Biodiesel and Renewable Diesel Workgroup

California Biodiesel Multimedia Revised Tier II Report

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Tiered Approach Refresher

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

Conclusions About Key Information Gaps

- Additives composition, use, and impact
  - How **biocides and anti-oxidants** impact biodegradation
  - How priority additive impact human and ecosystem health
  - How cold flow property controllers impact multiphase transport, etc.
  - *toxicity*
- **Subsurface fate and transport** properties
- Releases - **Material Compatibility**
- **Biodegradation** of all biodiesel components in soils and aquifers
- More information on **air emissions**
- Missing **toxicological** data

- **biocides and anti-oxidants**
  - cold flow, cetane booster, NOx reducer…

- **Subsurface fate and transport**
- **Material Compatibility**
- **Biodegradation**

- **Air emissions**
- **Toxicological**

Overview of the Biodiesel Tier II Plan

- **>Solubility of components<**
- **biocides and anti-oxidants**
  - cold flow, cetane booster, NOx reducer… >solubility<

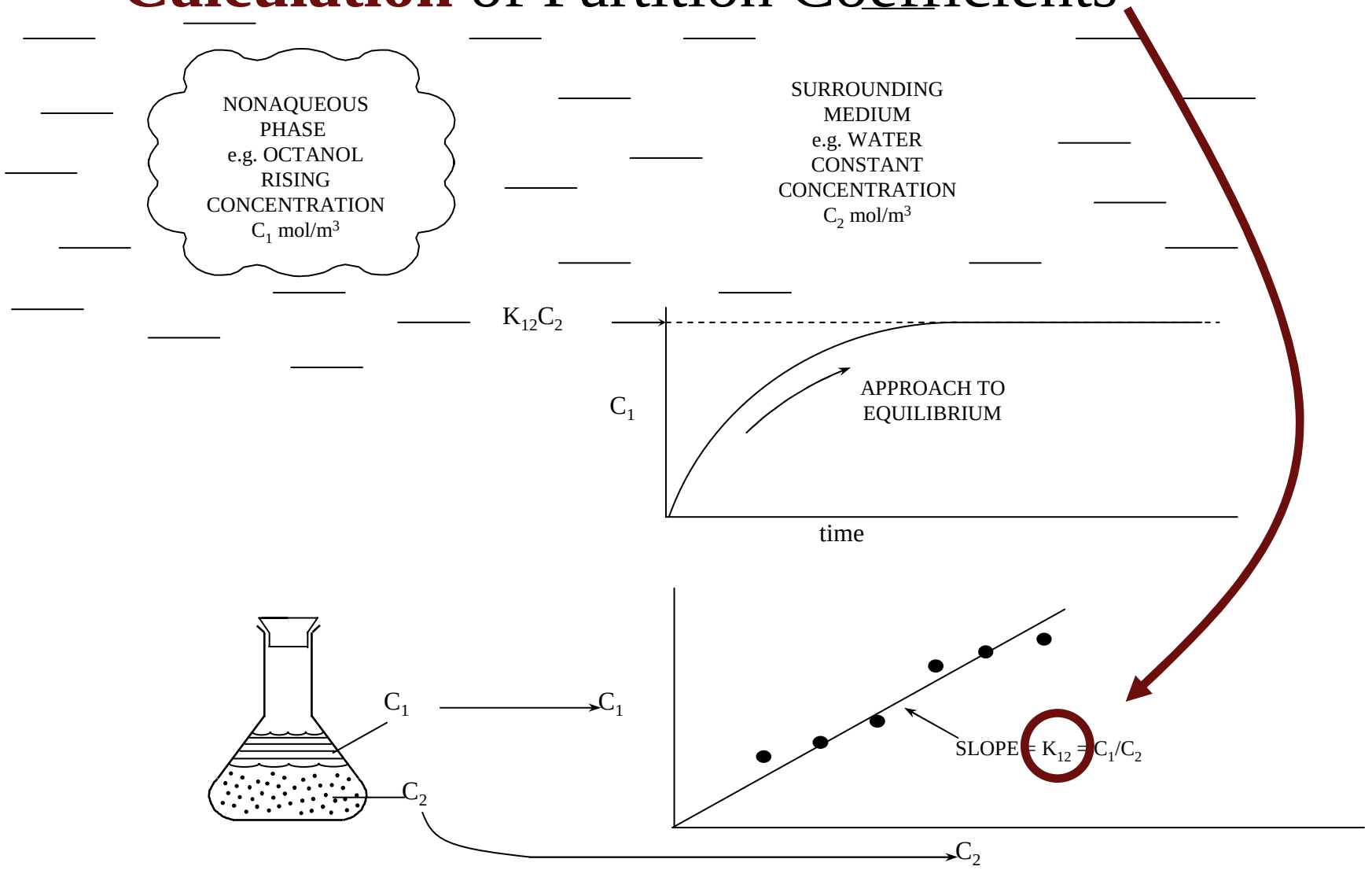
- **Subsurface fate and transport**
- **Material Compatibility**
- **Biodegradation**

