Oil Behaviour in Freshwater Environments: Weathering and Incorporation into Models

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Overview

- Behaviour in Fresh vs. Salt
- Evaporation
- Emulsification
- Natural Dispersion
- Dissolution
- Others
Fresh vs. Salt

- Most studies carried out on salt water
- …..despite fact that most spills occur in the freshwater environment
- --- but, freshwater spills aren’t that spectacular and don’t attract CNN
- There are some differences – but not completely different behaviours
Behaviour of Oil

- Evaporation is the single-most important component
- Emulsification is the second most important
- Natural Dispersion
- Dissolution
- Photooxidation
- Sedimentation/interaction with particles
- Biodegradation
Evaporation - Old Approach

- Presumed that oil evaporated like water
- Equations included wind speed, area (thickness), scale size, vapour pressure, inverse temperature, etc. etc.
- None of this information is available at a spill
- Further that evaporation should not be inverse of temperature!
New Studies

- Showed that oil evaporation was not air boundary-layer regulated like water.
- Oil evaporation does not increase with area, inversely with thickness, but increases with volume.
- Also found that a new simplified equation could be used.
Findings

- Studies showed that evaporation rate largely governed by temperature and time.
- Evaporation could be described by simple equation such as: \( \text{Evap} = a \times \ln(t) \)
  
  Where:
  - \( a \) = constant
  - \( t \) = time
- On short term basis some oils, eg. diesel fuel, are best modelled using square root of time.
Percentage Lost Through Evaporation (at 15°C)

- Gasoline
- Diesel
- Crude
- Heavy Crude
- IFO
- Bunker C

Time in hours
Distillation Data

- Is readily available because refineries need it
- For many crudes is similar and has similar slopes
- Gasoline and bunkers have different slopes and curve characteristics
- Diesel and similar products have a very narrow boiling range
Prediction Using Distillation

Combining with temperature correlations:

\[ \text{Evap}\% = [0.165(\%D) + 0.45(T-15)]*\ln(t) \]

Where: %D = percentage distilled at 180 °C
T = temperature, Celsius
\( t = \text{time in minutes} \)
Empirical Equations

- Have been developed for over 250 oils and products
- Are also available on web site www.etc-cte.ec.gc.ca/
- EC Continue to measure these
<table>
<thead>
<tr>
<th>Oil Type</th>
<th>Equation</th>
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<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adgo</td>
<td>(%Ev = (0.11 + 0.013T)\sqrt{t})</td>
<td>Jet Fuel (Anch) short term</td>
<td>(%Ev = (1.06 + 0.013T)\sqrt{t})</td>
</tr>
<tr>
<td>Adgo - long term</td>
<td>(%Ev = (0.68 + 0.045T)\ln(t))</td>
<td>Komineft</td>
<td>(%Ev = (2.73 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Alaska North Slope (2002)</td>
<td>(%Ev = (2.86 + 0.045T)\ln(t))</td>
<td>Lago</td>
<td>(%Ev = (1.13 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Alberta Sweet Mixed Blend</td>
<td>(%Ev = (3.24 + 0.054T)\ln(t))</td>
<td>Lago Treco</td>
<td>(%Ev = (1.12 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Amauligak</td>
<td>(%Ev = (1.63 + 0.045T)\ln(t))</td>
<td>Lucula</td>
<td>(%Ev = (2.17 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Amauligak - f24</td>
<td>(%Ev = (1.91 + 0.045T)\ln(t))</td>
<td>Main Pass Block 306</td>
<td>(%Ev = (2.86 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Arabian Medium</td>
<td>(%Ev = (1.89 + 0.045T)\ln(t))</td>
<td>Main Pass Block 37</td>
<td>(%Ev = (3.04 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Arabian Heavy</td>
<td>(%Ev = (1.31 + 0.045T)\ln(t))</td>
<td>Malongo</td>
<td>(%Ev = (1.67 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Arabian Heavy</td>
<td>(%Ev = (2.71 + 0.045T)\ln(t))</td>
<td>Marinus Turbine Oil</td>
<td>(%Ev = (-0.68 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Arabian Light</td>
<td>(%Ev = (2.52 + 0.037T)\ln(t))</td>
<td>Marinus Valve Oil</td>
<td>(%Ev = (-0.68 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Arabian Light</td>
<td>(%Ev = (3.41 + 0.045T)\ln(t))</td>
<td>Mars TLP</td>
<td>(%Ev = (2.18 + 0.045T)\ln(t))</td>
</tr>
<tr>
<td>Arabian Light (2001)</td>
<td>(%Ev = (2.4 + 0.045T)\ln(t))</td>
<td>Maui</td>
<td>(%Ev = (-0.14 + 0.013T)\sqrt{t})</td>
</tr>
</tbody>
</table>
Emulsion Formation

