blend(s) oils. The rate of water uptake for light crude oils, Cusiana and Caño Limon (S), rose higher percent of water, but presents an erratic behavior at the beginning of the process due to these crude oils has lack sufficient asphaltenes and resin to show a stable behavior [74]. Cusiana made a water entrainment emulsion, with high water uptake values, around 80%, but unstable with a  $R_{2/1}$  of 0.18. In previous studies made by Ramirez et, al.(2017), Cusiana reach a maximum quantity of water around the 20%, this diparity is a result of the lightly higher and better temperature control in the test, it is known that increases in temperature, under 60°C, advantage the water uptake and emulsion stability [75]. Otherwise Caño Limon (s), Vasconia and Castilla Blend got a water uptake on the stationary state of 86.6%, 81.8% and 63.3% respectively, both oils made a stable emulsion, with  $R_{2/1}$  of 0.98, 0.93 and 1.0 respectively. Both crudes oils had a similar behavior due to the resemblance in their S.A.R.A compositions, as it looks in the **Error! Reference source not found**, precisely in the resin and asphaltene fractions that plays an important role in the dispersion and capture of water in the oil phase [41]. The presence of resins

and asphaltenes fractions in oils have and surfactant-like behavior in the oil-water interphase, resins and asphaltenes are involve in interfacial processes that made water-oil emulsion stable [74].

The Table 6 shows the parameter acquired in the emulsion experiments that supply the COW model for the emulsion predictions over Colombian oils.

**Table 4** Oil emulsification parameter to COW model. Maximum water uptake ( $Y_{max}$ ), Half-life time ( $t_{1/2}$ )

<i>Parameters</i>	<i>Cusiana</i>	<i>Vasconia</i>	<i>Castilla Blend (s)</i>	<i>Caño Limon (s)</i>
$Y_{max}$	56 ± 13	88.22 ± 0.49	85.3 ± 0.8	90.2 ± 0.7
$t_{1/2}$	127.6 ± 113.4	15.23 ± 2.88	12.5 ± 2.5	23.8 ± 8.8

### 2.1.1 Dissolution

The dissolution experiments were carried out for Cusiana oil, due to its characteristic of being a light crude, that has a greater component of aromatic compounds highly soluble in water. Even so, it was not possible to determine the concentration of dissolved fractions because the implemented measurement method was not the correct one. For this reason, the dissolution was outside the scope of the investigation.

**Table 5** Absorbance for four samples of the dissolution experiment

<b>Sample</b>	<b>Absorbance</b>	<b>Concentration(mg l<sup>-1</sup>)</b>
2h	0.000	(<0.026)
4h	0.000	(<0.026)
8h	0.003	(<0.026)
24h	0.005	(<0.026)

**Error! Reference source not found.** shows the value of the first four samples taken in the Cusiana dissolution, as it is seen the absorbance was to low and it was out of the calibration curve made for Cusiana with the Beer-Lamber law. For this reason, was no possible to continue the dissolution experiment for Colombian oils.

## 2.1 Conclusion

The development of the sensitivity analyzed over COW allowed to find the more sensible parameter like the type of oil, this help the development of experimental setups that made easy to sample different types of oils. Because of that the methodology used for the emulsion testing and the small wind tunnel helps to develop a more accurately experimental methodology to characterized the evaporation and emulsion weathering processes, Mainly due to the good temperature control in both experiments. In addition to being able to characterize the behavior of other Colombian crude oils, Caño Lemon and Castile Blend, improve the experimental parameters used by COW for the oil spill

predictions. It was also possible to develop an operational wind tunnel, easy to use with a few raw material requirements to carry out several oil evaporation tests.

### **3 Conclusion and future work**

The wind tunnel designed for hydrocarbon evaporation showed great performance, it had a good temperature control and stable operating velocity. Until the moment of the review of the state of the art in this investigation it represented an innovation for the study of oil evaporation for atmospheric conditions. In addition, it is practical, since it does not require a large space for its operation and has a great advantage to evaluate the evaporation of hydrocarbons since it requires few amounts of crude per test, in this investigation this represented a great advantage due to the difficulty in obtaining enough raw material for the realization of the experimental matrix.

