Tiered Approach Refresher

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

**Tier 2**
- Multimedia Risk Assessment
  - 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
Overview of the Biodiesel Tier I Report

• Biodiesel Background Information
• Biodiesel Life Cycle
  – Biodiesel Feedstock Collection/Production
  – Production of Biodiesel
  – Storage and Distribution of Biodiesel
  – Use of Biodiesel
• Release Scenarios
• Environmental Transport and Fate of Biodiesel
• Biodiesel Toxicity
• Biodiesel Life Cycle Impacts
• Conclusions about Key Information Gaps
Biodiesel Background

• Biodiesel is composed of mono-alkyl esters of long chain fatty acids derived from:
  – a broad range of vegetable/seed oils
  – recycled cooking greases or oils
  – animal fats
  – algal oils

• Biodiesel can be used as a pure fuel or as a blend with petroleum diesel

• Our focus is on a blend of 20% biodiesel with 80% standard ULSD (B20) and on 100% biodiesel (B100), partial evaluation of B5

• A key goal of encouraging fuels such as biodiesel is to reduce California’s carbon “footprint”
Biodiesel Life Cycle

- Biodiesel Feedstock Collection/Production
- Production of Biodiesel
- Storage and Distribution
- Use of Biodiesel
Biodiesel Feedstock Collection/Production

• Primary biodiesel feedstocks expected to be used in California include:
  – soybean oil
  – animal tallow
  – yellow grease
  – canola
  – safflower
  – palm oil
  – algae
  – trap (brown) grease

• Biodiesel feedstocks are classified by their fatty acid profile
• Price, availability, origin, geography, and consistent quality generally dictate which feedstock biodiesel producers use
Production of Biodiesel

- To make biodiesel, a vegetable oil or fat is subjected to a chemical reaction known as transesterification.

\[
\begin{align*}
\text{Triglyceride} & \quad \text{Methanol} & \quad \text{Mixture of methyl esters} & \quad \text{Glycerin} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_1 & \quad \text{O} & \quad \text{CH}_3 - \text{O} - \text{C} - \text{R}_1 \\
\text{CH} - \text{O} - \text{C} - \text{R}_2 & + 3 \text{CH}_3\text{OH} + ? \quad \rightarrow \quad \text{CH}_3 - \text{O} - \text{C} - \text{R}_2 & + \text{CH} - \text{OH} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_3 & \quad \text{O} & \quad \text{CH}_2 - \text{OH} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

- Air emissions and hazardous wastes are important considerations for production operations.
Storage and Distribution

- Material compatibility is important to consider during the storage and distribution of biodiesel
- Biodiesel is susceptible to chemical changes during long-term storage
- Chemical additives to address
  - oxidative stability
  - microbial contamination
  - increased water affinity
  - cold-flow properties
  - increased NOx emissions of biodiesel
- Routine emissions and “off-normal” events (pipe-breaks, large spills) must be addressed
Use of Biodiesel

• In the fuel-use stage, the releases of greatest concern are emissions to air

• But there are also potential releases to water and soil

• Several studies have determined biodiesel blends exhibit reductions in hydrocarbons (HC), particulate matter (PM) and carbon monoxide (CO) emissions

• There are also vehicle operability issues with biodiesel blends:
  – cold fuel flow
  – fuel foaming
  – water separation
  – fuel oxidative stability

Figure from Julian Marshall University of Minnesota
Defining Release Scenarios

• Selection of biodiesel feedstock
• Selection of additives mix
• Identify normal (routine) releases during production for example
  – Hexane or CO2 released to the air during seed extraction.
  – Odors associated with waste biomass
  – Methanol releases to air or water
  – Used process water discharges of various pH and trace-chemical composition
• Normal releases during use include tailpipe emissions, both to air and to surface waters (marine vehicles)
• Identify off-normal releases, such as leak or rupture of:
  – an above-or below-ground storage tank and associated piping,
  – rail tank car, tanker truck, or tanker ship.
  – bulk fuel transport pipeline
Environmental Transport and Fate

- Emissions
- Transport and transformation
- Impact Characterization
- Toxicology
- Uptake and dose
- Exposures
The long-term behavior of chemicals in the environment is determined by their partitioning between three primary media:
Experimental Determination of Partition Coefficients

NONAQUEOUS
PHASE
e.g. OCTANOL
RISING
CONCENTRATION
C_1 \, \text{mol/m}^3

SURROUNDING
MEDIUM
e.g. WATER
CONSTANT
CONCENTRATION
C_2 \, \text{mol/m}^3

SLOPE = K_{12} = C_1/C_2

K_{12}C_2

C_1

APPROACH TO
EQUILIBRIUM

time

C_2

RISING
CONCENTRATION
C_1 \, \text{mol/m}^3

Experimental Determination of Partition Coefficients
Level III multimedia contaminant fate model
Biodiesel Toxicity

• Human and ecological risk
  – Hazard identification
  – Toxicity (dose-response)
  – Potential for exposure
  – Sensitive populations

• Toxic air pollutants

• Toxicity assessment to fill data gaps
Biodiesel Life-Cycle Impacts

- Life-Cycle Approach
  - Biomass production and harvesting or feedstock collection
  - Fuel production
  - Fuel transport and distribution
  - Fuel combustion
- Pollutant releases at each life stage
- Transport and fate
- Exposure and dose
- Toxicology and risk
Refining

Fuel transport

Fuel storage

Fuel distribution

CO
NO\textsubscript{x}
Ozone
Particulate matter
VOC
SVOC
Product leaks/spills

Fuel transport/storage

CO
NO\textsubscript{x}
Ozone
Particulate matter
VOC
SVOC

Combustion in vehicles

Fuel end use

emissions \rightarrow concentration \rightarrow exposure \rightarrow health effects \rightarrow damage

Graphic courtesy of Julian Marshall
University of Minnesota
Life Cycle Impact
Disability adjusted life years (DALYs)

Emissions [kg per joule fuel processed]

Biofuel production & location

Biodiesel from:
- Waste oil
- Plant oil

Renewable diesel from:
- Plant oil
- Other sources

Pollutant intake based on release scenario/location

1) Aldehydes
2) US EPA Criteria Pollutants (PM2.5, CO, etc.)
3) Other Air Toxics (e.g., PAHs)
4) Hazardous wastes

Potential disease burden

DALYs per joule biofuel processed

Urban
Rural

Total DALYs

DALYs per joule conventional diesel processed
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
  – 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