Tier II Results for Multimedia Risk Assessment of Biodiesel: Relative Mobility, Biodegradation, and Aquatic Toxicity

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Multimedia Risk Assessment
Tier I
Tier II
Tier III

Tier 1 Preliminary Review
- Define framework and approach
- Identify information needs and gaps
- Peer review

Tier 2 Multimedia Risk Assessment Design Review
- Experimental design developed and submitted
- Design peer reviewed,
- Feedback provided for Tier 3

Tier 3 Final Multimedia Risk Review
- Final report is used as the basis for recommendations submitted to the Environmental Policy Council
- Final report is peer reviewed

1 http://www.arb.ca.gov/fuels/multimedia/multimedia.htm
2 http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm
Multimedia Risk Assessment\(^1\)
Tier II\(^2\)
Experiments Performed

- **Mobility**
  - Side-by-side infiltration in 2D “ant farm” flow cells

- **Biodegradation Tests**
  - Microcosm respirometry in soil slurry, 29 day

- **Aquatic Toxicity**
  - Suite of freshwater/estuarine toxicity tests

1 [http://www.arb.ca.gov/fuels/multimedia/multimedia.htm](http://www.arb.ca.gov/fuels/multimedia/multimedia.htm)
2 [http://www.arb.ca.gov/fuels/diesel/diesel/biodiesel.htm](http://www.arb.ca.gov/fuels/diesel/diesel/biodiesel.htm)

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### Mobility

#### Fuel Blends

<table>
<thead>
<tr>
<th>Type</th>
<th>Blendblock</th>
<th>Total</th>
<th>Soro</th>
<th>Briland</th>
<th>Querry</th>
<th>Shearing</th>
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</thead>
<tbody>
<tr>
<td>RSOI</td>
<td>Soy</td>
<td>3</td>
<td>3</td>
<td>50 mL/min</td>
<td>50 mL/min</td>
<td></td>
</tr>
<tr>
<td>RSOI</td>
<td>Soy</td>
<td>3</td>
<td>3</td>
<td>50 mL/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSE</td>
<td>Soy</td>
<td>3</td>
<td>3</td>
<td>50 mL/min</td>
<td></td>
<td></td>
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<tr>
<td>LASSI</td>
<td>Petroleum</td>
<td>15</td>
<td>15</td>
<td>50 mL/min</td>
<td></td>
<td></td>
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</tbody>
</table>

Note: experiments are side-by-side comparison between ULSD#2 and Diesel w/ or w/o additive for consistency of sand construction.

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### Mobility

- Image analysis of biodiesel vertical infiltration in Sandbox
  - 50x20x2cm, #20 (course) sand, water table
  - Soy- and Animalfat-based 100% and 20% blends, 1 additive

- Sandbox preparation
  - Wet-pluviated sand
  - Drain to water table
  - simultaneous 50mL ULSD#2 and biodiesel side-by-side, both dyed

- Data collected
  - infiltration rate in vadose zone
  - redistribution
  - lens form & surface area, on water table
**Mobility**

Sample Results
Final Lenses

- Soy B20 least different

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**Summary**

- Minor differences in travel times
- AF B100a only shows moderate differences
  - Thicker lens formation
  - More residual

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**Mobility**

Sample Results
Final Lenses

- Animalfat B100
  - Strongest effect
  - Similar travel times
  - Less lateral dispersion
  - Thicker, deeper lens
  - More residual, less sfc area

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**Mobility**

Sample Results
Final Lenses

- Soy B20a CARB ULSD#2

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**Mobility**

Sample Results
Final Lenses

- AF B100a CARB ULSD#2

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Mobility

- Minor differences in travel times
- AF B100a only shows moderate differences
  - thicker lens formation
  - more residual
- Interfacial Tensions (mN/m):
  - ULSD: 7.4
  - Soy (B20/B100): 8.5/12.0
  - AF (B20/B100): 15.0/19.5
- Viscosity

Summary

- Soy- and Animalfat-based 100% and 20% blends, 2 additives
- Microcosm preparation
  - 250 mL flask that consists of 200 mL mineral medium
  - 2 g soil (Yolo silt loam) as bacterial inoculums
  - 5uL of test substrate
- For each fuel type:
  - triplicate batch
  - one sterile control (1% sodium azide) - showed no CO2.

