Terminal Velocity of Heavy Crude Oil in Aqueous Solution: Effects of pH and Salinity

Mohamed Azil Zain Zameek¹, Mee Wei Lim¹, Ee Von Lau¹⁺

¹ School of Engineering, Monash University Malaysia, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Abstract. The terminal velocity and the flow behavior of heavy crude oil droplet motion within different aqueous solutions were studied in terms of pH level and aqueous salt concentration. Results showed that the density difference between the oil droplet and the external phase has a significant effect over viscosities and the interfacial tension of each phase. On the other hand, the terminal velocity of oil droplets expresses a negative deviation compared to the theoretical values due to impurities in the aqueous solutions. The present study was conducted for diameters ranging from 5.18 mm to 11.88 mm which resulted in Reynolds number ranging from 590.19 to 1678.18. The transitional phase of deformation for crude oil in pH solutions and salt solutions have been presented as 11-13 mm and 6-8 mm respectively.

Keywords: terminal velocity, heavy crude oil, salinity, interfacial tension

1. Introduction

Crude oil is the most important natural resource of the industrialized nations. As it is such an important resource it is very important to expand our technical ability to discover new sources and extend the production lives of existing oil fields.

The oil magazine has revealed that the unexplored gas and oil potential in the Arctic is about 20% [1]. Furthermore, the effect of climate change which causes the melting of arctic ice will likely be the opening of a vast new drilling territory for countries that are thirsty for oil. However, it is widely agreed by many activists and scholars that there is still limited research done to address any oil spill in salty cold waters should oil drilling be carried out in the Arctic. Hence, it brings the need to research about the movement of a crude oil drops in these conditions.

At present, literature discloses that investigations have been carried out on the movement of oil drops at several conditions than the aforementioned. Almatroushi & Ghannam [2] has carried out a study on droplet motion, surface active material, salt concentrations and polymer concentrations and concluded that the presence of NaCl in the aqueous phase increases the droplet translation velocity for all droplet sizes. Researchers such as Myint et al. [3] and Kurimoto et al [4] claims that the initial shape deformation does not affect the terminal velocity due to strong viscous damping shape oscillations and that the surfactants in the external phase increase the drag co-efficient. Cai et al. [5] deems that the drag coefficient of bubbles increases until the Reynolds number is about 1200, while Borhan & Pallinti [6] claims that the walls of the experimental setups affects the kinetics of the crude oil particle. Extensive research on drop kinetics has been carried out by Clift et al. [7] who demonstrates that the aeration reduces the apparent density which can cause errors while calculating the terminal velocity.

Thus limited studies are known in the area of movement of the crude oil particle in salty cold waters. Hence, this paper aims to investigate the correlation of the terminal velocity of heavy crude oil in terms of the pH levels, Viscosity of crude oil and the salinity of the external phase with a notion of predicting the
movement and flow at different temperatures. This also opens paths to predict the movement through computational simulations in future studies that can be used to predict the flow of crude oil at the event of an oil spill.

2. Materials and Experimental Procedure

2.1. Experimental Procedure

Experiments were conducted in room temperature and at atmospheric pressure. Fig. 1 shows the experimental apparatus. The width, height and depth of the water tank were 0.20, 0.20 and 0.69 m which were large enough to avoid the wall effects [3]. Since all drops in the present experiment rose rectilinearly, two DSLR cameras with a resolution of 8 Mega pixels were stationed as shown. Camera 1 was used to capture the total movement of the oil drop and the time taken was analyzed by using a video editor (Cyber link power Director V8). This camera was stationed 700 mm away from the front face of the tank and was focused to range between 100 mm X 700 mm. Camera 2 was used to capture the crude oil drop at a higher resolution in order to measure the diameter. These diameters were measured using ImageJ-1.49n. This camera was stationed 400 mm away from tank and was focused between a ranges of 20 mm X 80 mm.

Experimental terminal velocities was calculated by the ratio of the length of each segment over the time taken to travel. This experimental procedure was based on studies carried out by Myint et al. [3].

![Experimental setup diagram](image)

**Fig. 1:** Schematic diagram of the experimental set up

2.2. Measurement of Parameters

Viscosities of sample was measured using a DV-III programmable Rheometer. All external phase sample viscosities were measured using Spindle CP 42 which has an operating range of 1.7 mPa.s to 32700 mPa.s. However, only the values between the accepted ranges of 10% -100 % was considered. Viscosities of crude oil samples were measured using the spindle CP 52 which had an operating viscosity range of 49.2 mPa.s to 98300 mPa.s. The experimental data reported is an average of three repeated data.

