FINAL REPORT

California Biodiesel Multimedia Evaluation

Tier I Report

Prepared

By

The University of California, Davis
The University of California, Berkeley

For the

California Environmental Protection Agency
Multimedia Working Group

December 2008

Table of Contents

Executive Summary 7
Background 7
Study Approach and Results 8
Key Information Gaps and the Tier-II Sampling Plan 10
1. Biodiesel Background Information 13
1.1. Introduction 13
1.2. History 15
1.3. Legislative Incentives for Biodiesel 16
2. Production of Biodiesel 17
2.1. Biodiesel Production Chemistry 17
2.1.1. Biodiesel Transesterification Reactants 17
2.1.2. Managing the Transesterification Process 19
2.2. Overview of Biodiesel Feedstocks 21
2.2.1. Primary Feedstocks for Multimedia Review 21
2.2.2. Feedstock Characteristics 25
2.2.3. Feedstock Economic Considerations 27
2.3. Biodiesel Standardization and Fuel Quality 27
2.3.1. Biodiesel Fuel Energy Content 29
2.4. Waste Generation and Waste Management 29
3. Storage and Distribution of Biodiesel 31
3.1. Material Compatibility 31
3.2. Biodiesel Solvency 32
3.3. Storage Stability 32
3.3.1. Biodiesel Oxidation 32
3.3.2. Residual Water 33
3.4. Distribution and Blending of Biodiesel 34
4. Use of Biodiesel 35
4.1. Vehicle Operability Issues 35
4.2. Biodiesel Cold Flow Characteristics 35
4.3. Use of Additives 35
4.3.1. Antioxidants 36
4.3.2. Cold-Flow Enhancement 37
4.3.3. Biocides 37
4.3.4. Cetane Enhancers and NOx Reduction Additives 38
4.3.5. Water Dispersants 39
4.3.6. Anti-Foaming Agents 39

4.4. Potential Impacts During Fuel Use 39
4.4.1. Biodiesel Impact on Air Quality 40
4.4.2. Exhaust Emissions 40
4.4.3. Effects on Ambient CO and PM Concentrations 44
4.4.4. Effect on Ozone 46
4.4.5. Effect on Toxic Air Pollutants 47
4.4.6. Summary Points on Biodiesel Emissions 48
5. Release Scenarios 50
5.1. Defining Release Scenarios 50
5.2. Normal Releases 51
5.3. Off-Normal Releases 51
6. Environmental Transport and Fate of Biodiesel 53
6.1. A Multimedia Framework for Fate, Transport, and Exposure 53
6.2. Data Needs for Multimedia Transport 54
6.3. Chemical Composition and Multimedia Transport Properties 56
6.3.1. Chemical Makeup of Biodiesel and Diesel 57
6.3.2. Solubility in Water 57
6.3.3. Sorption to Solids 58
6.3.4. Vapor Pressure 59
6.4. Biodegradation of Biodiesel Components 59
6.4.1. Biodegradability in Aquatic Environments 59
6.4.2. Biodegradation in Soil 61
6.4.3. Biodegradation Under Aerobic and Anaerobic Conditions 61
6.4.4. Biological and Chemical Oxygen Demand 61
7. Biodiesel Toxicity 63
7.1. Human and Ecological Risk Assessment 63
7.2. Acute Oral and Acute Dermal Toxicity 63
7.3. Toxic Air Pollutants and Human Health 64
7.4. Previous Toxicity Testing of Biodiesel Fuel Exhaust Emissions 66
7.5. Aquatic Toxicity 67
7.6. Toxicity in Aerated Soil 69
8. Biodiesel Life Cycle Impacts 70
8.1. Life Cycle Assessment 70
8.2. Emissions of Pollutants to Air 72
8.3. Solid Waste and Emissions to Water 74
8.4. Life Cycle Inventory Information Gaps 74
9. Tier I Conclusions 75

10. References 79
11. Appendices 85
11.1. Appendix A: ASTM D6751-07a Standard Property Descriptions for Biodiesel 86
11.2. Appendix B: Biodiesel Additive Chemicals 89
11.3. Appendix C: Biodiesel Web Links 92

List of Figures

Figure 1.1. Generalized summary of biodiesel life cycle impacts.

Figure 2.1. Transesterification reaction.

Figure 2.2. Biodiesel transesterification process.

Figure 2.3. Glycerol refining using acid to produce fatty acids and salt.

Figure 4.1. Relation between content of saturated fatty acids in biodiesel (without additives) and its CFPP value.

Figure 4.2. Rohm and Hass Kathon FP 15 biocide.

Figure 4.3. Average emission impacts of biodiesel for heavy-duty highway engines.

Figure 4.4. Biodiesel feedstock effect on CO emissions.

Figure 4.5. Biodiesel feedstock effect on NOx_x emissions.

Figure 4.6. Biodiesel feedstock effect on PM emissions.

Figure 4.7. Regression model showing effect of oxygen on particulate matter.

Figure 5.1. Biodiesel and renewable diesel process flow chart.

Figure 6.1. A conceptual illustration how pollutant emissions from each life-stage of biodiesel enter air, water, and or soil, undergo multimedia transport into exposure media, followed by contact with humans and ecosystems.

Figure 6.2. Phase distribution equilibria involving pure phase partition coefficients (solubility in water S_W, solubility in octanol S_O and vapor pressure p_V) showing the links for describing environmental phase partitioning (K_{AW} air/water partition coefficient, K_{OW} octanol/water partition coefficient, K_{OA} octanol/air partition coefficient). The octanol phase is used for soil, sediment, particles and biota).

Figure 6.3. Statistical significance of temperature and level of blending on moisture content.

Figure 6.4. BOD_5 values for biodiesel and diesel.

Figure 6.5. COD values for biodiesel and diesel.

Figure 7.1. 48 Hour Static, Non-Renewal, *Daphnia magna* EC_{50}.

Figure 7.2. 48 Hour Flow-Through, *Daphnia magna* EC_{50}.

Figure 7.3. Comparison of aggregated toxics and total HC.

Figure 8.1. An illustration of life stages and life-cycle impacts for biodiesel fuels.

Figure 8.2. Life cycle air emissions for B100 and B20 compared to petroleum diesel life cycle air emissions.

List of Tables

Table 2.1. Yield for each feedstock.

Table 2.2. Fatty acid percentages in biodiesel feedstocks.

Table 2.3. Comparison of iodine number and cetane number for different types of biodiesel.

Table 2.4. Economic considerations of biodiesel feedstocks.

Table 2.5. ASTM D6751-07a. Specifications for biodiesel (B100).

Table 2.6. Average energy content of 100% biodiesel.

Table 3.1. Biodiesel materials compatibility.

Table 4.1. Overall average change in mass emission effects due to use of biodiesel fuels in heavy-duty highway vehicles compared to standard diesel fuel.

Table 4.2. Peak estimated 1-hour and 8-hour carbon monoxide (CO) concentrations in the Las Vegas Valley, 100% B20, and 50% B20 emission scenarios and the differences in CO concentrations between the biodiesel fuel scenarios and the standard diesel base case.

Table 4.3. Estimated maximum increases and decreases in particulate matter (PM) concentrations ($\mu g/m^3$) in the Southern California air basin due to a 100% penetration of B20 biodiesel in the heavy duty diesel vehicle fleet.

Table 4.4. Maximum increases and decreases in daily maximum 1-hour ozone concentrations in three air basins.

Table 4.5. Maximum increases and decreases in daily maximum 8-hour ozone concentrations in three air basins.

Table 6.1. Physical and chemical properties of fuel oils.

Table 6.2. Biodegradation of fuel in biodiesel mixture and diesel alone.

Table 6.3. Percent degradation in different rapeseed ethyl ester (REE)/diesel mixtures.

Executive Summary

The purpose of this multimedia assessment is to provide the State of California information that will allow an informed decision as to the relative impacts posed by biodiesel to the State's resources, human health, and environment. Biodiesel and renewable diesel are names of alternative diesel-equivalent fuels, derived from biological sources (such as vegetable oils or tallow), which can be used in unmodified diesel-engine vehicles.

Background

Pure biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. To create biodiesel, a vegetable oil or animal fat is subjected to a chemical reaction known as transesterification. In this reaction, a feedstock (either oil or fat) is reacted with alcohol in the presence of a catalyst to produce glycerin and methyl esters (biodiesel).

