Effects of Mixing Energy and Hydrodynamics on Chemical Dispersion of Crude Oil in Bench-Scale Tests

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Advantages of Bench-Scale Testing

• Useful for empirical testing of dispersant effectiveness
  - screen dispersant-oil combinations
  - evaluate effects of oil weathering and environmental factors

• Simple, inexpensive replication
  - evaluate statistical significance of results
  - accurately reproduce experimental conditions in different labs and at different times

• Check data quality using mass balances
Disadvantages of Bench-Scale Testing

• Bench-scale tests cannot predict effectiveness at sea
  ➢ method for scaling results to predict at-sea performance is not clear
  ➢ energy dissipation rate has been suggested as fundamental scaling parameter

• Relatively poor correlation between effectiveness in different bench-scale tests
  ➢ energy dissipation rates have not been determined for many bench-scale effectiveness procedures at typical operating conditions
  ➢ differences in droplet-formation mechanisms may be responsible for variability among procedures
Objectives

• Measure dispersion effectiveness in two well-characterized experimental systems over wide range of energy dissipation rates

• Evaluate effects of mixing energy and hydrodynamics on droplet-size distributions of dispersed oil
Experimental Conditions

• Crude oil:
  - weathered Mars (Gulf of Mexico; initial API gravity ≈ 30)
  - evaporative mass loss = 18% (final API gravity ≈ 22)
  - oil-water ratio = 1:1200

• Dispersants:
  - sorbitan monooleate (Span 80; HLB = 4.3) and ethoxylated sorbitan monooleate (Tween 80; HLB = 15) in dodecane
    - HLB = 10 and HLB = 12
    - dispersant-oil ratio = 1:25 (pre-mixed)

• Mixing systems:
  - baffled flask and baffled paddle jar
  - mixing energy: 0.00017 to 0.16 J/kg-s
  - mix for 15 minutes; settle for 10 minutes
Baffled Flask
Paddle Jar
Analytical Methods

• Dispersion effectiveness ($\eta$):
  - extract dispersed oil into dichloromethane
  - measure oil concentration by integrated absorbance (340 to 400 nm)

\[
\eta = \frac{M_{\text{oil, extracted}}}{M_{\text{oil, added}}}
\]

• Droplet-size distribution:
  - dispersed oil droplets measured and counted (number distribution) using optical particle counter (OPC)
  - compute volume distribution and dispersed oil volume

• Quality assurance/quality control:
  - mass balances on $\geq 5\%$ of experimental units
  - effectiveness based on dispersed oil volume (OPC) not significantly different from effectiveness based on extraction
Effect of Mixing Energy on Dispersion Effectiveness: Baffled Flask

![Graph showing the effect of mixing energy on dispersion effectiveness. The graph plots dispersion effectiveness (%) against energy dissipation rate (J/kg·s) for HLB 10 and HLB 12.]
Effect of Mixing Energy on Dispersion Effectiveness: Paddle Jar

![Graph showing the effect of energy dissipation rate on dispersion effectiveness for HLB 10 and HLB 12. The graph has a y-axis labeled 'Dispersion effectiveness (%)' ranging from 0 to 100, and an x-axis labeled 'Energy dissipation rate (J/kg*s)' ranging from 0.00 to 0.20.]
Effect of Mixing Energy on Droplet-Size Distributions: Baffled Flask (HLB = 12)
Effect of Mixing Energy on Droplet-Size Distributions: Baffled Flask (HLB = 12)

- 0.0002 J/kg-s
- 0.0005 J/kg-s

Graph showing the relationship between droplet diameter (µm) and the normalized volume fraction of droplets ($V_i / (V_{tot} \Delta d_i)$) for different mixing energies.
Effect of Mixing Energy on Droplet-Size Distributions: Baffled Flask (HLB = 12)

![Graph showing the effect of mixing energy on droplet size distributions for a baffled flask with HLB = 12. The graph plots the volume fraction of droplets (V_i / V_total) against droplet diameter (µm) for different mixing energy levels: 0.0002 J/kg-s, 0.0005 J/kg-s, and 0.016 J/kg-s.](image)
Effect of Mixing Energy on Droplet-Size Distributions: Baffled Flask (HLB = 12)
Effect of Mixing Energy on Droplet-Size Distributions: Swirling Flask (HLB = 12)

![Graph showing droplet diameter distribution](image)
Effect of Mixing Energy on Droplet-Size Distributions: Swirling Flask (HLB = 12)

**Graph:**
- **Y-axis:** $V_i / (V_{tot} \Delta d_i)$ (µm³/ml·µm)
- **X-axis:** Droplet diameter (µm)
- **Legend:**
  - 36 rpm
  - 186 rpm