The interfacial tension of crude oil immersed both in salt water and pH solutions were measured using (goniometer) which has an operating range of drop diameter of 0.1 mm to 3 mm. The average of 500 data points at a time span of 500 s was considered as the IFT at that temperature.
The pH levels were controlled using 2 mol.dm$^{-3}$ of HCl and 0.5 mol.dm$^{-3}$ NaOH solutions. Both pH level and the temperature of sample solutions were measured using (pH Meter). Instrument accuracy is limited to ± 0.01 pH.

Salinity of the solutions were measured in terms of electric conductivity using a HI-9033 multi-range conductivity meter where, the average of three measurements was considered as the electrical conductivity of each sample. A limitation range of 0.001 mS.cm$^{-1}$ to 999 mS.cm$^{-1}$ was used to measure the salinity. However, A considerable fluctuations were observed at lower salinity levels.

2.3. Data Analysis

The velocity of drops in pure water could be expressed as a function of the drop equivalent diameter, $V_\infty$. The subsequent equations (Eq. 2 - 6) were proposed by Clip et al. [8] in order to calculate the terminal velocity in stagnant water.

$$V_\infty = \frac{\mu_f}{\rho_f D^{0.149}} Mo^{-0.149} (J - 0.857) \quad \text{(Eq. 1)}$$

$$\Delta \rho = \left| \rho_w - \rho_f \right| \quad \text{(Eq. 2)}$$

$$H = \left( \frac{4}{3} \right) Eo Mo^{-0.149} \left( \frac{\mu_f}{\mu_w} \right)^{-0.14} \quad \text{(Eq. 3)}$$

$$Eo = \frac{g \Delta \rho D^2}{\sigma} \quad \text{(Eq. 4)}$$

$$Mo = \frac{\mu_f^2 \Delta \rho}{\rho_f \sigma^3} \quad ; \quad \text{(Eq. 5)}$$

$$J = 0.94 H^{0.757} \quad \text{(2 < H ≤ 59.3)} \quad ; \quad J = 3.42 H^{0.441} \quad \text{(H > 59.3)} \quad \text{(Eq. 6)}$$

The theoretical terminal velocity could be further simplified into a mathematical model to obtain a linear regression that could ensure the accuracy of the results (Eq. 7). The constants and values to be adopted are summarized in Eq. 8 and Table I respectively.

$$\log(V_\infty D + 0.857B) = (a + 1) \log D + \log A \quad \text{(Eq. 7)}$$

$$B = \frac{\mu_f}{\rho_f} Mo^{-0.149} \quad \text{(Eq. 8)}$$

| Table I: Values to be substituted by considering the condition |
|----------------------|----------------------|
| When $2 < H < 59.30$ | When $59.3 < H$      |
| $a$ | 0.514 | -0.118 |
| $A$ | 0.94B $\times$ $\left[ \frac{4}{3} \right] Mo^{-0.149} \left( \frac{\mu_f}{\mu_w} \right)^{-0.14} \frac{g \Delta \rho}{\sigma}$ $^{0.757}$ | 3.42B $\times$ $\left[ \frac{4}{3} \right] Mo^{-0.149} \left( \frac{\mu_f}{\mu_w} \right)^{-0.14} \frac{g \Delta \rho}{\sigma}$ $^{0.441}$ |

The proposed deviation between the theoretical and experimental terminal oil velocities are calculated by Eq. 9, while the Re number of the drop is calculated by Eq. 10.

$$Z_m = \frac{V_{\text{theoretical}}}{V_{\text{experimental}}} \quad \text{(Eq. 9)}$$

$$Re = \frac{DV_\infty \rho_f}{\mu_f} \quad \text{(Eq. 10)}$$

3. Results and Discussion

3.1. Effect of pH in External Phase

Table II summarizes the data and the standard deviation which were measured experimentally at room temperature, while Fig. 2 represents the overall motion of terminal velocity respect to the diameter of 80 Cst oil droplets in aqueous solutions with pH ranging from pH 4 to pH 10. It is clearly visible that the terminal velocity increases with the increment of the diameter. However, when the diameter increases, the terminal velocities expresses a negative deviation from the theoretical values as shown in Fig. 2. Similar trends were observed at different pH levels, salinity levels and at crude oil viscosities.

