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

8 December 2010 MMRA Workshop

TR Ginn[1], ML Johnson[2], KM Scow[3], J Miller[4], L Rastegarzadeh[1], T Hatch[1], A Epple[1], V Nino[1], T Schetrit[1], T Barkouki[1], D Rice[5], T McKone[6]

[1] UC Davis Civil & Environmental Engineering
[2] UC Davis Aquatic Ecosystems Analysis Laboratory
[3] UC Davis Department of Land, Air, and Water Resources
[4] Aquascience Inc., Davis CA
[5] Consultant to UC
[6] UC Berkeley, Environmental Health Sciences

UCDAVIS
UNIVERSITY OF CALIFORNIA

Multimedia Risk Assessment

Tier 1
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

Multimedia Risk Assessment[1]

Tier 1
Tier II[2]
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

- Final report is used as the basis for

Tier 3

[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
[2] http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm

Mobility

Fuel Blends

Sandbox Experimental Matrix

Type	Feedstock	Totals	Additization			
			None		Bioextend	
			#	Quantity	#	Quantity
B100	Animal-fat	6	3	50 mL/test	3	50 mL/test
B100	Soy	3			3	50 mL/test
B20	Animal-fat	3			3	50 mL/test
B20	Soy	3			3	50 mL/test
ULSD	petroleum	15	15	50 mL/test		

Note: Experiments involve include side by side comparison between ULSD and Biodiesel within the same sandbox for consistency of sand compaction.

Mobility

- Image analysis of biodiesel vertical infiltration in Sandbox
- 30x20x2cm, #20 (coarse) sand, water table
- Soy- and Animalfat-based 100% and 20% blends, 1 additive

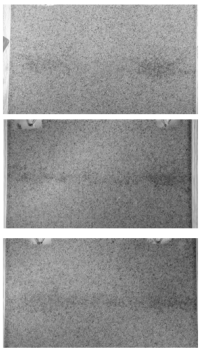
- Sandbox preparation
  - Wet-pluviated sand
  - Drain to water table
  - simultaneous 50mL ULSD#2 and biodiesel side-by-side, both dyed
- Data collected
  - infiltration rate in vadose zone
  - redistribution
  - lens form & surface area, on water table

Mobility

Sample Results
Final Lenses

- Soy B20 least different

Soy B20a CARB ULSD#2

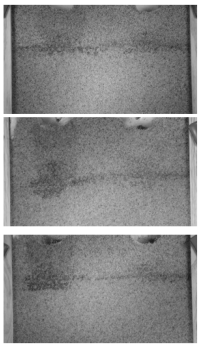


Mobility

Sample Results
Final Lenses

- Animalfat B100 strongest effect
  - similar traveltimes
  - Less lateral dispersion
  - thicker, deeper lens
  - more residual, less sfc area

AF B100a CARB ULSD#2



Mobility

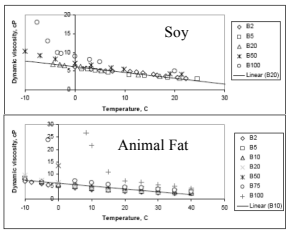
Summary

- Minor differences in traveltimes
- AF B100a only shows Moderate differences
  - thicker lens formation
  - more residual

Mobility

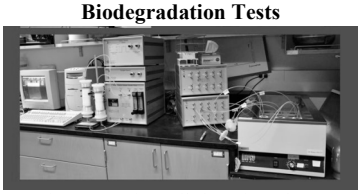
Summary

- Minor differences in traveltimes
- AF B100a only shows Moderate differences
  - thicker lens formation
  - more residual
- Interfacial Tensions[1] (mN/m):
  ULSD: 7.4
  Soy (B20/B100): 8.5/12.0
  AF (B20/B100): 15.0/19.5
- Viscosity[1]



1.Yang et al., ULSD/Biodiesel blend and its effect on fuel/ water separation, Amer. Filtration & Separation Soc. Annual Conf., May 19-22 (2008), Valley Forge, PA

Biodegradation Tests



- 29-day Respirometry using soil slurry inoculum
  - 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 sterilize control (1% sodium azide) - showed no CO2**.**

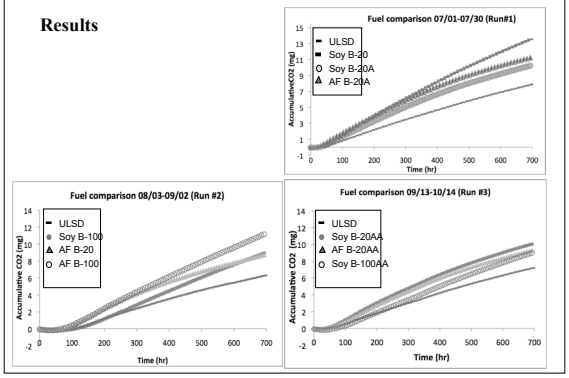
Biodegradation Tests

Fuel Blends

Experiment	Fuel Type	
	Description	Abbreviation
#1	Diesel	ULSD
	Soy biodiesel 20% blend + bioextend	Soy B-20 A
	Animal fat biodiesel 20% blend + bioextend	AF B-20 A
	Soy biodiesel 20% blend -no additives	Soy B-20
#2	Diesel	ULSD
	Soy biodiesel 100% - no additives	Soy B-100
	Animal fat biodiesel 20% blend - no additives	AF B-20
	Animal fat biodiesel 100% - no additives	AF B-100
#3	Diesel	ULSD
	Soy biodiesel 20% blend + bioextend + biocide	Soy B-20 AA
	Animal fat biodiesel 20% blend + bioextend + biocide	AF B-20 AA
	Soy biodiesel 100% + bioextend + biocide	Soy B-100 AA
#4	Diesel	ULSD
	Animal fat biodiesel 100% + bioextend + biocide	AF B-100 A
	Animal fat biodiesel 100% + bioextend	AF B-100
	Soy biodiesel 100% + bioextend	Soy B-100

