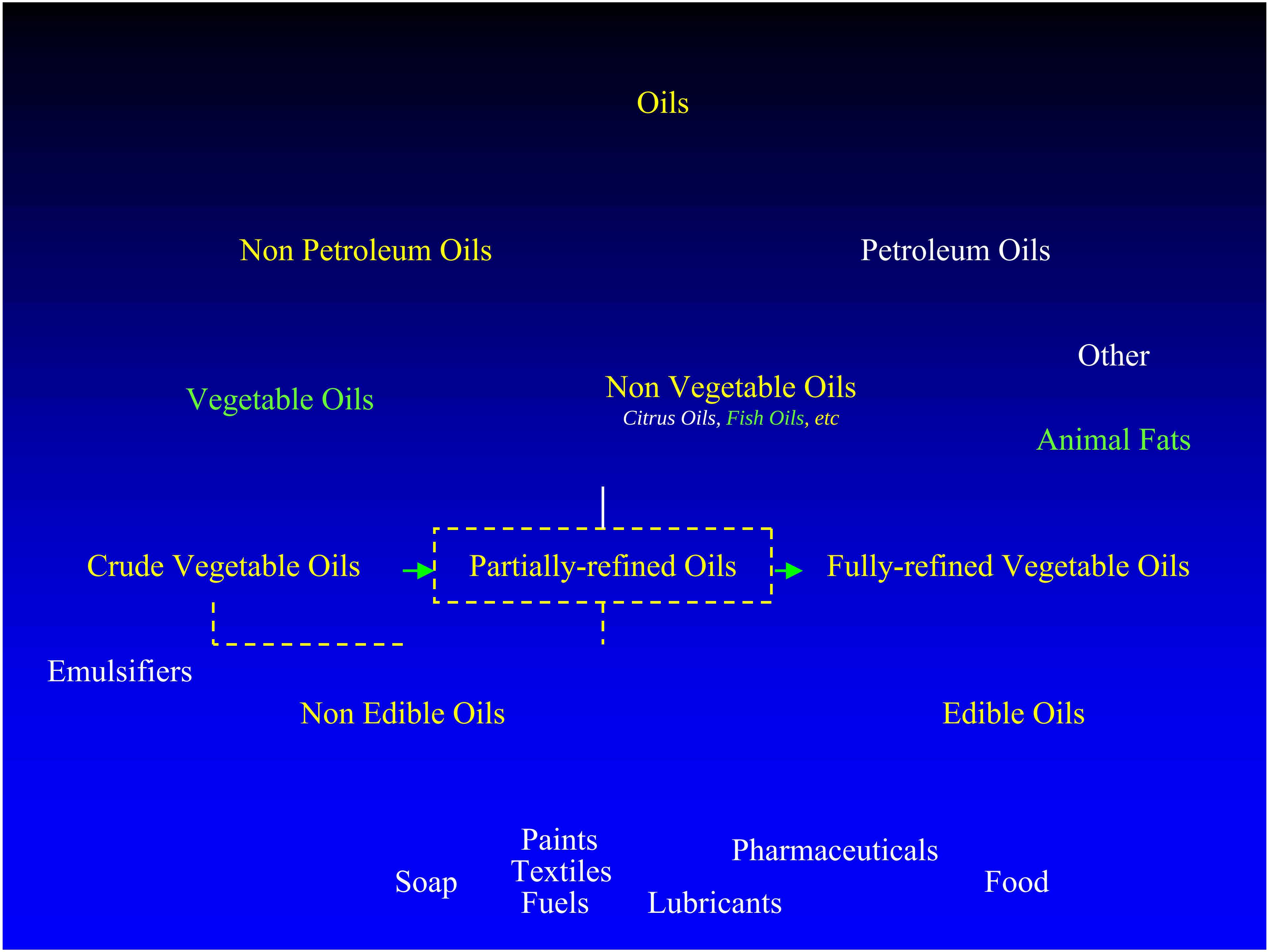
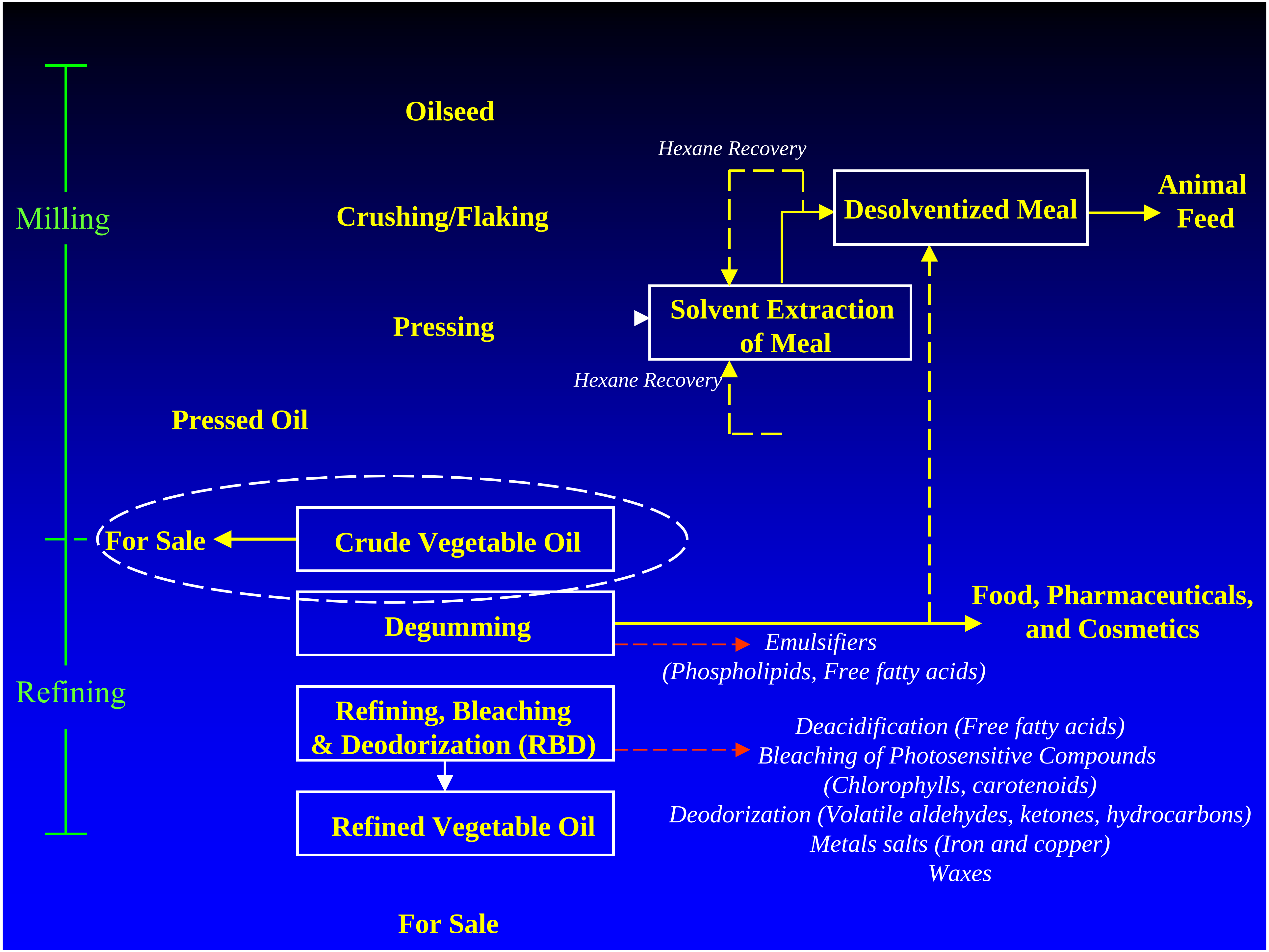
Consideration of Characteristics Influencing the Emulsification Factors for Vegetable Oil Spills

Greg Wilson, Ph.D.
Research Associate University of Cincinnati

Applicability of Emulsification Factors

- 40 CFR 112 Appendix E – Reponses Resources for FRPs
  - Table 7 – Emulsification Factors for AFVOs
- Used to calculate planning volumes for Worst Case Discharges (WCDs) – Appendix D
  - Accounts for increase in volume that results when discharged oil forms emulsions
- On-water recovery volume
  - WCD x (% Recovered Floating Oil) x (Emulsification Factor)
- Shoreline cleanup volume
  - WCD x (% Recovered Oil from Onshore) x (Emulsification Factor)