Alternatives to transesterified biodiesel are appearing rapidly. Renewable diesel (refinery co-processed diesel) is similar to biodiesel in that similar feedstocks are used in a traditional fractional distillation method to create a chemically different product. Thus, transesterification is not involved, and the result is a nonester renewable fuel. Thermal depolymerized diesel is another non-petroleum feedstock-based diesel that is produced through a hydrous-pyrolysis process that mimics the geological heat and pressures that naturally produce crude petroleum oil. Renewable diesel is the subject of another multimedia assessment, that is now in preparation.

Because biodiesel blends are new fuels, the California Air Resources Board (CARB) must provide a "multimedia assessment" of their potential impacts before adopting new fuel specifications (as required by California Health and Safety Code, Section 43830.8). Further, the "California Air Resources Board cannot adopt any regulation establishing a motor vehicle fuel specification unless a multimedia evaluation is conducted to determine whether the regulation will cause a significant adverse impact on the public health or environment" (California Senate Bill 140, 2007).

There are many steps involved in the transesterification production of biodiesel. Initially, the three reactants, alcohol, oil, and a catalyst, are mixed in a reactor. The next step involves separating the methyl esters and glycerin (a byproduct). The methyl esters are then neutralized with acid to remove any residual catalyst and to separate any soap that may have formed during the reaction. The mixture is washed with water and any alcohol is removed. The biodiesel may then be dried in a vacuum flash process that leaves a clear amber-yellow liquid with a viscosity similar to petroleum diesel.

Primary biodiesel feedstocks expected to be used in California include: soybean oil, palm oil, yellow grease, animal tallow, algae, trap (brown) grease, canola, and safflower. Biodiesel feedstocks are classified by their fatty acid profile; the fatty acid composition greatly influences a fuel's characteristics, as different esters of fatty acids have different physical and chemical properties. Price, availability, origin, geography, and consistent quality generally dictate which feedstock biodiesel producers use.

Generally, the quality of the fuel is dependent on the quality and fatty-acid composition of the feedstock, the production process, and post-production handling. Pure biodiesel fuels, regardless of feedstock, must meet the ASTM D6751 standards. When a biodiesel blend meets these requirements, it can be used in most modern engines without modifications.

Study Approach and Results

This Tier I report is the first step in evaluating the cumulative health and ecological impacts from releases to air, surface water, groundwater and soil at all stages of the life cycle of bio-diesel blends: feedstock production/collection, fuel production, fuel storage and distribution, and fuel use. The potential impact posed by diesel is assessed relative to the ultra low sulfur diesel (ULSD) currently in use. This report does not aim to address the direct and indirect environmental, ecological, and health impacts that biodiesel production may have due to changes in land use and the possible net gain in carbon emissions due to feedstock cultivation.

Our focus in this multimedia evaluation is on a blend of 20% biodiesel with 80% standard ULSD (B20). The B20 blend is designed to target the composition of fuel most frequently involved in on-site storage and distribution from fuel service stations. The transportation and storage of pure biodiesel (B100) as a distributed ingredient in on-site mixing are also considered. Biodiesel is typically transported via rail cars, tank trucks, and drums.

Material compatibility is an important property to consider during the storage and distribution of biodiesel. Since biodiesel can react with some metals and polymers, it is critical that the material of tanks, hoses, gaskets, and other parts that may come in contact with biodiesel, are compatible with the fuel's properties. Biodiesel is not compatible with brass, bronze, copper, lead, tin and zinc as these metals can initiate oxidation and sediment production. Nitrile rubber compounds, polypropylene, polyvinyl, and Tygon are particularly vulnerable to biodiesel. Biodiesel has higher solvency properties than petroleum diesel fuel and can act as a mild solvent. It can dissolve the residual sediments in diesel storage tanks and engine fuel tanks. These dissolved sediments can harm fuel systems as they plug fuel filters.

Biodiesel is susceptible to chemical changes during long-term storage. Fuel aging and oxidation by atmospheric oxygen can lead to increased acid numbers, increased fuel viscosity, and the formation of gums and sediments. Storage stability of biodiesel is also affected by the presence of water within the tank. Water can cause hydrolytic degradation of the fuel, contribute to microbial growth in the fuel, and can cause corrosion of fuel systems and storage tanks.

There are a number of vehicle operability issues associated with the use of biodiesel blends. These include cold fuel flow, fuel foaming, water separation, and fuel oxidative stability. Cold flow problems can result in fuel system clogging. Fuel foaming can result in difficulty during tank filling and can potentially increase the possibility of fuel spills. Reduced water separation can result in water/fuel mixtures that can clog fuel systems and promote microbial growth that can also clog fuel systems. Oxidative degradation of biodiesel can result in injector deposits, lacquer formation, and fuel systems corrosion. These impacts to the vehicle fuel system can result in reduced drive-ability, higher tailpipe emissions, and increased maintenance costs.

Chemical additives are commercially available to address the oxidative stability, cold-flow properties, microbial contamination, increased water affinity and increased NO_x emissions of biodiesel.

Releases associated with the production, storage and distribution, and use of biodiesel can be regarded as normal or off-normal. Different feedstocks and production processes may have different normal and off-normal releases and may affect different environmental media and human populations depending on geographic location. Normal or routine releases during the production of B100 may be:

- hexane or CO_2 released during seed-oil extraction residual oil washing.

- odors associated with waste biomass.
- methanol releases to air or water.
- used process water discharges of various pH.
- tailpipe emissions during combustion.

Normal releases during the use of biodiesel include combustion tailpipe emissions, both to the air and to surface waters in the case of marine use. The magnitude of these normal production and use releases within California is not clear yet.

Off-normal releases may include spills or leaks of bulk feedstock oil, production chemicals, such as methanol, hexane, acid, base, or blending stocks such as ULSD or B100, or finished B20 fuel. These off-normal releases may be the result of leak or rupture of:

- an above ground or below ground storage tank and associated piping.
- a liquid transportation vehicle such as rail tank car, tanker truck, or tanker ship.
- a bulk fuel transport pipeline.
- tank storing unprocessed glycerin.

In the fuel-use stage of the biodiesel life cycle, the releases of greatest concern are emissions to air, but there are also potential releases to water and soil from atmospheric deposition and from leaks and spills during fueling and vehicle use. Several studies have determined that use of biodiesel (as B100 or a B20 blend) instead of conventional diesel may be expected to exhibit large reductions in hydrocarbons (HC), particulate matter (PM) and carbon monoxide (CO) emissions. The type of feedstock and conventional diesel (used for blending) can influence these emissions. The NO_x emissions from biodiesel fuels increased with percent biodiesel blended and vary considerably with biodiesel feedstock used. Biodiesel containing feedstocks high in polyunsaturated fatty acids emit a greater percentage of NO_x than biodiesel high in saturated fatty acids.

Deploying a multimedia assessment framework to understand potential impacts requires basic information about the chemical/physical properties of the substances under consideration. These properties describe how a substance will distribute itself among the major phases of the environment—air, water, and organic phases such as lipids and organic materials in soil. The important multiphase transport properties identified include: chemical makeup of biodiesel diesel, solubility in water, sorption to solids, vapor pressure, and interfacial tensions. Here we summarize available information and knowledge gaps about these properties.

Biodegradation of hydrocarbons by microorganisms represents one of the primary mechanisms by which petroleum and diesel products are removed from the environment. The biodiesel biodegradation information evaluated in this report includes: biodegradability in aquatic environments, biodegradation in soil, biodegradation under aerobic and anaerobic conditions, and biological and chemical oxygen demand.

The greatest difficulty in determining the human and ecological toxicity of biodiesel fuels is that biodiesel fuel is not a defined chemical formulation or a defined mixture of components, but can be formulated from any of a very large number of feedstocks with different chemical components. In general, tests show that pure biodiesel is considerably less toxic than pure diesel fuel. Formulations of mixed biodiesel-diesel fuel such as B20 or B50 have shown results

consistent with the calculated diluent effect of the percentage of biodiesel fuel on the total toxicity of the mixture.

Life cycle inventory (LCI) comparisons between biodiesel and petroleum diesel show that overall, B100 biodiesel yields 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle. The fossil energy ratio of B20, however, is less than B100 with a ratio of 0.98 units. The LCI also included air pollutants: carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM), sulfur oxides (SO_x), non-methane hydrocarbons (NMHC), and toxic air pollutants. All tested pollutants, other than NO_x, hydrochloric acid (HCl), and total hydrocarbons (THC), show decreased emissions relative to diesel. Biodiesel produces 32% less total particulate matter (TPM) and 35% less CO than does petroleum diesel in its typical life cycle. A USDA/USDOE study estimated biodiesel life cycle wastewater flows as almost 80% lower than petroleum diesel. But one issue for PM and toxic air pollutants is that there is not just a reduction in emissions but a shift in chemical composition and it is not yet clear whether this composition is more or less toxic than petroleum diesel.