Once finished this research, as a future work is important to improve some detail in the wind tunnel, it is necessary to enhance the way as crude oil is charge in the weighting section, that is to say, make it more automated. Also it is important to made a turbulence study in the weighting section to understand and possible control variables that make difficult to follow the evaporation process.



# Appendix

## Appendix: Caño Limon and Castilla Blend surrogate

Fractions %w/w						
	Cusiana	Vasconia	Chichimene	Sum		
Castilla B	0.274	0.426	0.300	1.000		
Caño limon	0.739	0.030	0.231	1.000		
S.A.R.A.	Crudes			Crude objective		
	Cusiana	Vasconia	Chichimene	Castilla blend	Castilla blend-Surrogate	% Error
S	74.3	40.7	18.31	43.2	43.20	0.00
A	23	38.2	31.13	33.9	31.91	5.87
R	2.3	14.7	25.4	12.8	14.51	13.35
A	0.3	6.4	23.12	10.1	9.74	3.54
				100	Objetive cell	22.75739099
S.A.R.A.	Crudes			Crude objective		
	Cusiana	Vasconia	Chichimene	caño limon	Caño limon -Surrogate	%Error
S	74.3	40.7	18.31	60	60.36	0.60
A	23	38.2	31.13	24	25.33	5.56
R	2.3	14.7	25.4	8	8.01	0.10
A	0.3	6.4	23.12	8	5.75	28.07
					Objetive cell	34.33

The table below shows the fractions of crude oils Cusiana, Chichimene and Vasconia used to create the surrogate Castilla Blend and Caño Limon.

## ■ Appendix: Sensitivity

$$S_l^{(i)} = \frac{\partial y_i}{\partial \varphi_l}(t, \varphi_l) \left( \frac{\varphi_l}{y_i} \right) (1)$$

The sensitivity analysis was made using equation (1), where  $S_l^{(i)}$  is the relative sensitivity coefficient for variable  $i$ ,  $y_i$  is the dependent variable (model output),  $\varphi_l$  refers to parameter  $l$ , and  $t$  is the independent variable.

The first term in the Eq.1 was estimate using a MATLAB algorithm integrated with COW Fortran algorithm that calculated the rate of change of the dependent variable, Oils slick volumen ( $V_{OS}$ ), with each parameter define in the vector  $U$  ( $U_1 \dots U_7$ ), that contain the parameters previously shown. The simulation evaluated the influence of the parameter  $U$  in at time of 168 hour, where the value of  $V_{OS}$  was collect in windows of 10h, 24h, 48h and 168h. Each parameter was varied from -15% to 15% with steps of 5%, then using least squared methods (polyfit) from MATLAB was possible to get the  $\frac{\partial y_i}{\partial \varphi_l}(t, \varphi_l)$  function for each parameter  $U$ . Subsequently the sensitivity coefficient was calculated with Eq.1.

## Appendix: Stirring frequency to make of water in oil emulsion

The stirring frequency to make the water-oil emulsion should be such that be in agreement with the power given by waves over the spill in these 2 conditions:

- Deep sea:  $10^{-7}$ - $10^{-5}$  W/kg
- Surface near shore:  $10^{-5}$ - $10^{-2}$  W/kg
- Breaking waves: 1-10 W/kg

These power conditions were proposed by Fingas, et al (1994) [76]. In this order, the power number (Eq.1), was used to estimate the power of the linear shaker could impress over the emulsion at the range of operation frequency available in the equipment.

$$P = N'_e \rho n^3 d^4 V_l^{1/3} \quad (1)$$

Where,  $N'_e$  is the Newton number,  $\rho$  the density,  $n$  is the stirring frequency,  $d$  is the diameter and  $V_l$  is the volume of the flask

For the emulsion media, the Newton number was estimate using the (Eq.2), it is a correlation proposed by Klöcker and Büch (2012)[77] to estimate the power input in shake flasks.