Oils
Non Petroleum Oils
Petroleum Oils
Other
Vegetable Oils
Non Vegetable Oils
Citrus Oils, Fish Oils, etc
Animal Fats
Crude Vegetable Oils
Partially-refined Oils
Fully-refined Vegetable Oils
Emulsifiers
Non Edible Oils
Edible Oils
Paints
Textiles
Fuels
Soap
Pharmaceuticals
Lubricants
Food


Milling
Refining
Oilseed
Crushing/Flaking
Pressing
Pressed Oil
Hexane Recovery
Desolventized Meal
Animal Feed
Solvent Extraction of Meal
Hexane Recovery
For Sale
Crude Vegetable Oil
Degumming
Food, Pharmaceuticals, and Cosmetics
Emulsifiers
(Phospholipids, Free fatty acids)
Refining, Bleaching & Deodorization (RBD)
Deacidification (Free fatty acids)
Bleaching of Photosensitive Compounds
(Chlorophylls, carotenoids)
Deodorization (Volatile aldehydes, ketones, hydrocarbons)
Metals salts (Iron and copper)
Waxes
Refined Vegetable Oil
For Sale

Why study crude vegetable oils?

- Oilseed milling facilities produce crude vegetable oils
- Milling processes are often separate from refining processes
- Thus, crude vegetable oils may be transported to refining facilities
- Crude vegetable oils are often transported in bulk through waterways

Crude vegetable oil composition

- Triglycerides
- Free fatty acids *(organic acids)*
- Metal salts
  - Iron, copper
- Photosensitive compounds
  - Chlorophylls, carotenoids
- Phospholipids
  - Phosphatides *(inositol, serine, ethanolamine, choline)*
- Tocopherols *(Vitamin E)*
- Plant sterols *(phytosterols)*
- Sulfur

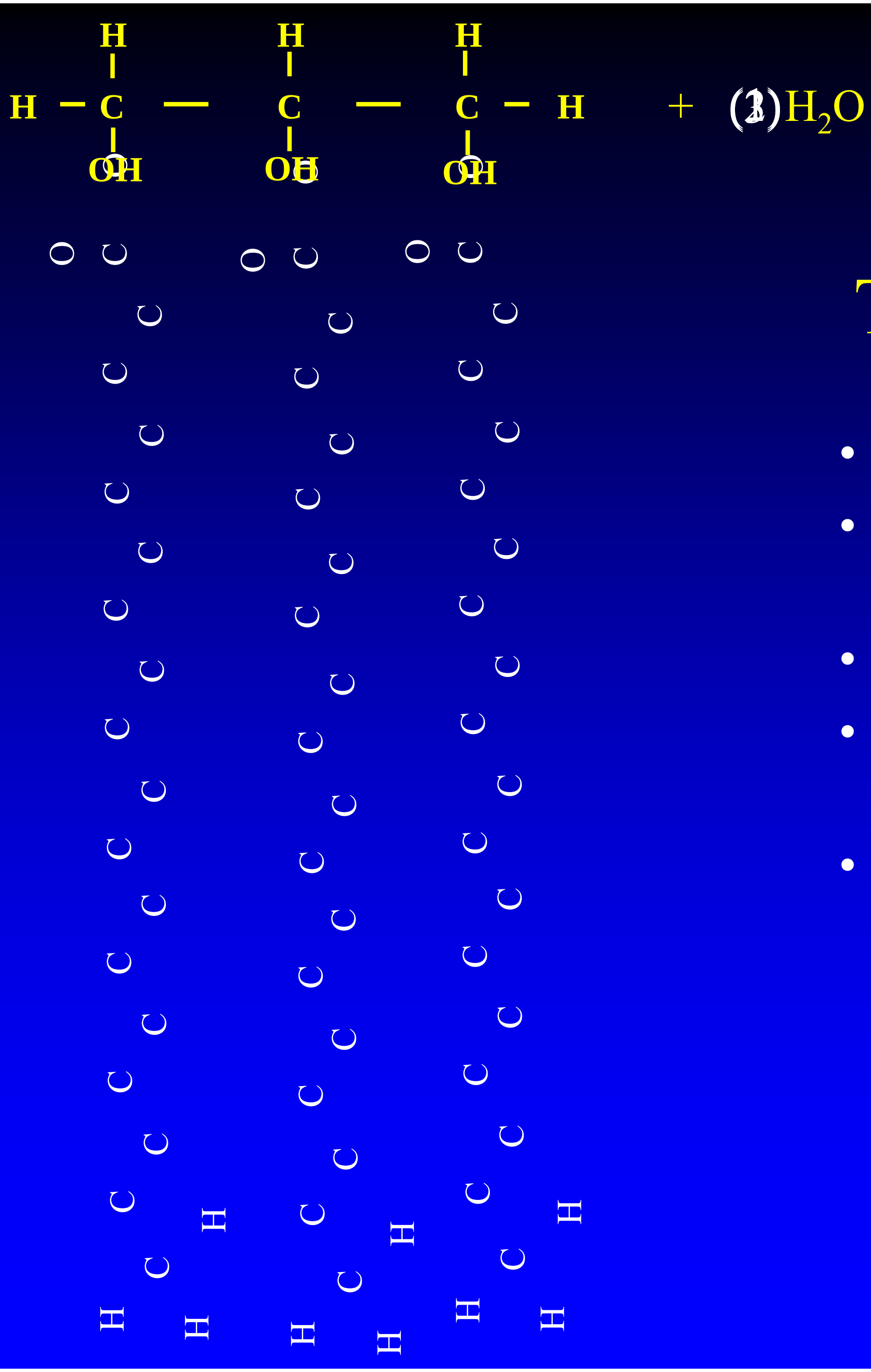
In the presence of oxygen, these compounds reduce the oxidative stability of unsaturated oils via autocatalytic and photocatalytic reactions

Partially-refined vegetable oils

- Usually degummed with some RBD
- May need further processing before use

Fully-refined vegetable oils

- RBD-processed oils



Triglycerides

- Triacylglycerols (TAGs)
- ~ 95% composition of crude vegetable oil
- Glyceryl esters of fatty acids
- Fatty acid composition makes the type of vegetable oil unique
- Fatty acid composition can vary with cultivar

Compounds in crude vegetable oils that have amphiphilic properties

- Phospholipids
  - Phosphatidyl Choline
  - Phosphatidyl Inositol
  - Phosphatidyl Ethanolamine
  - Phosphatidyl Serine
  - Phosphatidic Acid
- Glycerophospholipids
- Free Fatty Acids
- Monoacylglycerols (MAGs) and Diacylglycerols (DAGs)

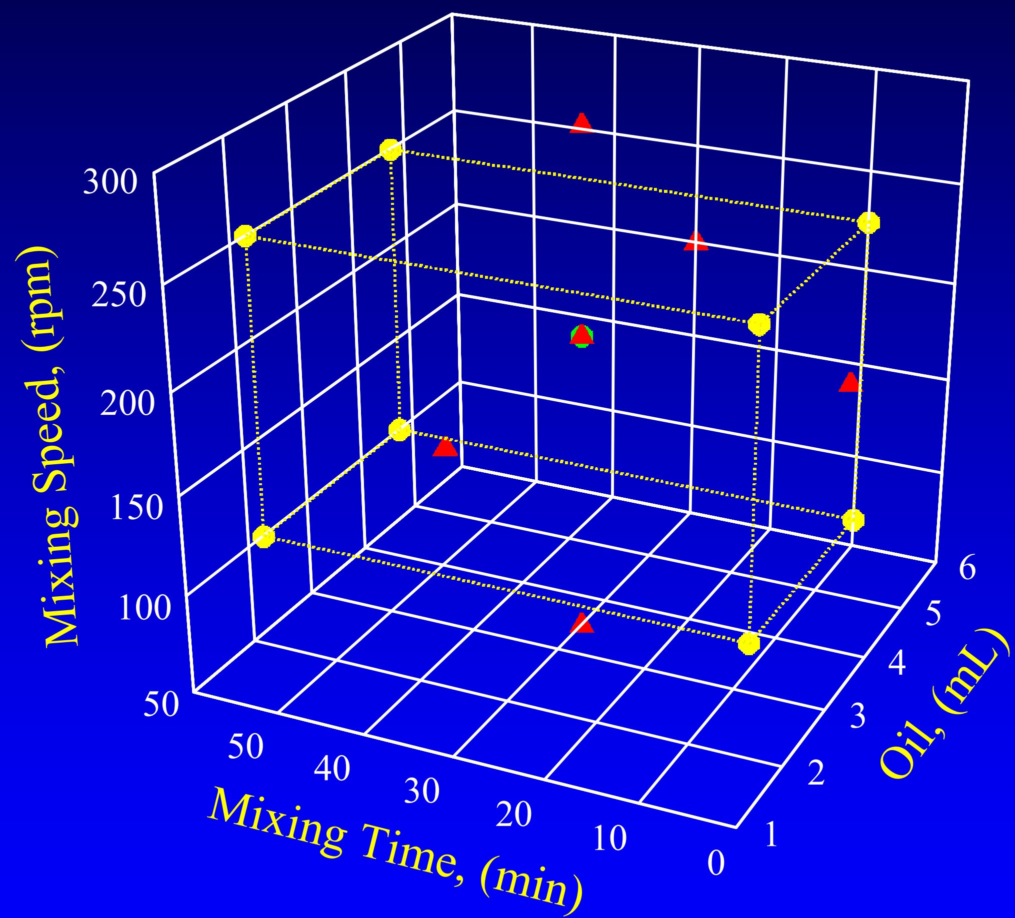
Experimental Setup
“modified” Central Composite Design