Key Information Gaps and the Tier-II Sampling Plan

1. Additives impacts. To provide a stable useful, and reliable fuel, additive chemicals will need to be introduced into almost all biodiesel blends. These additives will be required to control oxidation, corrosion, foaming, cold temperature flow properties, biodegradation, water separation, and NO_x formation. The specific chemicals and amounts used have not been well-defined for the emerging industry in California. A careful evaluation the possible chemicals would be beneficial to California and may lead to a "recommended list" or "acceptable list" that would minimize the uncertainty of future impacts as industry standards are developed.

The impact of various additives that may be used with biodiesel blends needs to be considered for releases to the air, water, and soils. Additives may affect fuel quality or storage stability in unintended ways. Because the properties of additives can potentially alter the characteristics of biodiesel, increasing its environmental and health risks, there is a need for additional tests on biodiesel with specific concentrations of additives. In particular it is necessary to assess the impact of

- cold flow property controllers on surface water- biodiesel interaction and on subsurface multiphase transport of biodiesel (see number 2 below).
- biocides and anti-oxidants on biodegradation (see number 3 below).
- all priority additives on human and ecosystem toxicity.

2. Subsurface fate and transport properties. The impacts of leaks and spills of biodiesel fuel product during transport, storage, and distribution have not been addressed. This is an important issue for California. Because the chemical composition of biodiesel differs significantly from that of petroleum diesel, it is expected that infiltration, redistribution, and lens formation on water tables will differ for the two fuels, leading potentially to significant differences in relative impacts to groundwater quality. Properties governing these processes are density, viscosity, and interfacial tensions. Component (including additive) solubility into the water phase ultimately governs water quality and so inter-phase solubilization of individual components also needs to be identified. To address these issues requires experiments with conventional soil column tests that will be used to establish relative transport behaviors among different fuel compositions and for site-specific analyses. But the relevance of these results for state-wide assessments should be

considered along with the value of full-scale comparative field tests with releases into the groundwater, or into the vadose zone just above the groundwater table.

3. Biodegradation in soils and aquifers. The anticipated use of biocides in B20 fuels may affect the biodegradation potential for biodiesel released into the environment. The impact of biocides added to blended biodiesel may reduce the biodegradation of biodiesel and other petroleum-based fuels leaked or spilled into the subsurface. Since subsurface biodegradation can play an important role in the remediation of fuel spills and leaks, an understanding of the fate of biodiesel with biocide additive is needed.

Not all biodiesel or renewable-diesel fuel blends have been tested for degradation under aerobic and especially anaerobic conditions. To our knowledge, only one alternate electron acceptor, nitrate, has been tested; others such as sulfate and methanogenic conditions should be explored, because these are the primary available electron acceptors expected in the reducing environments expected in deeper soil contamination and in aquifers.

Pure biodiesel (B100) without additives may be more biodegradable than ULSD and may be preferentially metabolized by subsurface microbes. The interaction of B100 with existing gasoline or conventional diesel previously released into the subsurface needs to be examined more closely.

4. Production and storage releases. In addition to impacts from released B100 or blended B20 biodiesel, increased production and associated feedstock processing may involve impacts from released reactants and by-products. There are potential impacts to California's air and water during the large-scale industrial operations used to extract seed oils. These impacts may result from air emissions of solvents used to extract the seed oil (e.g., hexane) and from leaking tanks containing chemicals to process the plant oils into biodiesel. There is also the issue of occupational exposures. Finally, UST material compatibility must be addressed: owner/operators are required by state health and safety codes to demonstrate material compatibility prior to storage of biodiesel. The impacts during seed extraction will become more of an issue for California as in-state production of plant-derived oils increases and may require further study. Currently, the possible impacts during seed extraction will be minimal in California since it is anticipated that most of the seed oils will be derived from soy grown and extracted out-of-state.

Among the most important current production reactants are: methanol, generic acid or base catalysts, feedstock oils, and post-processing water. As the biodiesel industry matures, release scenarios developed in this report need to be refined and prioritized.

5. Additional air-emission studies. There are not yet sufficient data to assert that the use of biodiesel will reduce the emissions of criteria and toxic air pollutants. Although considerable data is available on the effect of biodiesel on EPA-regulated pollutants (i.e., HC, CO, NO_x, and particulates), most of this data was generated using older technology engines. Further, very little detailed exhaust characterization data on biodiesel exists beyond a small number of regulated pollutants. Planned emission testing is based on newly blended B20 fuel stocks with only an anti-oxidant added and purged with nitrogen. B5, B50 and B100 will also be tested. The anti-oxidant and nitrogen purge are needed because the fuel used for the planned testing will be at least six month old-which is at the maximum recommended storage time for biodiesel. We note that these fuel mixes may not necessarily represent the general storage conditions expected throughout California. It is well established that fuel-handling practices have an important influence on engine performance and combustion emission. Additionally, the impact of various additives on combustion air emissions needs to be evaluated. Given the wide variety of oils and fats that

might be used to make biodiesel fuel and the potential additives, the actual emissions of PMs and toxic air pollutants will have to be determined for each proposed formulation of biodiesel fuel to be used in California. This situation demands a systematic and ongoing effort to assess emissions from diesel engines. In particular, there is a need for more controlled combustion studies to assess how the spectrum of toxic air pollutants, such as the spectrum of PAHs, will shift both in terms of volatile and particle-bound fraction but also in terms of any changes in toxic equivalency.

6. Tier II Sampling Plan. Many of the data gaps identified above will be addressed in the sampling plan developed for the Tier II study and report. In preparing this report, we had a number of discussions with Cal-EPA staff that provide important insight for developing the Tier-II sampling plan. First there is the issue of differences in emissions from different vehicle/engine classes such as on and off road vehicles. Where possible, this information should be included in the Tier two assessment. Next there are a number of issues of coordination among samples for different media and different objects. Samples used to test fate, transport, and toxicity should come from the same batch and be stored (aged) under the same conditions. When making comparisons of ULSD and biodiesel, all fuels should be subjected to the same tests. One example includes efforts to assure that fuel samples tested for water quality include the same types of fuel samples used by CARB for air emissions tests to evaluate the effects and toxicity of the antioxidant additive. A second example is that the biodiesel formulation used to approve underground storage tank components for material compatibility should be the same formulation used in material compatibility tests. Fatty-acid-methyl-ester-derived-biodiesel samples used in fate, transport, and toxicity testing should represent the vegetable oil and the animal-fat feedstock most widely found in biodiesel marketed in California. Finally, samples used in fate studies should, where possible, represent both an ideal biodiesel composition that meets ASTM D6751-07a specifications, as well as a more real-world example of fuel stored in an underground storage tank—containing water, peroxide and ammonia nitrogen levels attained through natural aging of biodiesel without antioxidants.

7. Life Cycle Impacts. Only differences in emissions inventories were considered during recent studies comparing life cycle inventories (LCI) of biodiesel to petroleum diesel. Differences in health and environmental impacts associated with these LCI differences needs to be evaluated. Additionally, current LCI studies have been limited to only soybean oil feedstocks. It is well established that different feedstocks can have an important influence on life cycle emissions. Information is needed for other feedstocks as well as for renewable diesel.

8. Priority list of biodiesel formulations. Because the number of potential feedstocks, the number of fuel blends, and the number of additive choices and mixes makes for an unmanageable suite of permutations of cases for consideration, it is critical to identify the priority feedstocks, fuel blends, and additives requiring study for our impacts assessment. Not specifically addressed in this Tier I evaluation are the environmental impacts from the increased use of fertilizers and water and land resources as the production of plant oils increases in the State. These factors may be some of the most important eventual impacts to California as the biofuels industry expands. More sustainable sources of biodiesel such as yellow or brown grease may be preferable and should be encouraged.

Finally, a key goal of encouraging fuels such as biodiesel is to reduce California's carbon "footprint" as part of a global strategy. To consider only the environmental impacts to California and disregard the impacts that may be occurring nationally or internationally during the production of the biofuels feedstock that is used in California is short-sighted.

1. Biodiesel Background Information

1.1. Introduction

The purpose of this multimedia assessment is to provide the State of California information that will allow an informed decision as to the relative health and environmental impacts to the State's resources, human health and environment posed by the use biodiesel. Biodiesel and renewable diesel are the names of alternative diesel-equivalent fuels, derived from biological sources (such as vegetable oils or tallow), which can be used in unmodified diesel-engine vehicles.