- **Air emissions**
- **Toxicological**

Relative to ULSD

Experimental Determination (coming)

Calculation of Partition Coefficients



Solubility Calculations

- **Assumptions:**
  - **Raoult's law**
    - **Solubility proportional to mole fractions in biodiesel**
  - **Assume activities =1**
    - **(conservatively assumed based on knowing that the greatest partitioning of oil into the water phase will be achieved through this assumption).**
  - **FAMES and additives partition according to Raoult's Law**
  - **Raoult's law implies the absence of cosolvency effects.**
    - **(This may not be a conservative assumption when additives are involved, some of which are completely soluble in water and may affect solubility of other components of biodiesel)**

Solubility Calculations

Biodiesel-water Partition Coefficient, K_o for kth component from Raoult's law

$$K_o = \frac{\omega_k \sum_{j=1}^{N} \frac{c_{oj}}{\omega_{oj}}}{S_k \gamma_k}$$

Where, per kth component:

- **ω_o= the molecular weight (g/mol)**
- **c_o = component concentration in biodiesel (g/L)**
- **S = the solubility of the component in water (g/L)**
- **γ = the activity coefficient of the component (assumed to be 1)**
- **component = FAME or additive compound.**

…Will Compare with GC-MS

Experimental Plan Summaries

Subsurface Fate & Transport

- Ant Farm

Material Compatibility

- Immersion batch

Biodegradation

- Multi-batch respirometry

Aquatic Toxicity

- 6 species marine & freshwater

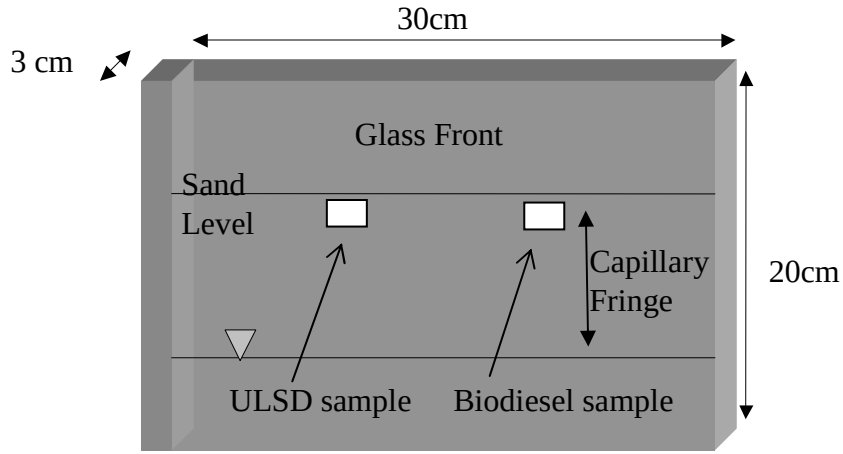
Subsurface Fate & Transport

Approach:

- Ant Farm
- 2D infiltration vadose zone
  - Visual observation, dyes
- Lens formation

Permutations:

- Two soils
  - Medium sand
  - Silty-sand-loam
- B100 (Soy and animalfat)
  - antioxidant+biocide
- B20 (Soy and animalfat)
  - antioxidant+biocide
- ULSD



Subsurface Fate & Transport

Experimental Matrix

	ULSD	Animalfat B100	Animalfat B20	Soy B100	Soy B20
Reference	50-200 mL				
biocide and antioxidant		50-200 ml two soils	50-200 ml	50-200 ml two soils	50-200 ml
Totals	50-200mL	200-800 ml	100-400 ml	200-800ml	100-400ml

Subsurface Fate & Transport

Material Compatibility

Approach:

- Prelude to anticipated UL testing
  - Broad indicators
- Batch exposures
  - 1-4 months
  - Aerobic immersions

Permutations:

- B100, B20, B5 x Animalfat, Soy
  - With/without low salinity water
  - All with antioxidant additive
- Materials
  - Bimetal copper-steel coupons
  - Fiberglass
  - elastomers

Material Compatibility

Experimental Matrix

Low-salinity water

Material	ULSDx2	Animalfat			Soy		
		B100	B20x2	B5	B100	B20x2	B5
Copper-steel	.2 L	.2 L	.2 L	.2 L	.2 L	.2 L	.2 L
Fiberglass 1	.2 L	.2 L	.2 L	.2 L	.2 L	.2 L	.2 L
Fiberglass 2	.1 L	.1 L	.1 L	-	.1 L	.1 L	-
Elastomer 1	.2 L	.2 L	.2 L	.2 L	.2 L	.2 L	.2 L
Elastomer 2	.1 L	.1 L	.1 L	.1 L	.1 L	.1 L	.1 L
Elastomer 3	.1 L	.1 L	.1 L	-	.1 L	.1 L	-
Elastomer 4	.1 L	.1 L	.1 L	-	.1 L	.1 L	-
Totals	2 L	1 L	2 L	1 L	1 L	2 L	1 L