- Not much understood until recently
- Old model equations are totally wrong
- Is somewhat complex and very oil composition dependent
Overview of Stabilization

- There are two fundamental mechanisms by which oil retains water:
  1. Viscosity – water cannot coalesce
  2. Surfactant action of asphaltenes and resins – chemical action
Emulsions have been studied since 1968
Information on how they are formed not clear until early 90’s
Several workers now have many papers on formation mechanisms and stability
Unfortunately – some of older, incorrect hypotheses still float around
Stabilization Mechanisms

- Viscosity – if oil is viscous enough – water droplets injected cannot coalesce or sink through oil mass
- Correspondingly – too little viscosity, the droplets are not held, too much they cannot enter
Oil layer is sufficiently viscous to prevent oil droplets from coalescing.
Surfactant Stabilization

- Resins and asphaltenes act to stabilize water droplets in oil.
- Polar constituents reside in the water and non-polar in the oil, thus locking up the droplet.
- Asphaltenes form much more stable emulsions, but take a longer time to migrate to oil/water interface.
Resins and Asphaltenes Stabilizing Water Droplets in Oil
Asphaltene and Resin Stabilization

- Is aided by viscosity – the water droplets need to be held in place long enough for the surfactants to migrate to the interface.
- Asphaltene migration still continues after one month.
Water Content

- Surfactant stabilized emulsions begin at about 70% - this is the maximum packing of one sphere size inside a space.
- With some water loss this can drop to about 60%.
- With some water particle size differences could be initially as high as 90%.
More on Water Content

- Emulsions therefore have about 60 to 90% water initially - typically 60 to 70% after a period of time.
- Water content less than 60% initially indicates viscosity entrainment of water with little stability – this is not an emulsion.
Types of Water-in-oil States

- Emulsions – two types – stable and meso-stable (defined by how long they last, electric and viscoelastic measurements)
- Entrained – simple viscosity-bound water in oil – lasts only minutes to a few hours
- Unstable – oil that simply doesn’t hold water either way
Studies of Various Types

- Over 200 oils were studied as to type of emulsion they form
- All forms were studied over periods as long as 1 year
- Some stable emulsions have been in lab for over 10 years!
- Studies of real emulsions confirm lab studies
<table>
<thead>
<tr>
<th></th>
<th>Stable</th>
<th>Meso</th>
<th>Entrained</th>
<th>Unstable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/mL</td>
<td>0.85-0.97</td>
<td>0.84-0.98</td>
<td>0.97-0.99</td>
<td>0.8-1.03</td>
</tr>
<tr>
<td>Viscosity mPa.s</td>
<td>15-10000</td>
<td>6-23000</td>
<td>2000-60000</td>
<td>2 - 5.1 X 10^6</td>
</tr>
<tr>
<td>Saturates %</td>
<td>25-65</td>
<td>25-65</td>
<td>19-32</td>
<td>23-80</td>
</tr>
<tr>
<td>Aromatics %</td>
<td>20-55</td>
<td>25-40</td>
<td>30-55</td>
<td>5-12</td>
</tr>
<tr>
<td>Resins %</td>
<td>5-30</td>
<td>6-30</td>
<td>15-30</td>
<td>0-32</td>
</tr>
<tr>
<td>Asphaltenes %</td>
<td>3-20</td>
<td>3-17</td>
<td>3-22</td>
<td>0-32</td>
</tr>
<tr>
<td>Asphaltenes/Resins</td>
<td>0.74</td>
<td>0.47</td>
<td>0.62</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Old Myths

- Waxes have a role.
- All water-in-oil states are emulsions.
- Water content can vary from 0 to 90.
- All emulsions are the same.
- Water content is relevant or a discriminator.
- RIP - hopefully.