Biodiesel is defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (NBB, 2007). Biodiesel has been derived from a broad range of vegetable oils, recycled cooking greases or oils, animal fats and algal oils. It can be used as a pure fuel or as a blend with petroleum diesel, as biodiesel is miscible with petroleum diesel at all ratios (Knothe et al., 2005). The most common blend is B20 (20% biodiesel mixed with 80% ultra-low sulfur diesel, ULSD). In this report, the word *biodiesel* refers to pure biodiesel (B100) and meets the specific biodiesel definition and standards approved by ASTM (American Society for Testing and Materials) D6751.

Pure biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Alternatives to of biodiesel are also appearing rapidly. Renewable diesel (co-processed diesel) is another alternative fuel that has potential in California. Renewable diesel is comparable to biodiesel in that similar feedstocks are used in a traditional fractional distillation method that creates a chemically different product. Thermally depolymerized diesel is non-petroleum feedstock-based diesel that is produced through a hydrous pyrolysis process that mimics the geological heat and pressures that naturally produces crude petroleum oil.

Since biodiesel is a new fuel, the California Air Resources Board (CARB) must provide a "multimedia risk assessment" before adopting new fuel specifications (as required by California Health and Safety Code, Section 43830.8). Further, existing law states that the "California Air Resources Board cannot adopt any regulation establishing a motor vehicle fuel specification unless a multimedia evaluation is conducted to determine whether the regulation will cause a significant adverse impact on the public health or environment" (California Senate Bill 140, 2007).

As a result, the California Environmental Protection Agency (Cal-EPA) has initiated a program to assess the multimedia life-cycle impacts of biodiesel fuels used in California. This Tier I report is the first step in a three tier process evaluating the cumulative health and ecological impacts from releases to air, surface water, groundwater and soil at all stages of the biodiesel life cycle: production, storage and distribution, and use. The risk posed by biodiesel is assessed as a relative risk compared to ultra low sulfur diesel currently in use.

The goal of this Tier I report is to identify what is currently known about biodiesel along with a discussion of key uncertainties and data gaps, including:

- Physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel and additive components,
- Summary of all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios,

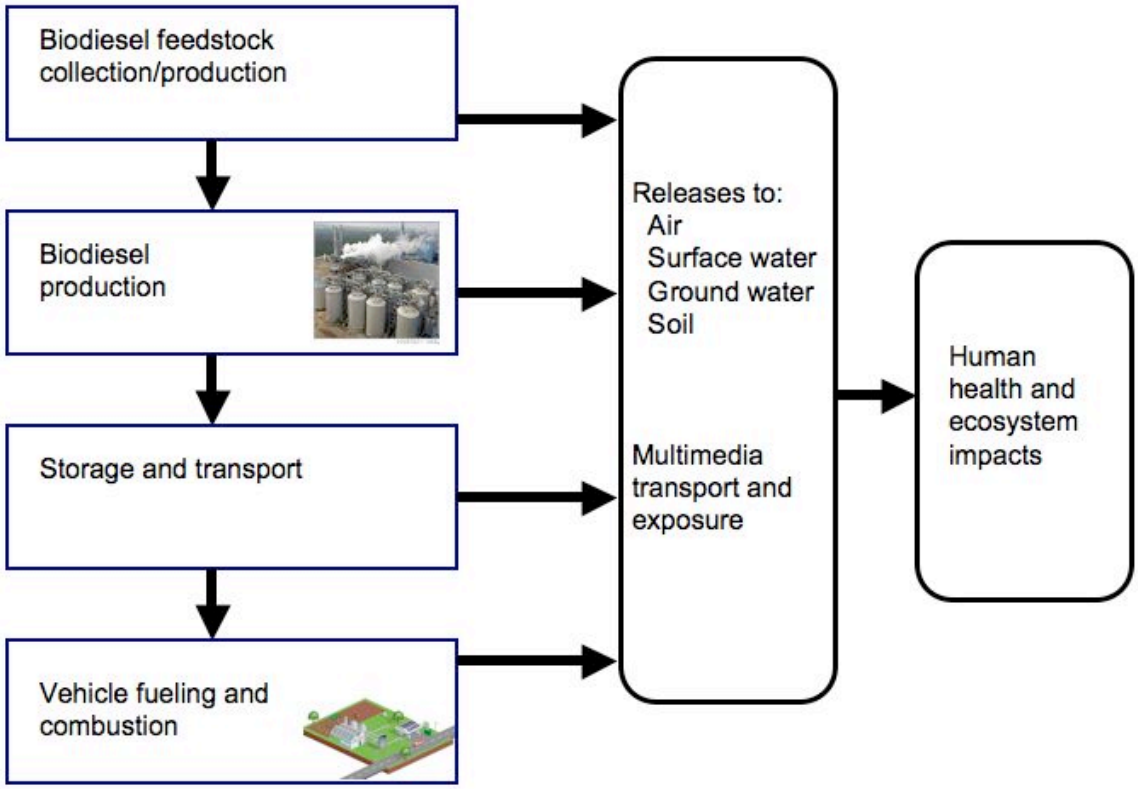
- Summary of the expected environmental behavior (transport and fate conceptual models associated with release scenarios) of proposed fuel or fuel components that may be released, and
- Comparison of physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components.

This report excludes the direct and indirect environmental, ecological, and health impacts associated with biomass production such as changes in land use and the possible net gain in carbon emissions due to feedstock cultivation. There is a scientific debate concerning the sustainability of wide scale energy conversion from fossil fuels to biofuels (Wang & Haq, 2008). Controversial findings suggest that the clearing of virgin rainforests and grasslands to make land for biofuel production will produce high initial "carbon debts" that are estimated to have decades or even centuries long pay-back periods due to the modest savings in carbon emissions from burning biofuels (Searchinger et al., 2008; UMN, 2008; The Wall Street Journal, 2008). Such issues have lead the European Union to propose a ban on certain biofuel sources such as palm oil from Southeast Asia due to associated deforestation and habitat loss, and due to non-sustainability of palm tree monoculture (Kantor, 2008; Rosenthal, 2007). Some end-users (e.g., Virgin Atlantic airlines) seek only sustainable sources of biofuels that are not produced in ways that compete for food grain production and/or add to deforestation (Clark, 2008). It is clear that the issue of sustainability and complete life cycle costs of biofuels are important aspects of the impacts biofuels will have. However, such evaluation is beyond the current scope that includes the risks associated with the production, transportation, storage, and use of biofuels and not the broader impacts of increased/decreased use of various raw feedstocks.

This Tier I report sets the stage for this multimedia assessment and follows the guidance set forth in the "Guidance Document and Recommendations on the Types of Scientific Information to be Submitted by Applicants for California Fuels Environmental Multimedia Evaluations" (2008).

During Tier II activities, a plan of action is developed to address these uncertainties and data gaps and conduct a life-cycle based assessment of the potential impacts biodiesel may have to the State's resources, human health and environment. During Tier III activities, the life cycle based assessment is performed and the results reported to California Environmental Policy Council. Figure 1.1 provides an overview of the life-cycle stages that we will be discussing in this report. We consider four major life stages—feedstock production/collection, biodiesel production, transport and storage, and fuel use (combustion).

Figure 1.1. Generalized summary of biodiesel life cycle impacts.



1.2. History

The first appearance and demonstration of an oil based diesel fuel was at the Paris Exhibition in 1900. The French Government requested the Otto Company to use Arachide (earth-nut or peanut) oil as a fuel in one of their small diesel engine cars. The demonstration went so well that few spectators were aware that the car was running on vegetable oil. This sparked interest in vegetable based fuels for many European countries. France, Italy, Belgium, the UK, and other countries with territories or colonies in Africa, saw potential for Arachide oil because it was readily abundant within the region (Knothe et al., 2005). It was thought that if Arachide could be used as a fuel, it would not only be economically feasible, but also result in a sustainable fuel source.

The use of crude vegetable oil as a fuel was explored until 1937 when Walton discovered that the viscosity of vegetable oil was too high for use in a combustion engine and that vegetable oil required a refining process to reduce its viscosity. In this process, oil was reacted with an alcohol to transform the triglycerides to esters with glycerin as a by product. Walton's work established the first research on biodiesel and a patent was granted for the "transformation of vegetable oils for their use as fuels" (Knothe et al., 2005).

World War II sparked an added interest in biodiesel. With limited oil supplies, many nations resorted to vegetable oil based fuels and used oil from locally grown plants to fuel large tankers and other war machinery (Knothe et al., 2005). Another wartime benefit of biodiesel was its byproduct, glycerin, used as a main ingredient for explosives. However, following the war, a steady supply of cheaper diesel became available again and the production of biodiesel was essentially curtailed.