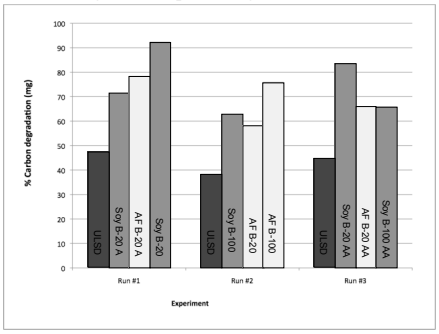
Biodegradation Tests

Results



Biodegradation Tests

29Day Cumulative degradation percentages

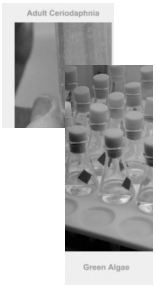


Biodegradation Tests

Summary

- All fuel blends more readily degrable than ref. fuel
- Soy-based blends somewhat more degrable than Animalfat-based blends
- 20% biodiesel blends somewhat more degrable 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_{25}
- **"Toxicity" as TU = 100/EC_{25}**
  # 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

Fuel Type[c]	*Code*
100% Ultra-Low Sulfur Diesel	ULSD
100% Soy Biodiesel	Soy B-100
20% Soy Biodiesel + 80% ULSD (w/w)	Soy B-20
20% Soy + 80% ULSD (w/w) amended with additive[c]	Soy B-20A
100% Animal Fat Biodiesel	AF B-100
20% Animal Fat Biodiesel + 80% ULSD (w/w)	AF B-20
20% Animal Fat + 80% ULSD (w/w) amended with additive	AF B-20A

Aquatic Chronic Toxicity Tests

Test Species

Category	*Test Species*	*Test Type*	*Test Endpoints*	*Replicates*	*Temp.*
Freshwater	Green algae (*S. capricornutum*)	96-hour static	Cell growth	10,000 cells/rep 4 reps/conc	25 ± 1 °C
	Water flea (*C. dubia*)	7-day daily renewal	Survival Reproduction	1 flea/rep 10 reps/conc	25 ± 1 °C
	Fathead minnow (*P. promelas*)	7-day daily renewal	Survival Growth	10 fish/rep 4 reps/conc	25 ± 1 °C
Estuarine/ Marine	Red abalone (*H. rufescens*)	48-hour static	Normal shell development	5 reps/conc 2000 embryos/rep	15 ± 1 °C
	Mysid shrimp (*M. bahia*)	7-day daily renewal	Survival Growth Fecundity	5 fish/rep 8 reps/conc	25 ± 1 °C
	Topsmelt (*A. affinis*)	7-day daily renewal	Survival Growth	5 fish/rep 5 reps/conc	20 ± 1 °C

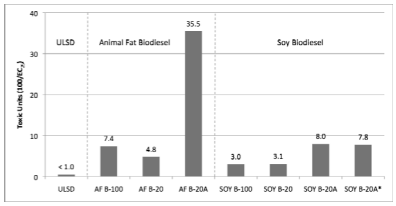
Aquatic Chronic Toxicity Tests

Results

- 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

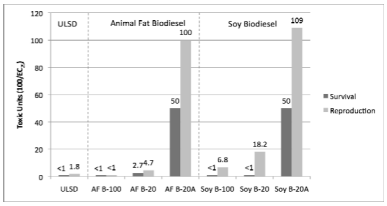
Examples



Red Abalone (*Haliotis Rufecens*) shell development

Aquatic Chronic Toxicity Tests

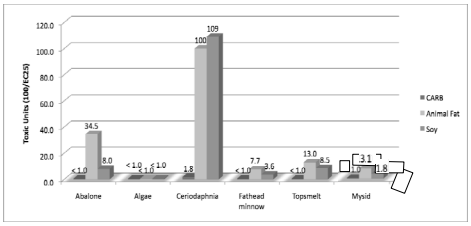
Examples



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

Tier II for Biodiesel Blends Tested

Summary

- Mobility
  - AFB100a shows thicker lens, more residual
  - due to higher viscosity, IFT
- Biodegradation
  - All biodiesel blends more readily degrable than ULSD
  - Soy-based blends, or 20%s, somewhat more degrable
  - 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

Tier II for Biodiesel Blends Tested

Summary

- Mobility
  - AFB100a only shows smaller lens, more residual
- Biodegradation
  - All biodiesel blends more readily degrable than ULSD
  - Soy-based blends, or 20%s, somewhat more degrable
  - 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