- Widely used technique in exploratory experiments
- Central Composite Designs (CCD) are good screening tools
- Multiple independent factors can be evaluated from few sampling events
- Data can be fitted to a response surface model to identify key factors
- Eliminating unresponsive factors allows researchers to refocus limited resources
- This experimental setup used a “modified” CCD design: “star” elements are offset

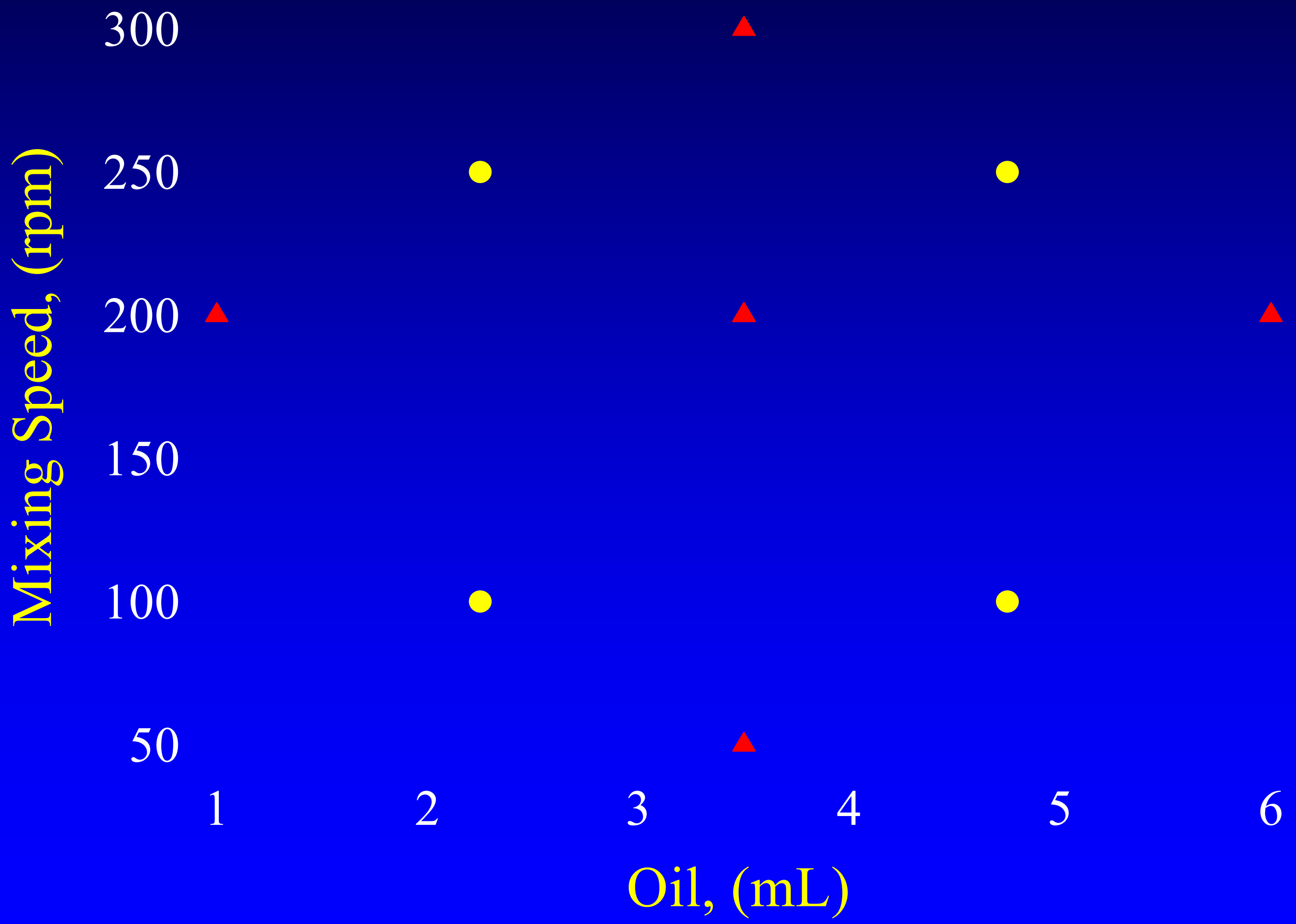
Experimental Setup: Factors Considered

- Five factors considered
  - Mixing time (1, 5, 30, 60, 180 minutes)
  - Mixing speed (50, 100, 200, 250, 300 rpm)
  - Oil:water ratio (1.00, 2.25, 3.50, 4.75, 6.00 mL oil) : (30 mL water)
  - Salinity (0, 16, 32 g/L NaCl)
  - Temperature (10^{o}C and 25^{o}C)
- Main elements = 2^k
- Since temperature is considered separately, k = 4
- 8 elements apiece at 0 and 32 g/L salinity satisfy the 2^k requirement
- "Star" elements = 2k - 1(or 7), satisfied at 16 g/L salinity
- Two "center" points for 0 and 32 g/L salinities
- Total of 25 samples (or elements) for each experimental run