The oil crisis in the 1970s and 1980s revived an interest in biodiesel. At that time, as the price of fuel doubled, it became clear that an alternative fuel was needed to reduce the nation's dependence on foreign oil. Early experiments on the production and use of biodiesel were conducted at the University of Idaho, University of Missouri, the National Renewable Energy Laboratory, and a handful of other institutions. In 1991, the first small-batch-process pilot plant was set up in Kansas City, Missouri to supply limited quantities of biodiesel. Today biodiesel continues to attract attention with the expectation that this renewable resource will provide environmental benefits with lower emissions (Kemp, 2006).

1.3. Legislative Incentives for Biodiesel

To reduce our nation's dependence on imported oil, Congress passed the Energy Policy Act of 1992 (EP Act). This Act required 75% of new vehicle purchases made by federal and state governments, and alternative fuel providers to be alternative fuel vehicles. Compliance was mandatory for these agencies that operated, leased, or controlled 50 or more light-weight vehicles. The alternative fuels on which these vehicles could run included: pure biodiesel (B100), blends of 85% or more of alcohol with gasoline, natural gas and liquid fuels domestically produced from natural gas, hydrogen, electricity, coal-derived liquid fuels, and liquefied petroleum gas (USDOE, 2005).

Energy Conservation and Reauthorization Act of 1998 amended and updated many elements of the 1992 EP Act. The 1998 amendment allowed "qualified fleets to use B20 in existing vehicles to generate alternative fuel vehicle purchase credits, with some limitations" (USDOE, 2006). This amendment significantly increased the use of B20 by government and alternative fuel provider fleets.

The Energy Policy Act of 2005 was signed into law in August 2005. This legislation supports the growth of the biodiesel industry. Consumer and business federal tax credits for biodiesel were extended to 2008 and the credits were provided to small agri-biodiesel producers. This legislation also requires a comprehensive two-year "analysis of impacts from biodiesel on engine operation for both existing and expected future diesel technologies, and provides recommendations for ensuring optimal emissions reductions and engine performance with biodiesel." (Federal Record, 2005).

In 2007, California Senator Christine Kehoe introduced Senate Bill 140 which, if passed will require all diesel sold in California to contain two percent renewable fuel. Two years after implementing this requirement, all diesel fuels will be required to contain at least five percent renewable fuels (California Senate Bill 140, 2007).

2. Production of Biodiesel

2.1. Biodiesel Production Chemistry

To make biodiesel, a vegetable oil or animal fat is subjected to a chemical reaction known as transesterification. In this reaction, a feedstock (either oil or fat) is reacted with alcohol in the presence of a catalyst to produce glycerin and methyl esters (known as biodiesel). This reaction is shown below.

Figure 2.1. Transesterification Reaction*.

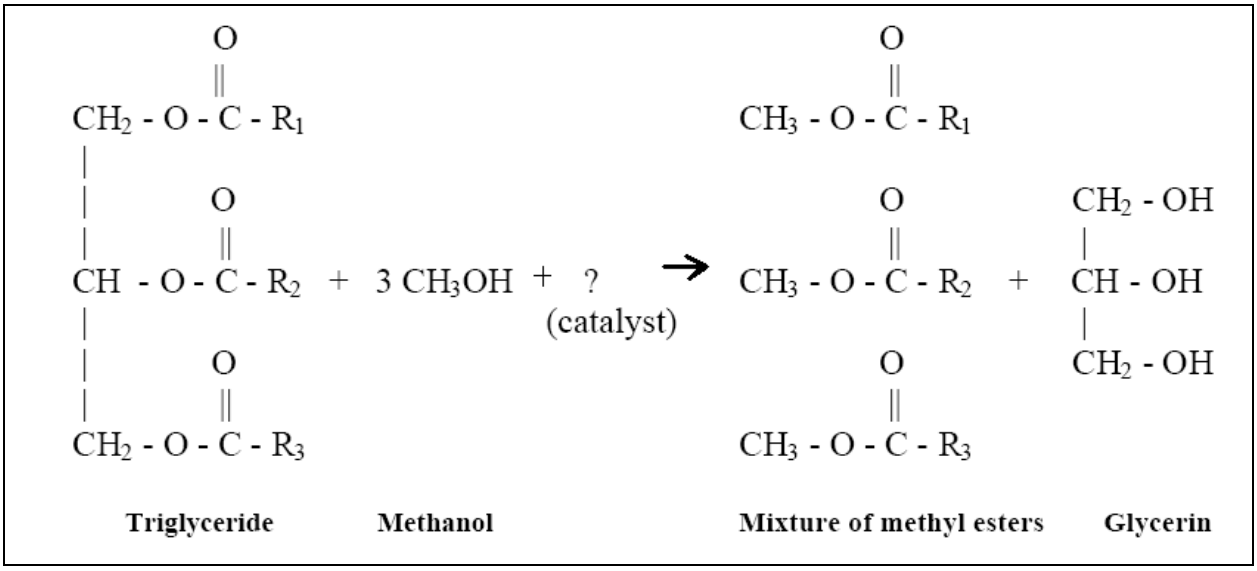


*Figure from Van Gerpen (2004)

In Figure 2.1, the R_1, R_2, and R_3 represent long-chain hydrocarbon fatty acid associated with the feedstock; these are largely palmitic, stearic, oleic, and linoleic acids from naturally occurring oils and fats (NBB, 2007). In theory, the transesterification reaction is reversible, however, "the back reaction does not occur or is negligible largely because the glycerin formed is not miscible with the product, leading to a two-phase system" (Knothe et al., 2005).

2.1.1. Biodiesel Transesterification Reactants

There are a variety of alternative reactants available for producing biodiesel. Reactants are selected based on economic considerations and on the chemical and physical properties of the feedstock.

Alcohol

Either methanol or ethanol can be used as a reactant alcohol in the transesterification process. Economic considerations generally dictate which one is selected because the chemical characteristics of biodiesels do not depend greatly on the particular alcohol used in this process (Van Gerpen et al., 2004). Compared with methanol, ethanol is currently more expensive and about 44% more ethanol is required for the transesterification reaction (Van Gerpen et al., 2004). But the alcohol recovery process is also an important factor in selecting between ethanol and methanol. Excess alcohol must be recovered to minimize operation costs and environmental

impacts. Although the stoichiometric molar ratio for alcohol to triglycerides is 3:1, a 6:1 molar ratio is typically used to ensure a total conversion of the fat or oil to its esters, leaving residual (unreacted) alcohol. Since methanol has a low boiling point, the unreacted alcohol can be removed fairly easily through distillation. Ethanol is more difficult to recover and return to the process because ethanol in water forms an azeotrope, i.e. a mixture for which there is little change in chemical composition through distillation (Van Gerpen et al., 2004).

Triglyceride (Feedstock)

Fats and oils (commonly referred to as the feedstock) are composed of organic compounds made up of three fatty acid units attached to a three-carbon backbone, known as "triglycerides" (Van Gerpen et al., 2004). Each feedstock has a different fatty acid unit. The properties of the final biodiesel product can vary greatly based on the composition of the unit. Feedstock is further discussed in Section 2.2.

Feedstock extraction

Currently the feedstock for biodiesel is grease obtained from restaurants or other recycled sources, but there is also the option of obtaining biodiesel feedstock from agricultural sources such as seeds. Once a feedstock is harvested, the oil-bearing component (such as seeds) must be crushed to extract the oil (which is then transesterified). Crushing facilities extract the oil in a two-step process. First, the biomass is pressed with expellers to extract 60 to 70% of the oil. Since the resulting product still contains between 14 and 20% oil, a second step is required. The product is sprayed with a solvent (typically hexane) and the oil, which is soluble in the solvent, is removed. The solvent is then distilled off, leaving crude oil.

While this oil extraction process is relatively simple, in California there are some additional challenges. Currently there are only two crushing facilities in the state: the J.G., Boswell Company in Corcoran and Adams Grain in Woodland (Kaffka, 2007). To support large-scale biodiesel production in California, additional facilities must be built.

The biggest challenge for increasing the number of oil extraction facilities in the state is obtaining the environmental permits for building them. Solvent losses to the atmosphere during several points in the production process range from 0.2 to 2.0 gallons per ton of biomass (seeds) processed. Since the solvent is composed of 100% volatile organic compounds, the process produces potentially harmful VOC releases. For example, hexane is classified under the Clean Air Act as a Hazardous air pollutant and emissions are highly restricted. With California's strict regulations, obtaining a permit to build a large VOC producing plant can be difficult.