$$N'_e = 70Re^{-1} + 25Re^{-0.6} + 1.5Re^{-0.2} \quad (2)$$

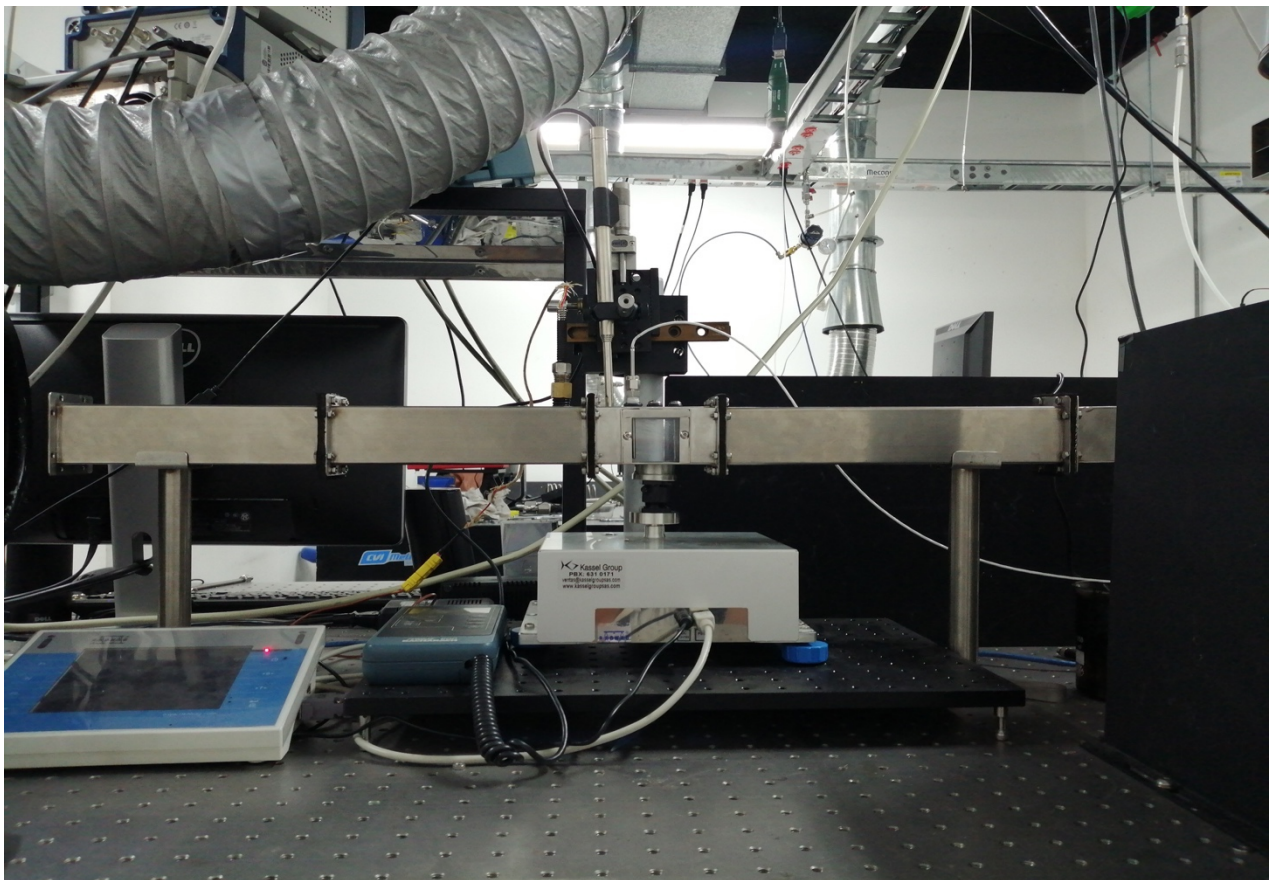
Where  $Re$  is the Reynolds number.

The calculation was made for an emulsified volume of 220ml, the power impress by the shaker was 0.0220 W at 180 rpm. The power impress by the shaker cover the surface near shore and Deep sea wave conditions and was 1 order below for breaking waves, for the study carrie out in this thesis it was a good approximation.

- Breaking waves: 0,22W
- Surface near shore: 0.0000022W
- Deep sea: 0.000000022 W

## Appendix: Wind tunnel

Photograph of the wind tunnel





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