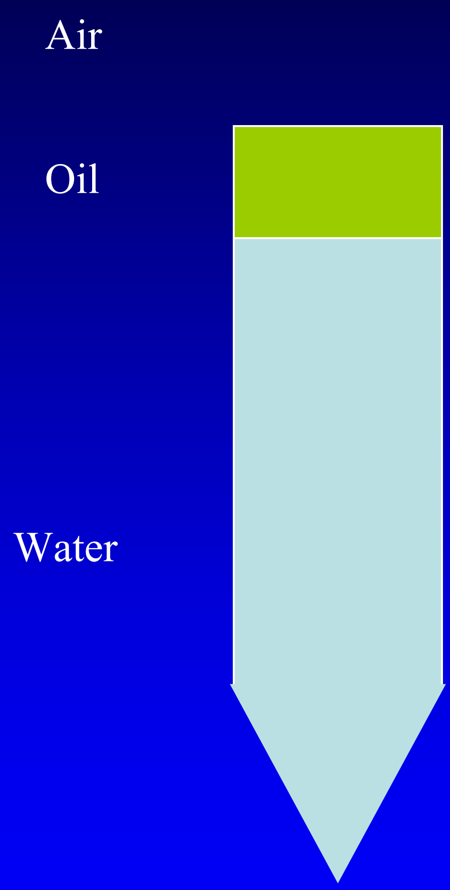
Experimental Design: mCCD



Experimental Design: mCCD - Plane View

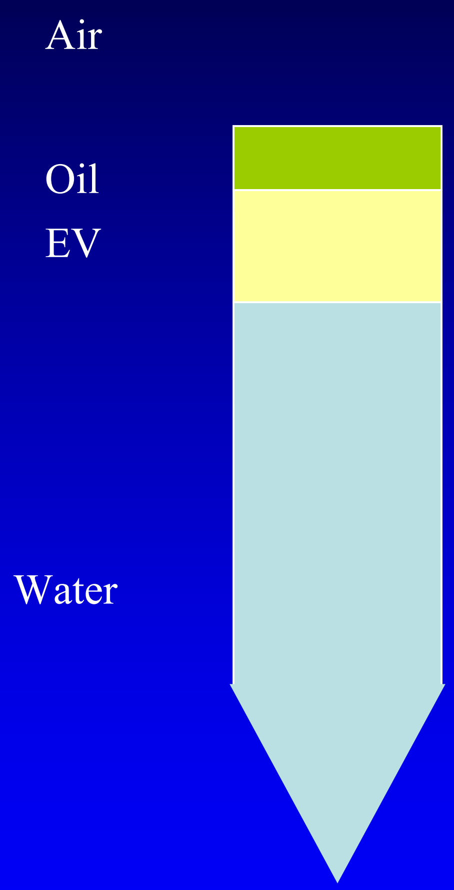


Initial Conditions



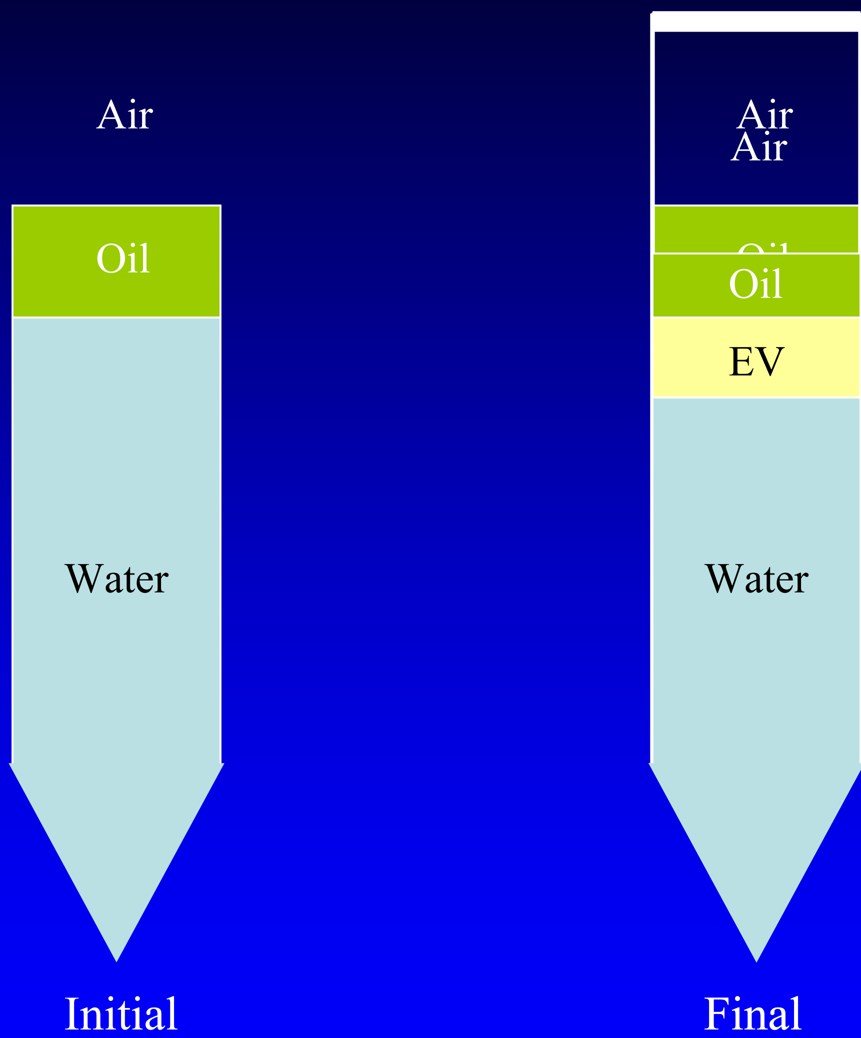
- Five vegetable oils
  - Canola, cottonseed, corn, soybean, peanut, sunflower
- Two petroleum oils
  - South Louisiana Crude, No. 2 Fuel Oil
- Water = 30 mL
- Oil = 1.00, 2.25, 3.50, 4.75, or 6.00 mL Oil
- Air = balance

Analyses



- Each sample was allowed to settle for one hour prior to analyses
- Dissolved organic carbon (DOC) in the water phase was measured
- Emulsification volume (EV) was recorded