Catalyst

Both acids and bases are used as catalysts in biodiesel production. The content of free fatty acids (FFAs) within the feedstock predominately determines the type of catalyst used in the transesterification process. For feedstocks with FFA levels around 1%, such as soybean oil, canola (rapeseed) oil, and higher grades of restaurant waste oils a base catalyst is used. Animal tallow, palm oil, and other feedstocks that are higher in FFA content (> 2%) can be treated either with an acid catalyst, or with a two-step process using an acid followed by a base catalyst. It is critical to use the appropriate catalyst as it can dictate the type of reaction that occurs. For example, when a base catalyst is mixed with a feedstock high in FFAs, the base catalyst will react with the FFAs to form soap and water (instead of biodiesel). This reaction happens "very fast and [goes] to completion before any esterification begins" (Van Gerpen et al., 2004).

Base catalysts are most commonly used to produce biodiesel. They provide many advantages including: relatively inexpensive production costs since only low temperatures and pressures are required; a high conversion rate (98% typically) with a short reaction time; no requirement for intermediate compounds to yield a direct conversion; minimal side reactions; and no need for exotic construction materials (NBB, 2007).

Base catalysts are typically sodium hydroxide, potassium hydroxide or other similar alkoxides with concentrations ranging from 0.3 to 1.5% based on the weight of oil (Knothe et al., 2005). An alkali catalyst yields fast reactions "with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol/triglyceride ratio" (Van Gerpen et al., 2004). Most commercial operations use sodium hydroxide (NaOH) because of its low cost, but some operations benefit from use of potassium hydroxide (KOH) because the potassium can precipitate as K_3PO_4, which can then be used as a fertilizer (when neutralized with phosphoric acid).

When an acid catalyst is used, a byproduct of the esterification reaction is water. The presence of water can create problems as it "reduces the yield of fatty acids to biodiesel and leaves too many fatty acids behind in the feedstock. Water also reduces yields in the transesterification step" (Van Gerpen et al., 2004) and result in additional treatment costs. Biodiesel producers must take precautions that the water from the acid catalyst is removed prior to the addition of a base catalyst.

Triglycerides and FFAs require different processes for biodiesel production. Acids (such as H_2SO_4 or H_3PO_4) are very effective catalysts for converting FFAs to methyl esters. However, the "acid-catalyzed reaction of triglycerides and methanol is very slow, typically taking 2-3 days to reach completion" (Van Gerpen et al., 2004). To speed up the reaction, a two-step approach is typically used. First, the feedstock is pretreated with an acid catalyst to convert FFAs to esters and then an alkaline catalyst is used to convert the remaining triglycerides to methyl esters. The conversion of FFAs to esters during the first step prevents the formation of soap from the use of a base catalyst in the second step.

2.1.2. Managing the Transesterification Process

There are many steps involved in the production of biodiesel. As described above, three reactants--alcohol, oil, and a catalyst, are mixed in a reactor. Small production plants use batch reactors to mix the reactants while "larger plants (>4 million L/yr) use continuous flow processes involving continuous stirred-tank reactors (CSTR) or flow reactors" (Knothe et al., 2005). For a more complete reaction with a lower alcohol requirement, the reactor step (where the reactants first enter the biodiesel production) can be divided into two steps. First, approximately 80% of the methanol and catalyst are added to the first CSTR to react with the oil, then the excess glycerin is removed and the esters are transferred to a second CSTR, where the remaining 20% of the methanol and catalyst are added.

The next step involves separating the methyl esters and glycerin. Due to the "low solubility of glycerin in the esters, this separation generally occurs quickly and can be accomplished with either a settling tank or a centrifuge" (Knothe et al., 2005). Both products use a substantial amount of excess methanol; the methanol is not removed in this separation process because there is concern that the transesterification process may reverse without it.

The methyl esters are then neutralized with acid to remove any residual catalyst and split any soap that may have formed during the reaction. Figures 2.2 below illustrate the stages of the

transesterification process. Figure 2.3 shows the reaction of the soap with the acid to form FFA and water-soluble salts.

Figure 2.2 Biodiesel transesterification process*.

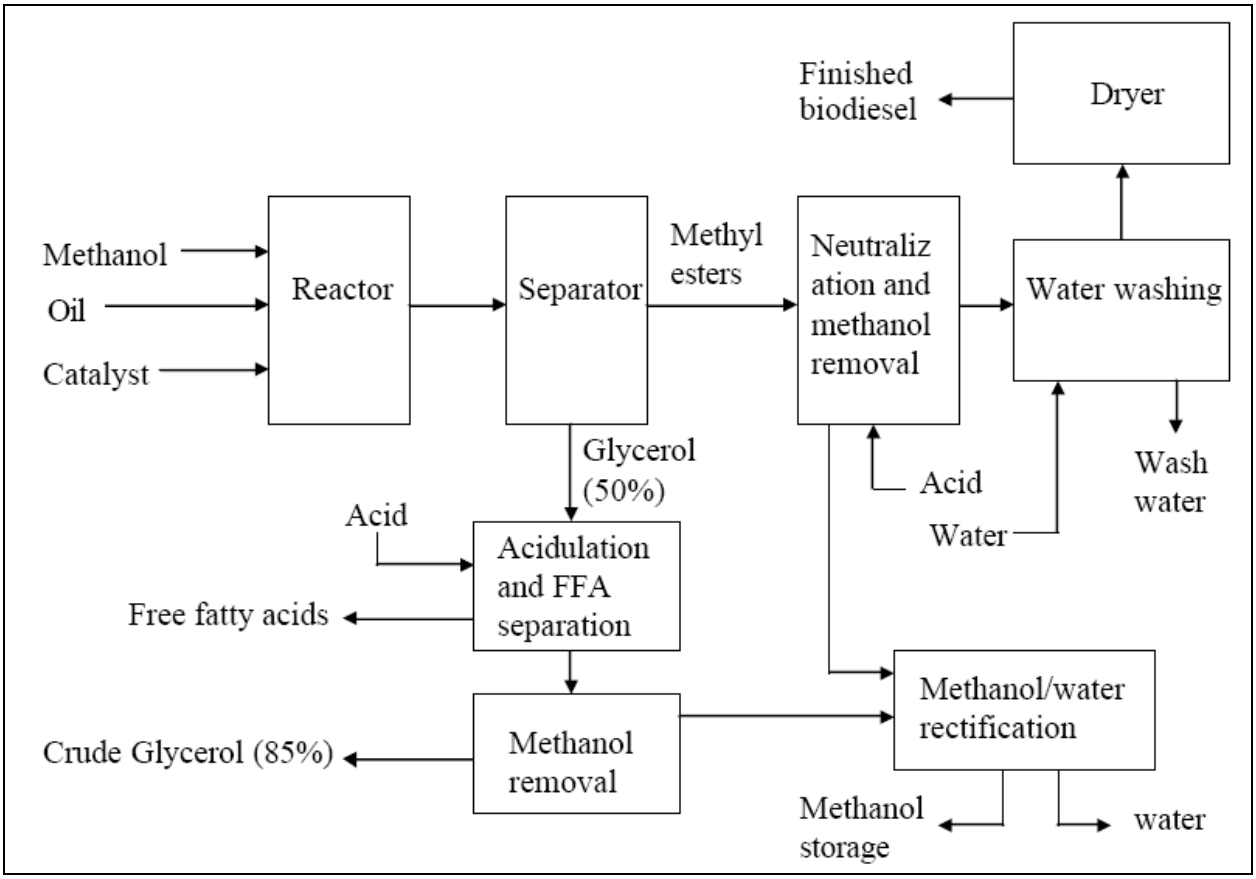
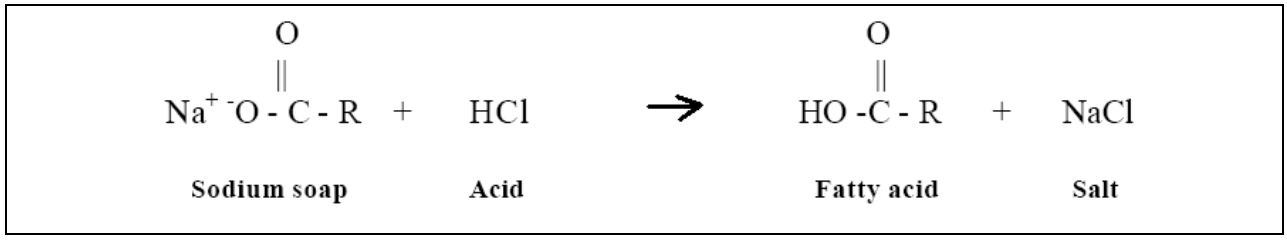


*Figure from Knothe et al. (2005).