The increasing deviation at larger deviations is suggested to be due to contaminants in the aqueous solutions, whereby these surface active contaminants affects the surface tension forces [8]. Moreover, as the
Reynolds number increases the drop starts to deform. For the present study, the data ranges of diameter, Re, \(E_o\) and \(Z_m\) is shown in Table III. By analyzing the Eotvos number and the corresponding Reynolds number in Table 3, it is understood that a considerable amount of data lies in the transitional phase of deformation, especially between aqueous solutions of pH 4 to pH 6. Thus, the negative deviation has taken place.

### Table II: Summary of oil characteristics with respect to pH and salinity

<table>
<thead>
<tr>
<th>Liquid Phase</th>
<th>Density (g/cm(^3))</th>
<th>Viscosity (mPa.S)</th>
<th>Interfacial Tension (mN/m)</th>
<th>Salinity (mS/cm)</th>
<th>API Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH aqueous solutions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 4</td>
<td>1.010 (0.21)</td>
<td>1.80 (0.30)</td>
<td>2.98</td>
<td>-</td>
<td>2.18 (0.21)</td>
</tr>
<tr>
<td>pH 5</td>
<td>1.006 (0.19)</td>
<td>1.75 (0.06)</td>
<td>18.00</td>
<td>-</td>
<td>2.10 (0.22)</td>
</tr>
<tr>
<td>pH 6</td>
<td>1.007 (0.22)</td>
<td>1.70 (0.23)</td>
<td>32.39</td>
<td>0.017 (0.007)</td>
<td>2.11 (0.21)</td>
</tr>
<tr>
<td>pH 8</td>
<td>1.000 (0.10)</td>
<td>1.13 (0.03)</td>
<td>103.00</td>
<td>-</td>
<td>2.01 (0.19)</td>
</tr>
<tr>
<td>pH 9</td>
<td>0.999 (0.03)</td>
<td>1.10 (0.09)</td>
<td>66.03</td>
<td>-</td>
<td>2.17 (0.31)</td>
</tr>
<tr>
<td>pH 10</td>
<td>0.998 (0.01)</td>
<td>1.08 (0.08)</td>
<td>42.31</td>
<td>-</td>
<td>2.12 (0.10)</td>
</tr>
<tr>
<td>Salt Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>1.016 (0.02)</td>
<td>2.20 (0.03)</td>
<td>18.98</td>
<td>1.333 (0.008)</td>
<td>2.15 (0.02)</td>
</tr>
<tr>
<td>Moderate</td>
<td>1.026 (0.02)</td>
<td>2.38 (0.14)</td>
<td>83.28</td>
<td>13.433 (0.267)</td>
<td>2.05 (0.01)</td>
</tr>
<tr>
<td>High</td>
<td>1.058 (0.02)</td>
<td>2.50 (0.07)</td>
<td>110.66</td>
<td>22.200 (0.200)</td>
<td>2.17 (0.11)</td>
</tr>
</tbody>
</table>

The Data presented is for 80 Cst oil only.

Clip et. al [8] reports that the drag is dominated by deformation over 1.3mm. However, in this experiment crude oil deformation is seen over 11 mm to 13 mm in pH solutions and at a range between 7-8
mm in salt solutions. It’s also apparent that the spherical shapes are seen in lower Eotvos and Reynolds number. This confirms that at higher viscous medium and at higher interfacial tension drop becomes spherical. Thus, this reduces the drag and increases the terminal velocity [9].

A drastic decrease from 1.7 mPa.S to 1.13 mPa.s in viscosity of pH solutions is observed at a pH range 6 to 8 and also seen that the viscosity was a constant in both acidic and alkaline solutions with value of 1.7 mPa.S and 1.1 mPa.S respectively. This occurrence agrees with the trend presented in the literature [10]. On the other hand, the increase in the pH level from pH 4 - 8 of a liquid increases the interfacial tension from 2.98 mN/m to 103 mN/m. However, further increase in pH demonstrated an inverse effect on the interfacial tension between bitumen and water, with a significant decrease to 42.31 mN/m at pH 10. This was attributed to the presence of natural surfactant molecules such as surface active materials carboxylic acids [7]. This phenomena was in good agreement with previous literature works [11]-[13]. The change in the interfacial tension at low pH levels is because of the vicinity of alphaltenes in crude oil. Thus, the drastic decrease is observed at 80 Cst where the higher asphaltene concentration is at the highest [14].

In summary the viscosity of the external phase has decreased, the interfacial tension between the crude oil and the solution has decreased and the density of the external phase has decreased with the augmentation of pH value. For this experiment the terminal velocity is determined by the viscous and inertial conditions [3]. Thus, resulting that the terminal velocity depends on the density and the viscosity of the external phase. Furthermore the Eotvos number has increased with pH, giving notion that the buoyancy forces are dominant.