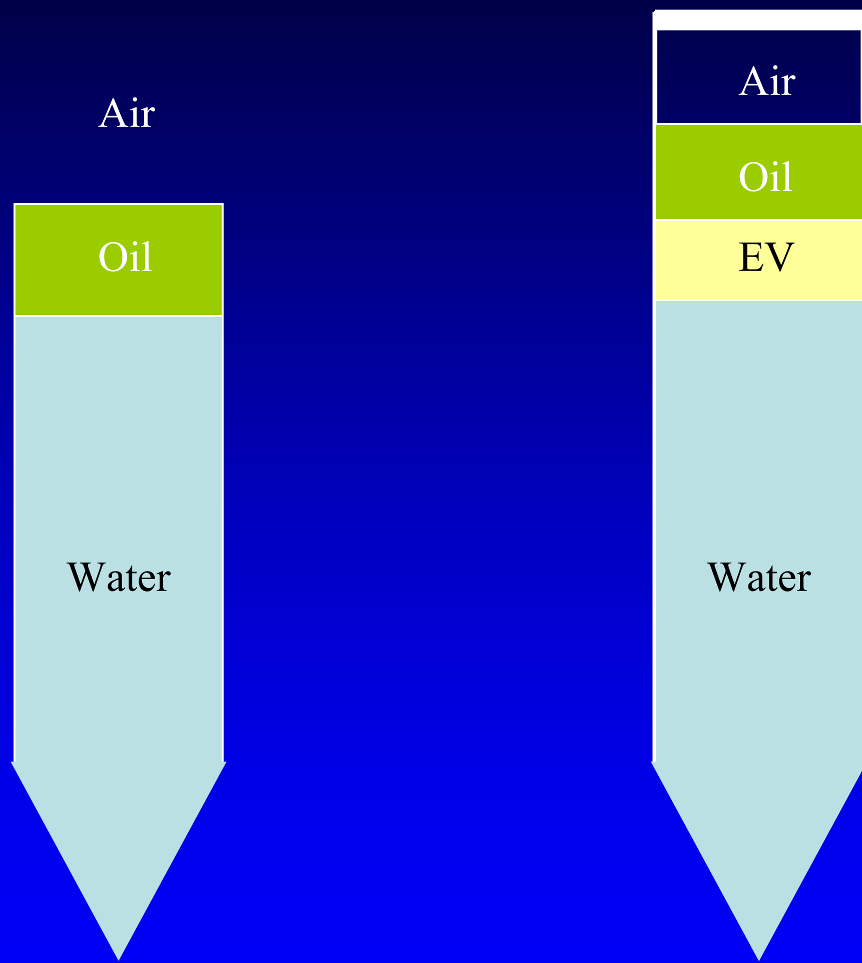
Possible Outcomes



Water-in-Oil (w/o) emulsion
Leak

Oil-in-Water (o/w) emulsion

Possible Outcomes



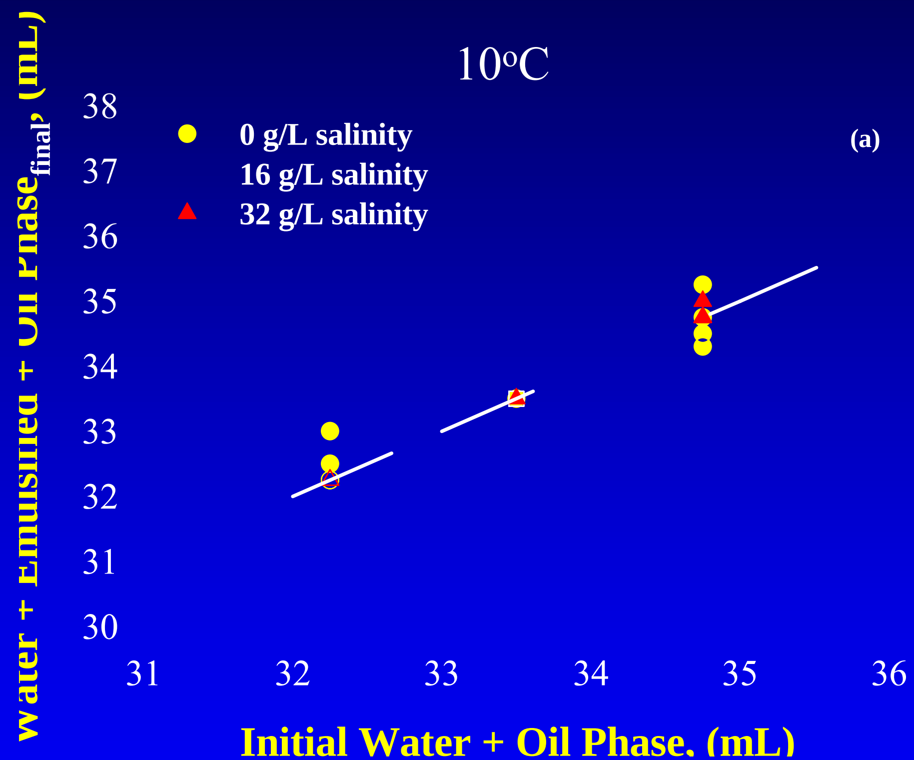
Initial

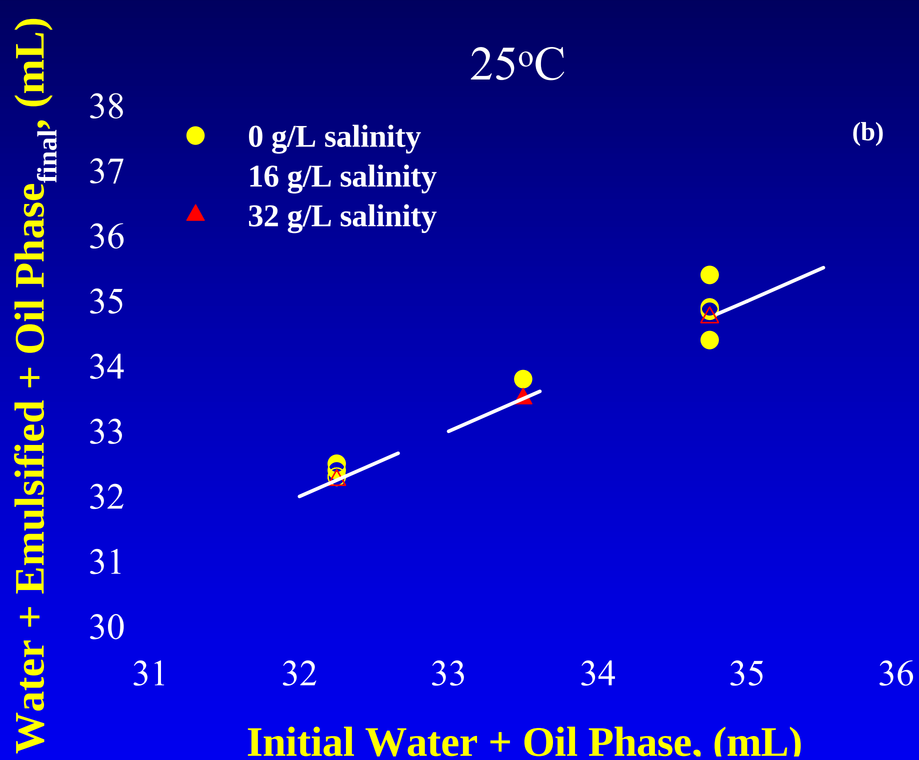
Final

Air entrainment

$$\Sigma\,(\mathrm{Vol}_{\mathrm{Oil}} + \mathrm{Vol}_{\mathrm{Water}})_{\mathrm{Initial}} \leq \Sigma\,(\mathrm{Vol}_{\mathrm{Oil}} + \mathrm{Vol}_{\mathrm{Water}} + \mathrm{Vol}_{\mathrm{EV}})_{\mathrm{Final}}$$