US EPA ARCHIVE DOCUMENT
'Emulsion' implies stability and therefore it should only be used for stable or meso-stable emulsions.

- Entrained water states should be called that.

- Very important to distinguish between types because countermeasures depend very much on stability.
### Distinguishing Typical Properties for the Water-in-Oil States

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<th>Meso</th>
<th>Entrained</th>
<th>Unstable</th>
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</thead>
<tbody>
<tr>
<td><strong>Day of Formation Appearance</strong></td>
<td>brown solid</td>
<td>brown viscous liquid</td>
<td>black with large droplets</td>
<td>like oil</td>
</tr>
<tr>
<td><strong>Water Content on first day</strong></td>
<td>%</td>
<td>80</td>
<td>62</td>
<td>42</td>
</tr>
<tr>
<td><strong>Appearance after one week</strong></td>
<td>brown solid</td>
<td>broken, 2 or 3 phases</td>
<td>separated oil and water</td>
<td>like oil</td>
</tr>
<tr>
<td><strong>Water Content after week</strong></td>
<td>%</td>
<td>79</td>
<td>38</td>
<td>15</td>
</tr>
<tr>
<td><strong>Stable time</strong></td>
<td>days</td>
<td>&gt;30</td>
<td>&lt;3</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td><strong>Properties on day of formation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Ratio of Viscosity Increase</td>
<td>1100</td>
<td>45</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td><strong>Properties after one Week</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Ratio of Viscosity Increase</td>
<td>1500</td>
<td>30</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>Properties after one Year</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Ratio of Viscosity Increase</td>
<td>1400</td>
<td>15</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Differences from Salt to Fresh

- Salt water produces more stable emulsions than fresh water
- Paper shows some numeric examples of differences
- Emulsification is not as frequent in freshwater environments – probably because of types spilled more frequently and energy differences
Summary

- Four water-in-oil states exist: stable and meso-stable emulsions, entrained and unstable
- The four states are easily distinguished by: colour, appearance, lifetime, rheological measures
- Each state has a ‘window’ of starting oil viscosity, density, asphaltene/resin content
Natural Dispersion

- Has been studied by Delvigne in Holland and algorithms developed
- These algorithms over-predict what goes into the water
- Much more research needed here
- Problem is measurement and accurate simulation
Natural Dispersion

- Is known to be very significant with light oils in heavy seas – but in freshwater??
- Several spills large dispersed naturally: Braer off Scotland, Ecofisk Bravo blowout in Norway
- Several spills inland have dispersed somewhat in rapid rivers, over dams
- Heavier oils not subject
Dissolution

- No good model
- Solubility of several oils measured
- Solubility of oils ranges from about 1 to 200 ppm – most crudes are in range of 2 to 40 ppm
- Needs more research
Photooxidation

- Poorly understood at this time
- Are some old tid-bits of work – but may not be accurate
- Requires research
Photooxidation

- What is known – does occur with some oils more than others – results in oxygenates which can promote emulsification – products may be more toxic than starting oil
Sedimentation/Interaction with Particles

- Lot of activity lately – but little quantitative prediction work
- It is known in several spills that oil has often sedimented to a large degree (e.g. Amoco Cadiz) – but no good quantitative data at this time
- Relation to freshwater somewhat studied
Interaction with Particles

- Oil-fines interaction has been studied and field kits even available to examine the phenomena
- Oil-fines interaction can remove oil from a slick or even from a shoreline
- No quantitative prediction information available however
- Has been tested on Great Lakes
Biodegradation

- Is a remover of diesel and light fractions
- Effect of biodegradation on old spills can be as little as 1 to 2%
- Asphalt and tar do not readily biodegrade
- Biodegradation competitive to evaporation – especially C12 to C18
- Long-weathered oil can even lose biomarkers to degradation
Closing Remarks

- Behaviour and fate of oil is dominated by the composition – but also a function of the environment
- Differences between fresh and salt water environments are small – but in emulsification may be significant
- Some significant new work which can be incorporated into models