Figure 2.3. Glycerin refining using acid to produce fatty acids and salt.



Methanol is also removed in the methyl esters neutralization step, since it passes through a methanol stripper that is "usually a vacuum flash process or a falling film evaporator" (Van Gerpen et al., 2004). This neutralization process reduces the water required for the washing and "minimizes the potential for emulsions to form when the wash water is added to the biodiesel." During the water washing, salts are removed and the FFAs remain. The biodiesel is then dried in a vacuum flash process; this leaves a clear amber-yellow liquid with a viscosity similar to petroleum diesel.

Figure 2.2 also shows that, after the glycerin (glycerol) is separated from the methyl esters, it still must be treated. The amount of glycerin actually leaving the separator is ~50% of the remaining product which also contains methanol, catalyst and soap. At this stage, the methanol content is so high that glycerin must be treated as a hazardous waste. To refine glycerin, acid must be added to split the soaps into FFA and salts (Figure 2.3). Since the FFAs are not soluble in glycerol, they can easily be removed and recycled. The last step is to remove methanol by using a vacuum flash process (or another type of evaporator). The resulting glycerin is about 85% pure and can be sold to glycerin refiners who can increase the purity, often as high as 99.5 – 99.7%.

2.2. Overview of Biodiesel Feedstocks

Biodiesel is produced from a variety of feedstocks including: common vegetable oils (soybean, palm, rapeseed/canola, sunflower, safflower, algae, cottonseed, peanut), animal fats (usually tallow), and waste oils (used frying oils, trap grease). The greatest difference among feedstocks is the amount of free fatty acids that are associated with triglycerides. FFAs can form during the "recovery process for fats and oils, or when there is water present to break the glyceride-fatty acid bond. Hence, the FFA content is a significant measure of feedstock quality, because it indicates the degree of processing required" (Van Gerpen et al., 2004). Typically feedstocks high in FFAs contain greater levels of impurities and require a costly pretreatment to convert the FFAs to esters.

According to the Biodiesel Council of California, "of the 75 million gallons of biodiesel produced in the United States [in 2006], only 6 million gallons were produced in California" (Krauter, 2006). This minimal production is due to the lack of feedstock available within the state. As of 2006, no California farmers were known to be growing feedstock for biodiesel production (Krauter, 2006). Instead, feedstock has to be transported from outside sources to California, increasing the overall costs of the fuel.

The future of wide-scale biodiesel production in California may be dependent on the capacity for local feedstock production. Because of California's arid climate, limited water resources, and fragile ecosystems, determining appropriate feedstock crops for cultivation is crucial. Feedstocks such as canola, sunflower, safflower, cotton, and Chinese tallow tree show potential. However, canola and rapeseed seem to show the greatest promise for wide-scale biodiesel production, as discussed below.

The four primary feedstocks--soybean, palm, yellow grease, and animal tallow--and the two alternatives (algae and trap grease) for multimedia review are described below. Additional crops that grow (or have potential to grow) in California and show promise as feedstocks with wide scale biodiesel production, are also discussed.

2.2.1. Primary Feedstocks for Multimedia Review

Yellow Grease

Yellow grease consists of waste vegetable oils (WVO) such as soy, peanut, canola, and sunflower that are recycled from industrial cooking, franchise cooking operations, or other large scale cooking projects. It is estimated that recycling and processing waste oils can generate over 2.75 billion pounds of yellow grease annually (Kemp, 2006). Since yellow grease is a waste product, it is relatively inexpensive and available in all regions.

The FFA level ranges from 1% to 20%, with the median approximately 10%. "The low end of this range corresponds to an oil recently used in cooking and the high end is an oil that may have been stored for a considerable time before it is processed" (Van Gerpen et al., 2004). Yellow grease requires pre-treatment with an acid catalyst before transesterification can take place (Canacki and Van Gerpen, 2001).

With any WVO, there will always be variability in the quality of the oil. During the cooking process, varying amounts of water, solids and other impurities can be incorporated into the oil. These contaminants can cause difficulties in the transesterification process. This can be one of the greatest hurdles for producers since "having an oil supply of consistent quality is possibly the most important step in manufacturing biodiesel and eliminating excessive waste due to rejected batches" (Kemp, 2006).

A drawback to yellow grease is that it contains substantial quantities of saturated oils that exhibit cold flow problems. Yellow grease is generally solid at room temperature, and requires preheating to maintain it in fluid phase. The biodiesel made from yellow grease feedstock therefore tends to gel in cold climates, plugging fuel filters and fuel injection systems (Kemp, 2006). It is possible to improve the cold flow performance if producers use WVOs that are produced from unsaturated canola or soy oil. Another possible disadvantage for the use of yellow grease is the competition for this feedstock as an additive in animal feed. Competition could cause a price increase in the WVO.

Trap (Brown) Grease

Trap grease (also known as brown grease) is the oil that is recovered from the bottom of commercial frying systems and from grease traps. Typically restaurants install grease traps as part of a discharge system to collect the grease that is washed down the drain. The trap collects grease before it enters the sewer, where it can congeal on the pipe walls and restrict flow. Restaurants normally pay to have these traps emptied and for the grease to be disposed of. Since the grease currently has no other market value, its cost is extremely low.

Converting trap grease to biodiesel can be a daunting process. It is highly variable in composition, containing an assortment of fats, oils, greases, food particles, dirt, water and anything else that washes down the drain. This grease requires "dewatering, filtering, grit removal, and may also require deodorization and bleaching prior to use" (Van Gerpen et al., 2004).

Trap grease also has extremely high levels of FFAs ranging from 40 to 100%. The extensive pretreatment that is required can lead to a costly production. Another hurdle is odor control. Modifications to the production process must be made to adapt to the very volatile feedstock.

Animal Tallow

Animal tallow is a triglyceride material that is recovered by a rendering process, where the animal residues are cooked and the fat is recovered as it rises to the surface. Since it is a waste by-product, it is relatively inexpensive, sustainable, and is available locally. Rendered animal fats typically have a FFA content between 5% and 30%, mostly depending on the time of year. "In winter, when animals carcasses cool quickly with little decomposition, the FFA will be low. In hot summers, the FFA can be quite high" (Van Gerpen et al., 2004).

Since the tallow content is high in saturated fatty acids, it is generally semi-solid or solid at room temperature (Van Gerpen et al., 2004). This saturated fat produces good engine efficiency and

subsequently reduces exhaust emissions (Hilber et al., 2007). Biodiesel derived from animal fats also exhibits high cetane numbers and good oxidation stability. However, the high levels of FFAs can pose some drawbacks. Animal tallow has a high melting point that can lead to precipitation and poor engine performance in cold weather.

Soybean Oil

Soybean oil is the most popular biodiesel feedstock in the United States. Approximately 75% of the virgin plant-based feedstock used in biodiesel production is soy oil (Van Gerpen, 2004). This is largely because soybeans are a major domestic crop with massive production and infrastructure and tend to be the least expensive vegetable oil available in the U.S.

The composition of soy oil is relatively constant with few contaminants (including water) affecting biodiesel production. Its low FFA level (less than one percent) simplifies the refining process. Since soybean oil is composed primarily of unsaturated fatty acids, it has beneficial cold flow properties. However, it also has a lower performance as a fuel compared to other plant oils.

Currently, the primary challenge for the use of soy oil as a biodiesel feedstock is agricultural competition. With the high demand for ethanol, many farmers are shifting their focus to corn. Generally, as the price and demand for corn increase, the production of soy decreases; USDA reported that "soybean ending stocks for 2007-2008 are projected to be 320 million bushels, or nearly 50 percent lower than the 2006-2007 stocks." Similarly, prices for soy oil are expected to increase with demand. The average "soybean prices for 2007-2008 are projected at $6.65 to $7.65 per bushel, up 15 cents on both ends of the range" (Sioux City Journal, 2007).

Palm Oil

Palm oil is grown primarily in tropical or subtropical areas such as Malaysia and Indonesia. It is characterized by high concentrations of medium-chain saturated (palmitic acid) and monosaturated (oleic acid) fatty acids. One of its greatest advantages as a biofuel feedstock is high oil yield (Kemp, 2006). Palm plantations "typically produce about 610 gallons per acre of palm oil plantings, compared with 122 gallons per acre for rapeseed and 46 gallons per acre for soybeans"(Jessen, 2007). Also, the production costs of palm oil are low, providing a moderate world-market price compared to other edible vegetable oils.

Palm oil does have significant drawbacks. Its high levels of free fatty acids require an additional costly pretreatment. The oil also has a high saturated fatty acid content which corresponds with increased cold filter plugging and cloud point. This prevents the winter use of neat (100%) palm oil methyl esters in temperate climates (Mittelbach, 2004).