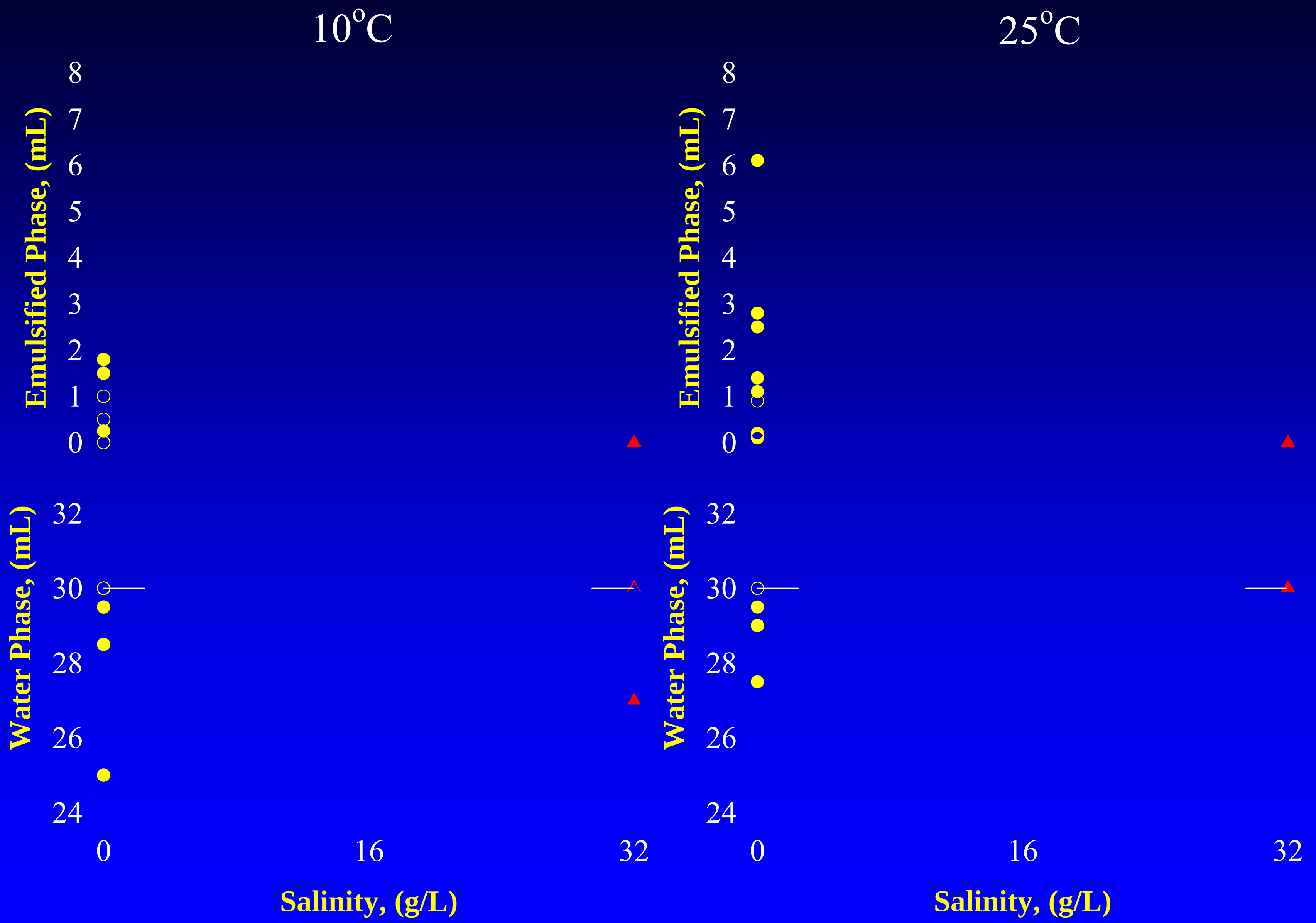
Canola oil



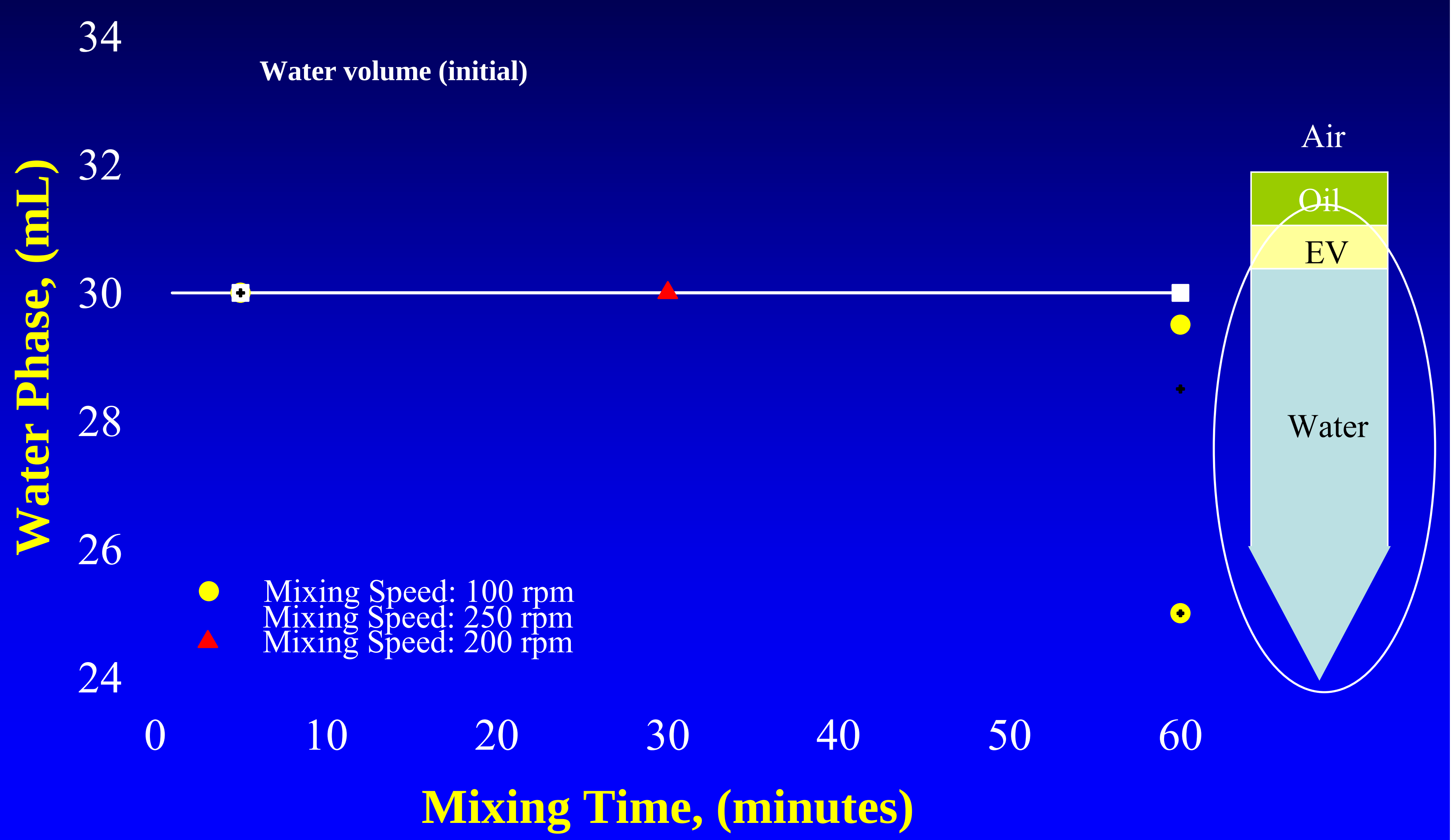


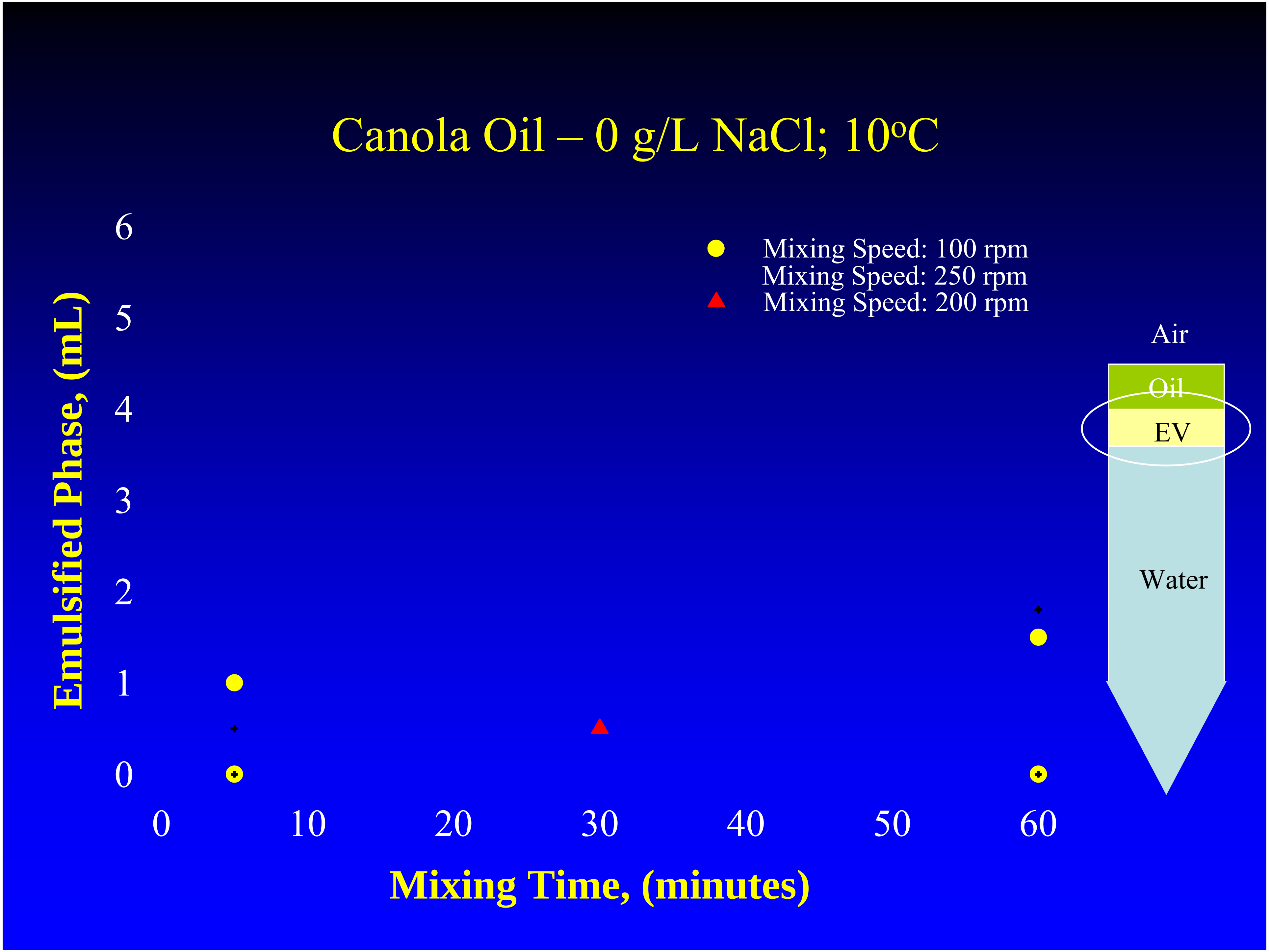
$$\Sigma\,(Vol_{Oil} + Vol_{Water})_{Initial} \leq \Sigma\,(Vol_{Oil} + Vol_{Water} + Vol_{EV})_{Final}$$