Consequently, the terminal velocity has decreased with the augmentation of pH level. However, it’s also noted that at constant densities and viscosities the terminal velocity will rise as the pH increases because interfacial tension forces becomes dominant as a result, the Eotvos number increases. As a result, the Reynolds number increases. Thus terminal velocity escalates.

3.2. Effect of Salinity in the External Phase

A considerable increase of the electrical conductivity was observed at the event of increasing the salt concentration. The highest electric conductivity was marked at 22.2 mS/cm and lowest at 0.017 mS/cm. this occurrence completely agrees with the literature with states at the event of augmentation in salt concentration the electric conductivity increases [15]. Moreover, the term salinity refers to the presence of the major dissolved inorganic solutes, essentially Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻, HCO₃⁻, and CO₃⁻, in aqueous samples [16], [17]. Consequently, the salinity has directly influenced the density, viscosity and the interfacial tension of the external phase.

The viscosities of salt samples increased as with respect to the augmentation of salinity of water. Salt sample 4 (High) marked the highest viscosity of 2.50 mPa.s while the salt sample 1 (pH 6) marked the lowest viscosity of 1.70 mPa.S. It was safely assumed that the salt water consists of chemical ion compositions of NaCl, MgCl₂, and KCl accordance to Millero et al. [18]. Thus, the trend agreed well with the literature values presented by Zang et. al [19].

Fig. 3: Measured Terminal Velocities of Various 80 Cst oil droplet diameters in different salt solutions at room temperature
The interfacial tension against the salinity content agrees well with the literature [17]-[20]. The authors clarified that the impurities such as brine solutions and bentonite increases the surface tension when inorganic salts are introduced into the medium since water molecules form a cage like structure bonded by hydrogen molecules, which makes the water molecules intact with the water-oil interface.

The higher interfacial tension is achieved due to the event of salts at the interface turn into negative polarity. Fig. 3 depicts the terminal velocities of 80 Cst oil droplet diameters in different salt solutions at room temperature. It is clearly seen that as the salinity increases, the terminal velocity increases as well.

For the present experimental conditions, it is clear that the terminal velocity is highly dependent on the viscous and inertial forces [3] and also it’s apparent that the Eotvos number has increased. Thus, buoyancy forces become more dominant. Nevertheless, change in the viscosity is negligible compared to the change in the density. Consequently, the terminal velocity has increased with the increment of the density of the external phase. Therefore, it could be concluded that the terminal velocity increases due to salinity. The deviation of the terminal velocity follows the reason due to the contamination effects as explained in the previous section.

4. Conclusions

A range of terminal velocities of heavy crude oil at stagnant aqueous solutions was plotted against its respected diameter at different pH levels, salt solutions and varying crude oil viscosities. All parameters were experimentally measured and have been compared with the literature value. The accuracy of data points have been analyzed by using a mathematical model. The model has resulted with $R^2$ value more than 0.8896. The terminal velocity of heavy crude oil is shown to increase with salinity and decrease with pH and viscosity. However, it is also predicted that the terminal velocity will increase when the viscosities and densities in the external phase become a constant. The drag dominate deformation for crude oil is between a diameter range of 11mm-13mm and it’s between 6 mm to 8 mm for crude oil in salt solutions. The effects of density difference between the drop phase and the external phase towards the terminal velocity of the oil drop has been shown to be more pronounced over other parameters, whereby the terminal velocity is highly governed by the buoyancy effect for heavy crude oil. This occurrence has been apparent in all observations. However, at constant densities and viscosities, the surface tension dominates, resulting in an increase in terminal velocity with decreasing surface tension. As the diameter increases a negative deviation is observed in the terminal velocities due to contaminations. It is noted that this deviation is are prominent at larger diameters.

5. Nomenclature

- $\rho_f$: Density of the continuous phase in kg.m$^{-3}$
- $\mu_f$: Dynamic Viscosity in the continuous phase, in Pa.s
- $\sigma$: Interfacial Tension, in N.m$^{-1}$
- $\Delta \rho$: Absolute value between particle and continuous phase, in kg.m$^{-3}$
- $V_o$: Terminal velocity of drops, in m.s$^{-1}$
- $D_e$: Diameter
- $E_o$: Eotvos Number
- $M_o$: Morton Number
- $Re$: Reynolds Number
- API: American Petroleum Institute
- Cst: Centistokes

6. References