Biodegradation Tests

- 29-day Respirometry using soil slurry inoculum
- Microcosm preparation
- For each fuel type:
  - triplicate batch
  - one sterile control (1% sodium azide) - showed no CO2.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Fuel Type</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Soy biodiesel 20% blend + inoculum</td>
<td>ULSD + soy 20%</td>
<td>soy 20 A</td>
</tr>
<tr>
<td>1B</td>
<td>Soy biodiesel 10% blend + inoculum</td>
<td>ULSD + soy 10%</td>
<td>soy 10 A</td>
</tr>
<tr>
<td>2A</td>
<td>Animal fat biodiesel 20% blend + inoculum</td>
<td>AF 9-20 A</td>
<td>AF 9-20 A</td>
</tr>
<tr>
<td>2B</td>
<td>Animal fat biodiesel 10% blend + inoculum</td>
<td>AF 9-10 A</td>
<td>AF 9-10 A</td>
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<tr>
<td>3A</td>
<td>Soy biodiesel 20% blend + sterile + inoculum</td>
<td>soy 20 AA</td>
<td>soy 20 AA</td>
</tr>
<tr>
<td>3B</td>
<td>Soy biodiesel 10% blend + sterile + inoculum</td>
<td>soy 10 AA</td>
<td>soy 10 AA</td>
</tr>
<tr>
<td>4A</td>
<td>Animal fat biodiesel 20% blend + sterile + inoculum</td>
<td>AF 9-20 AA</td>
<td>AF 9-20 AA</td>
</tr>
<tr>
<td>4B</td>
<td>Animal fat biodiesel 10% blend + sterile + inoculum</td>
<td>AF 9-10 AA</td>
<td>AF 9-10 AA</td>
</tr>
</tbody>
</table>
Biodegradation Tests

Results

Biodegradation Tests

29Day Cumulative degradation percentages

Biodegradation Tests

Summary

• All fuel blends more readily degradable than ref. fuel
• Soy-based blends somewhat more degradable than Animalfat-based blends
• 20% biodiesel blends somewhat more degradable than 100% biodiesel
• Additives effect are minor
Aquatic Chronic Toxicity Tests

- 6 fuel blends
- 3 freshwater and 3 estuarine organisms
- 6 dilutions plus a control per species/fuel
- Using published USEPA chronic toxicity testing protocols
- “100% solutions” produced using the “slow stir” method, defining equilibrium solubility conditions
- All tests met protocol QA/QC requirements

Aquatic Chronic Toxicity Tests

Details

6 Blends in addition to reference fuel (ULSD)
- Animalfat biodiesel (100% 20%, 20% w/additive)
- Soy biodiesel (100% 20% 20% w/additive)

100% solubility solution by slow stir method
- solutions 100%, 50%, 25%, 10%, 5%, and 1%, w/stock
- 2 samples/test archived frozen for later analysis
- Replicates for particular combinations.

Interpolate among dilutions to determine EC<sub>25</sub>
- “Toxicity” asTU = 100/EC<sub>25</sub>
  - TU<1 no effects
  - TU<1 effects seen only at 100% solution
  - TU<100 effects seen at 1% solution

Aquatic Chronic Toxicity Tests

Fuel Blends

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Ultra Low Sulfur Diesel</td>
<td>ULSD</td>
</tr>
<tr>
<td>100% Soy Biodiesel</td>
<td>Soy B-120</td>
</tr>
<tr>
<td>30% Biodiesel + 70% ULSD (w/w)</td>
<td>Soy B-20</td>
</tr>
<tr>
<td>20% Biodiesel + 80% ULSD (w/w) amended with additive</td>
<td>Soy B-25A</td>
</tr>
<tr>
<td>100% Animal Fat Biodiesel</td>
<td>AT B-120</td>
</tr>
<tr>
<td>20% Animal Fat Biodiesel + 80% ULSD (w/w)</td>
<td>AT B-20</td>
</tr>
<tr>
<td>30% Animal fat + 70% ULSD (w/w) amended with additive</td>
<td>AT B-25A</td>
</tr>
</tbody>
</table>
Aquatic Chronic Toxicity Tests

Test Species

- ULSD - low but detectable toxicity on mysid growth (1.0 TU) and Ceriodaphnia reproduction (1.8 TUc) only.
- No unadditized Animalfat or Soy Biodiesel blends produced detectable toxicity to the mysid, topsmelt or fathead minnow.
- Animal Fat and Soy B-100 and B-20 mixtures caused toxicity to algae cell growth, abalone shell development, and Ceriodaphnia survival and/or growth.
- Except for algae, the additized Biodiesel B-20 test materials were substantially more toxic than the corresponding unadditized material.

Aquatic Chronic Toxicity Tests

Examples

Red Abalone (Haliotis Rufecens) shell development
Aquatic Chronic Toxicity Tests

Examples

Water flea (Ceriodaphnia dubia) survival and reproduction

Aquatic Chronic Toxicity Tests

Summary Toxicity with additive

Toxicity apparent in all 6 species per growth endpoint

Aquatic Chronic Toxicity Tests

Summary

- Biodiesel blends are significantly more toxic than CARB ULSD#2
  - algae cell growth
  - abalone shell development
  - Ceriodaphnia survival and growth

- Biodiesel 20% blends with antioxidant additive were substantially more toxic than the corresponding unadditized blend
  - abalone shell development
  - Ceriodaphnia survival and growth
Summary

- Mobility
  - AFB100a shows thicker lens, more residual
  - due to higher viscosity, IFT

- Biodegradation
  - All biodiesel blends more readily degradable than ULSD
  - Soy-based blends, or 20%<sub>s</sub>, somewhat more degradable
  - Additives effect are minor

- Aquatic Toxicity
  - Biodiesel blends are more toxic than ULSD#2
  - Biodiesel 20% blends with antioxidant additive are more toxic than the corresponding unadditized blend