Biodegradation

Approach:

- OECD (2004) recommended testing
- Batch respirometry (CO2)
  - Mineral medium,
  - inoculumn activated sludge
  - Tested substrate (same slow stir method as aquatic tox)

Permutations:

- B100 (Soy and animalfat)
  - Antioxidant, antioxidant+biocide
- B20 (Soy and animalfat)
  - Antioxidant, antioxidant+biocide
- ULSD

Biodegradation

Experimental Matrix

	ULSD		Animalfat B100	Animalfat B20	Soy B100	Soy B20
Reference	.2 L					
antioxidant			.2 L	.2 L	.2 L	.2 L
antioxidant and biocide			.2 L	.2 L	.2 L	.2 L
subTotals	.2 L		.4 L	.4 L	.4 L	.4 L
Replication factor	3		3	3	3	3
Totals	.6 L		1.2 L	1.2 L	1.2 L	1.2 L

Biodegradation

Experimental Matrix And submatrix

	ULSD		Animalfat B100	Animalfat B20	Soy B100	Soy B20
Reference	.2 L					
antioxidant			.2 L	.2 L	.2 L	.2 L
antioxidant and biocide			.2 L	.2 L	.2 L	.2 L
subTotals	.2 L		.4 L	.4 L	.4 L	.4 L
Replication factor	3		3	3	3	3
Totals	.6 L		1.2 L	1.2 L	1.2 L	1.2 L

Description	**Content**				**# of Rep.**	**# of Microcosm**
	Substrate	*Inoculum*	*Mineral*	*Reference*		
Test suspension	X	X	X		3	3x9 = 27
Inoculum blank		X	X		3	3
Procedure control		X	X	X	1	1
Abiotic + Adsorption control	X Sterilized	X Sterilized	X Sterilized		1	1x9 = 9
				TOTAL Microcosms:		50

Aquatic Toxicity

Approach: 6 Species

EPA methods for Chronic Toxicity

- W Coast Marine EPA 600/R-95-136, 1995
- Marine and Estuarine, EPA 821-R-02-014, 2002
- Freshwater EPA 821-R-02-013, 2002.

Slow-stir aqu. prep (Schluep et al. 2001)

- 10:1 aqu:biodiesel, 24hrs, 2 hrs, decant
- GC-MS for solubility, stability
- 100%, 50%, 25%, 10%, 5%, 1%, 0% dilutions

Multiple chronic and Acute endpoints

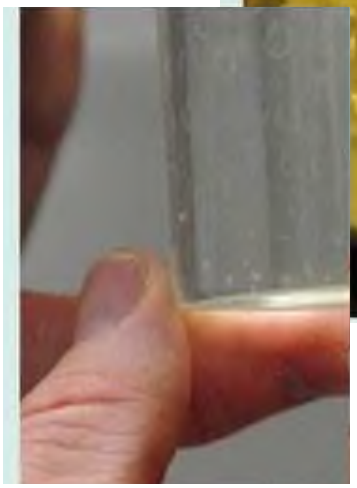
Permutations:

B20 Soy, B20 Animalfat

Antioxidant and biocide

B100/no biocide as feasible

ULSD



Green Algae

Ceriodaphnia Dubia

Aquatic Toxicity

Experimental Matrix

Test Species	Test Type	Test chemical				
		ULSD	B20S A	B20S A+B[a]	B20A A	B20A A+B
Green algae *(Selenastrum capricornutum)*	96-hr chronic cell growth	1L	1L	1L	1L	1L
Water flea *(Ceriodaphnia dubia)*	7-day chronic (survival and reproduction)	1L	1L	1L	1L	1L
Fathead minnow *(Pimephales promelas)*	7-day chronic (survival and growth)	1L	1L	1L	1L	1L
Red Abalone (*Haliotis rufescens*)	48-hr chronic (shell development)	1L	1L	1L	1L	1L
Mysid *(Mysidopsis bahia)*	7-day chronic (survival and growth)	1L	1L	1L	1L	1L
Topsmelt (*Atherinops affinis*)	7-day chronic (survival and growth)	1L	1L	1L	1L	1L
Totals		6L	6L	6L	6L	6L

Summary

Relative to ULSD

Broad Scope - Limited depth (time, $)

- **Conservative design**
  - **Potential risk = potential impact x potential frequency of use**

Present

- **Soy, animalfat feedstocks**
- **B100 storage, B20 storage & use, B5 use**
- **Biocide, antioxidant**

Absent

- **Other feedstocks (yellowgrease, canola, etc.)**
- **Other additives (coldflow, cetane booster, NOx reducer)**
- **Anaerobic biodegradation, NAPL biodegradation**
- **Coupled processes (SRB in UST)**