The graph shows the distribution of droplet sizes for different mixing energies. The data points are presented for two different speeds: 36 rpm and 186 rpm. The distribution peaks at different droplet diameters, indicating the influence of mixing energy on the droplet size distribution.
Effect of Mixing Energy on Droplet-Size Distributions: Paddle Jar (HLB = 12)

Graph showing the droplet diameter distribution for mixing energy of 0.0002 J/kg·s.
Effect of Mixing Energy on Droplet-Size Distributions: Paddle Jar (HLB = 12)

The diagram shows the distribution of droplet diameters in micrometers (µm) for two different mixing energies: 0.0002 J/kg-s (represented by white circles) and 0.0005 J/kg-s (represented by yellow circles). The x-axis represents the droplet diameter in µm, while the y-axis represents the volume fraction of droplets, $V_i/(V_{tot} \Delta d_i)$, in microliters per milliliter ($\mu l/ml$). The graph illustrates how the mixing energy affects the droplet size distribution, with higher energy resulting in a different droplet size profile compared to lower energy.
Effect of Mixing Energy on Droplet-Size Distributions: Paddle Jar (HLB = 12)

![Graph showing the effect of mixing energy on droplet-size distributions. The x-axis represents droplet diameter (μm) ranging from 0 to 100, and the y-axis represents $V_i / (V_{tot} \Delta d_i)$ (μm³/ml-μm) ranging from 0.000 to 0.100. The graph includes lines for different mixing energies: 0.0002 J/kg-s (black dots), 0.0005 J/kg-s (yellow dots), and 0.016 J/kg-s (green dots).]
Effect of Mixing Energy on Droplet-Size Distributions: Paddle Jar (HLB = 12)

![Graph showing the effect of mixing energy on droplet-size distributions. The x-axis represents droplet diameter in micrometers (µm), and the y-axis represents the fraction of total volume (V/V_total). Lines of different colors and markers represent different mixing energies: 0.0002 J/kg-s (black), 0.0005 J/kg-s (yellow), 0.016 J/kg-s (green), and 0.16 J/kg-s (red). The graph illustrates how increasing mixing energy affects the distribution of droplet sizes.]
Effect of Mixing Energy on Droplet Size Modes: Baffled Flask (HLB = 12)
Effect of Mixing Energy on Droplet Size Modes: Paddle Jar (HLB = 12)
Effects of Mixing System and Dispersant HLB on Droplet Size Modes

![Graph showing the effects of mixing system and dispersant HLB on droplet size modes. The graph compares the mean diameter of droplets for different HLB values (10, 12) and mixing systems (Swirling Flask, Baffled Flask, Paddle Jar) for small, medium, large, and extra large droplet sizes. The x-axis represents the HLB values and mixing systems, while the y-axis represents the diameter of mean volume (μm). The graph indicates varying trends in droplet size depending on the HLB and mixing system used.]
Effect of Mixing Energy on Distribution of Oil Among Size Modes: Baffled Flask (HLB = 12)
Effect of Mixing Energy on Distribution of Oil Among Size Modes: Paddle Jar (HLB = 12)
Effect of Mixing Energy on Distribution of Oil Among Size Modes: Swirling Flask

![Graph showing distribution of oil among size modes for different HLB values and rpm settings. The x-axis represents droplet-size mode (small, medium, large, extra large), and the y-axis represents the fraction of initial oil (%). The graph compares four conditions: HLB 10/36 rpm, HLB 10/186 rpm, HLB 12/36 rpm, and HLB 12/186 rpm.]
Conclusions

• Dispersion effectiveness increased with mixing energy but did not necessarily approach 100%.

• Energy dissipation rate alone was not sufficient as scaling parameter.
  - Hydrodynamic differences between baffled flasks and paddle jars resulted in different relationships between mixing energy and dispersion effectiveness.
  - Small differences in dispersant formulation affected performance; relative effectiveness was not consistent across all mixing systems.

• Droplet size distributions were (largely) tri-modal; the means of the major modes were unaffected by mixing energy and mixing system.
  - The distribution of oil among modes was affected by mixing energy and mixing system.
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Questions?
Effect of Mixing Energy on Distribution of Oil Among Size Modes: Baffled Flask (HLB = 10)
Effect of Mixing Energy on Distribution of Oil Among Size Modes: Paddle Jar (HLB = 10)
Effect of Mixing Speed on Dispersion Effectiveness: Swirling Flask

- HLB = 10
- HLB = 12

Mixing speed:
- 36 rpm
- 186 rpm

Dispersion effectiveness (%)
Effect of Mixing Energy on Droplet Size Modes: Baffled Flask (HLB = 10)
Effect of Mixing Energy on Droplet Size Modes: Paddle Jar (HLB = 10)