Effect of Salinity on Emulsification: Canola Oil

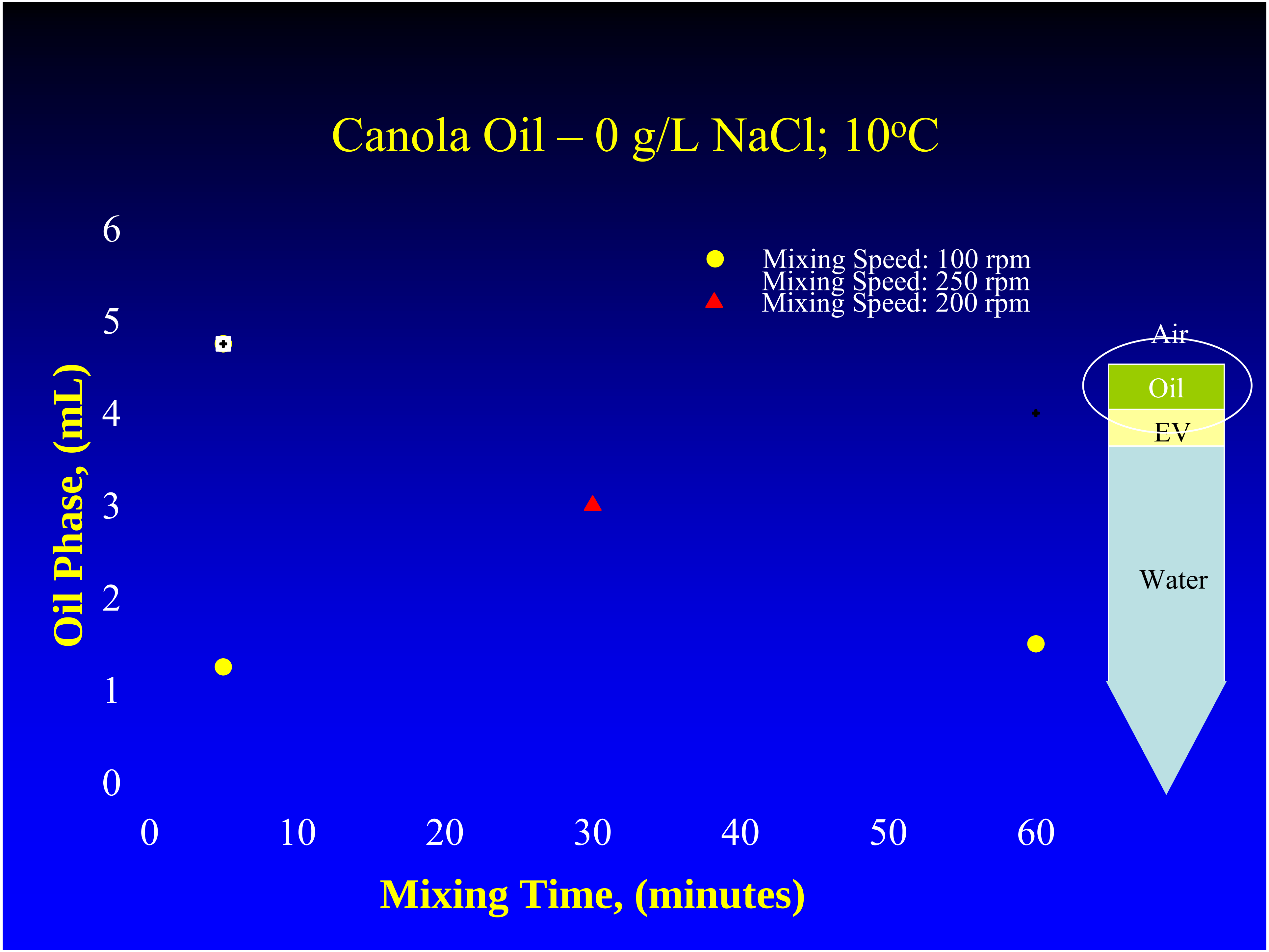


Canola Oil – 0 g/L NaCl; 10°C



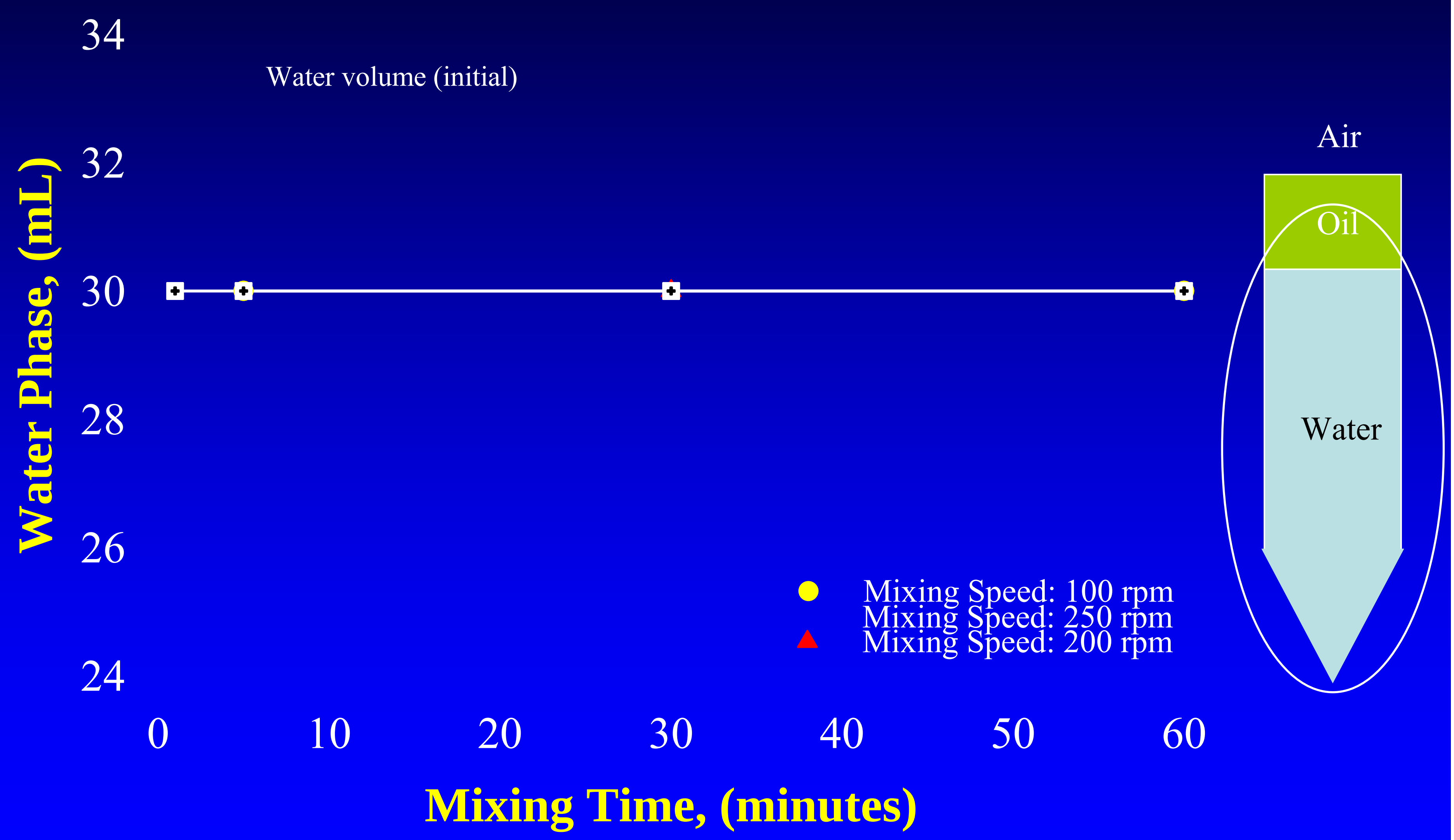


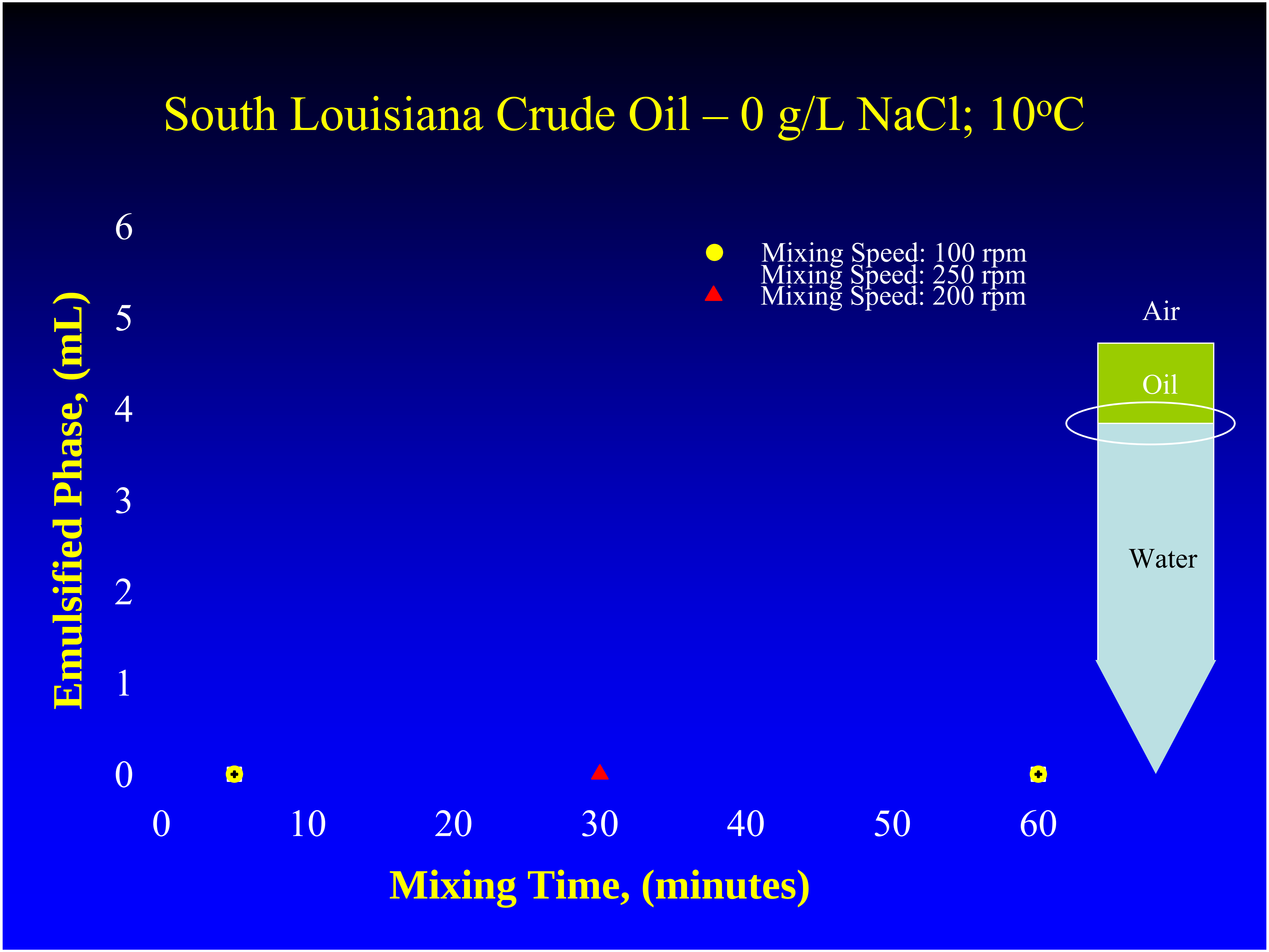
Canola Oil – 0 g/L NaCl; 10oC
Emulsified Phase, (mL)
6
5
4
3
2
1
0
Mixing Speed: 100 rpm
Mixing Speed: 250 rpm
Mixing Speed: 200 rpm
Air
Oil
EV
Water
0
10
20
30
40
50
60
Mixing Time, (minutes)



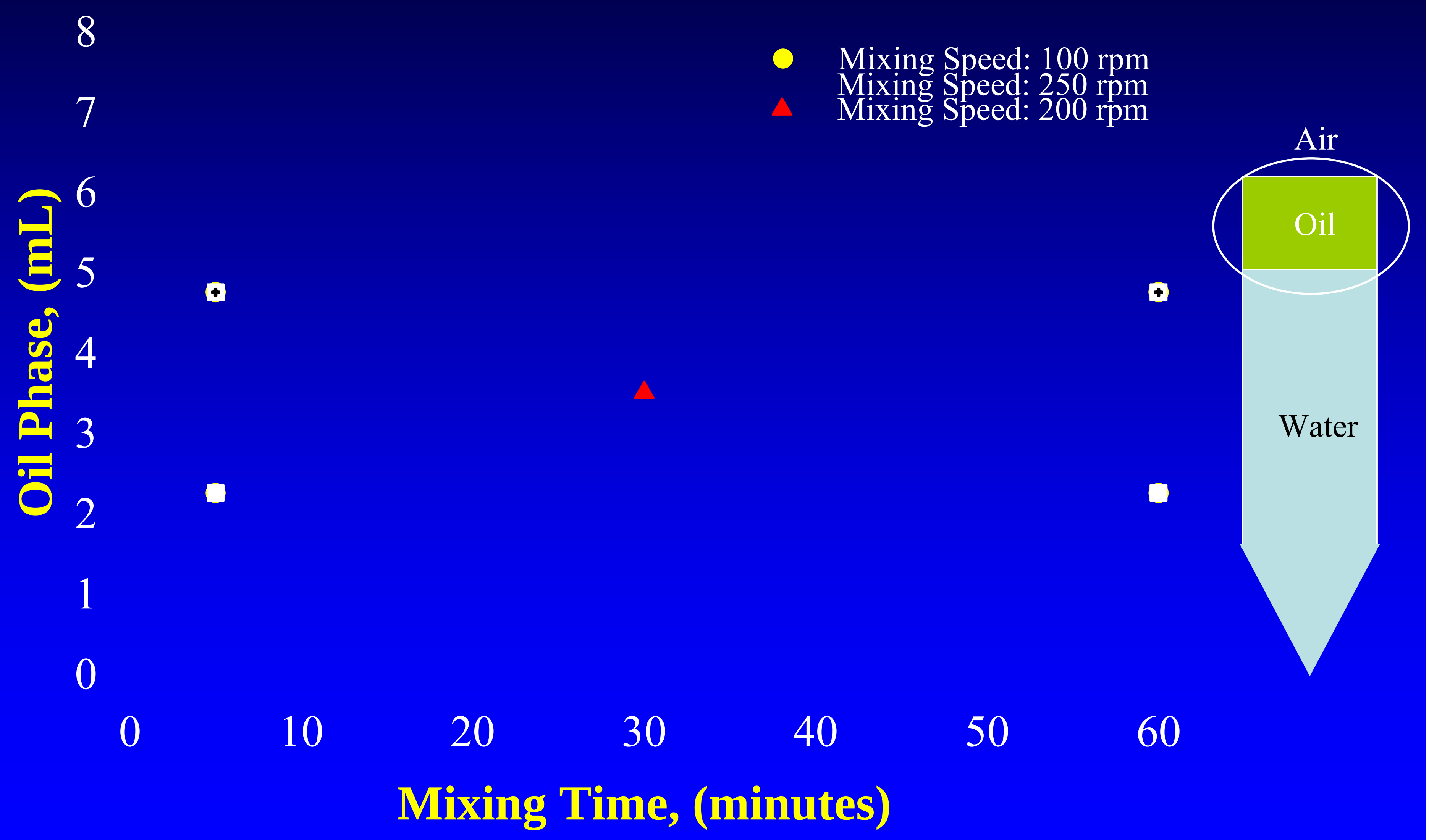
Canola Oil – 0 g/L NaCl; 10oC
Mixing Speed: 100 rpm
Mixing Speed: 250 rpm
Mixing Speed: 200 rpm
Air
Oil
EV
Water
Oil Phase, (mL)
Mixing Time, (minutes)
0
1
2
3
4
5
6
0
10
20
30
40
50
60

South Louisiana Crude Oil – 0 g/L NaCl; 10°C




South Louisiana Crude Oil – 0 g/L NaCl; 10oC
Mixing Speed: 100 rpm
Mixing Speed: 250 rpm
Mixing Speed: 200 rpm
Air
Oil
Water
Emulsified Phase, (mL)
0
1
2
3
4
5
6
0
10
20
30
40
50
60
Mixing Time, (minutes)

South Louisiana Crude Oil – 0 g/L NaCl; 10^{o}C



Summary of results

- Data suggest a correlation between the volume of emulsified oil and the measured dissolved organic carbon
- Mixing time and salinity are important factors for emulsification
- Highest emulsification volumes were observed at the lowest salinity
- EV and DOC values for the petroleum oils were smaller than that for the vegetable oils

What is needed to determine Emulsification Factors

- Characterization of crude vegetable oils is needed
    - Identify emulsifying agents prior to experimental use
- Compare results from crude vegetable oil experiments with similar experiments using refined vegetable oils of similar triglyceride composition
- Consider longer mixing time
- Determine the effect of water hardness on emulsification
- Consider coconut and palm oils for high salinity experiments

Acknowledgment

- Original experimental data provided by Battelle