Issues of palm oil sustainability also are of concern. With the recent increased demand for feedstock, Indonesia and Malaysia, the world's top palm oil producers, are clear-cutting and burning forests to build palm plantations. This deforestation releases greenhouse gas emissions and threatens the rich biodiversity of the ecosystem (Jessen, 2007).

Greenhouse gas emissions from existing palm oil forests are also a concern. After the forests are destroyed, the lands are filled to make peat bogs where the palm oil trees can be grown. A four-year study conducted by the Wetlands International, Delft Hydraulics and Alterra Research Center of Wageningen University in Holland examined the carbon release from peat swamps in Indonesia and Malaysia in recent years. It was determined that on average, 600 million tons of carbon dioxide seep into the air each year from these peat bogs. It has been estimated that these

carbon dioxide releases, combined with releases from burning of rain forests during clearing, equate to approximately 8% of the world's current carbon output from fossil fuels (Max, 2007).

To help efforts towards sustainability, a global, nonprofit organization known as the Roundtable on Sustainable Palm Oil (RSPO) was formed in April 2004. It is composed of 144 members who represent growers, processors, consumer goods companies, retailers and other non-governmental organizations. In November, 2005, the RSPO adopted eight criteria for sustainable palm oil production which include:

1. Commitment to transparency;
2. Compliance with applicable laws and regulations;
3. Commitment to long-term economic and financial viability;
4. Use of appropriate best practices by growers and millers;
5. Environmental responsibility and conservation of natural resources and biodiversity;
6. Responsible consideration of employees, individuals and communities affected by growers and mills;
7. Responsible development of new plantings;
8. Commitment to continuous improvement in key areas of activity.

Canola

Canola was developed through conventional plant breeding with rapeseed. To improve the characteristics of rapeseed, breeders created cultivars with reduced levels of erucic acid and glucosinolates. The end product, canola, is now widely grown in Canada, with some production in the United States. North Dakota is the leading state in the production of canola and typically grows approximately 90% of the total U.S. canola.

While there is little experience with canola in California, much may be learned from Australia's success in cultivating the crop. The climate where canola is grown in Australia is similar to the California Central Valley from Bakersfield to Redding (Kaffka, 2007). Canola is considered to be a relatively drought tolerant crop that typically requires around 18 inches of water a year (under Australian conditions) (Johnson, 2007). California's similar climate and the crop's relatively low water requirement suggest that canola could be widely produced within the state. Steve Kaffka, a University of California Cooperative Extension agronomist, is conducting a UC study on the conditions required to grow canola efficiently in California. As part of the study, trial canola varieties have been planted in Chico, Davis, the West Side Field Station and the Imperial Valley.

Canola oil shows promise as a feedstock; it has properties similar to soy oil with a composition primarily of unsaturated fatty acids and a low content of FFAs. The oil yield of canola, however, is much higher than soy; the seed contains 45% oil. Canola feedstock can produce fuel with beneficial cold flow properties; its 24°F CFPP is superior to almost all other feedstocks (soy is 28 degree CFPP, palm is 55 degree CFPP, and tallow is 58 degree CFPP) (Kotrba, 2007). On the negative side, canola does have a higher risk for oxidation and it exhibits poor storage stability.

Safflower

Safflower is the most common oil seed produced in California. It can tolerate extreme weather conditions and is considered a low input and drought tolerant crop. Little fertilizer is needed as

the crop is extremely deep rooted and can recover lost nutrients. In fact, an advantageous trait of the crop is its ability to aggressively recover nitrogen from the soil. Safflower could also be beneficial to the California agricultural industry as tests have shown that safflower can tolerate irrigation with saline water (Kaffka, 2007).

There are two types of safflower varietals--those high in monounsaturated fatty acid (oleic) and those high in polyunsaturated fatty acid (linoleic). In both varietals, the fatty acid profiles are so similar that they possess the same characteristics: poor storage stability, low cetane number and good cold flow characteristics. Another advantage of safflower is that its seed has a high oil concentration of 42 to 48%.

Algae

Algae is a single-celled organism that contains a relatively large volume of plant oil. According to the National Renewable Energy Laboratory, there are more than 300 algae strains demonstrating potential for use as fuel feedstock and some contain more than 50 percent oil. While there are multiple species of algae, all generally share similar fatty acid profiles. The majority of fatty acids present are oleic (36%), palmitic (15%), stearic (11%), and linoleic (7.4%). There are other saturated and monounsaturated fatty acids that can be present but they typically represent less than 5% each of the total fatty acids (Van Gerpen et al., 2004). Algae's high level of saturated and monounsaturated fatty acid content provides for optimal fuel quality.

High-oil algae species have been studied since 1978 by the US Department of Energy as part of its biodiesel fuels research. Intensive production of algae can lead to production of as much as 10,000 gallons of feedstock per acre per year (Kram, 2007). Algae is sensitive to temperature fluctuations, pH, atmospheric levels of CO_2, and competition between promising strains and less prolific strains of algae. If limitations associated with a narrow range of growing and harvesting conditions can be addressed, "enough algae-based biodiesel can be produced each year to power the current US fleet of vehicles (140 billion gallons or 500 billion liters) using a mere 9.5 million acres [3.8 million hectares] of cultivation space" (Cox, 2006). This acreage is minimal compared to the 3 billion acres of farmland required to produce the same amount of oil from soybeans. Competition with food production is also reduced due to minimized use of farmland.

Air pollutants can be reduced with the production of algae. Since algae thrives on high concentrations of carbon dioxide and nitrogen oxide, atmospheric emissions from power plants can be used to feed the algae. This creates a sustainable energy system that could "enable a power plant to meet emerging state regulations for both CO_2 reduction and renewable power generation" (Cox, 2006).

2.2.2. Feedstock Characteristics

Biodiesel feedstocks are classified based on fatty acid profile (Table 2.2); the fatty acid composition greatly influences a fuel's characteristics, as different esters of fatty acids have different physical and chemical properties. The carbon chain length and the degree of saturation of the raw material can affect key properties including--pour point, cloud point, centane number, viscosity, and storage stability. Typical values of fatty acid compositions of different feedstocks are shown below. The numbers describing each acid indicate the number of carbon atoms in the chain, followed by the number of unsaturated carbon-carbon bonds in the chain. For example, Oleic acid, 18:1, has 18 carbon atoms and one unsaturated bond.

A saturated oil or fat has no double bonds; instead, all of its carbon atoms (in the fatty acid portion) are bound to two hydrogen atoms (except at one end, which has 3 H atoms attached). This allows the chains of fatty acids to tightly align together, resulting in solidification at higher temperatures. Conversely, unsaturated fatty acids contain carbon-to-carbon double bonds and will exhibit lower cloud points as they resist solidification at low temperatures.

Table 2.2. Fatty acid percentages in biodiesel feedstocks*.

	Myristic 14:0	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3	Arachidic 20:0	Erucic 22:1
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-62	trace		
Hi linoleic Safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Oleic Rapeseed		4.3	1.3	59.9	21.1	13.2		
Hi Erucic Rapeseed		3	0.8	13.1	14.1	9.7	7.4	50.7
Tallow	3-6	24-30	20-25	37-43	2-3			
Yellow Grease	1.3	17.4	12.4	54.7	8	0.7	0.3	0.5

*Data from Van Gerpen et al. (2004) and Van Gerpen (2004).

Feedstock such as animal tallow and some recycled vegetable oils are high in saturated fatty acids, whereas oils including soy and canola are composed of unsaturated fatty acids. The degree of saturation is indicated by the iodine number of the oil. Iodine is used to break any double bonds as it attaches itself to each carbon atom that holds together the double bonds. The value of the iodine number corresponds to the degree of saturation; feedstock with a high composition of unsaturated fatty acids will demonstrate a high iodine value (since more iodine is needed to break apart the double bonds).

The cetane number of biodiesel is positively affected by an increased amount of saturated fatty acids. Biodiesel fuels with low iodine numbers (composed of saturated fatty acids) exhibit greater efficiency and maintain high cetane numbers. However, “the greater the fraction of saturated fatty acids, the poorer the cold weather performance” tends to be. (Van Gerpen et al., 2004) While the cold flow properties are better for biodiesel with high iodine numbers, the centane number is low (indicating poor performance), and there is poor storage stability (as there is a higher risk for oxidation). The correlation between iodine and cetane number can be seen in Table 2.3.

Table 2.3. Comparison of iodine number and cetane number for different types of biodiesel*.

	Rapeseed/ Canola Oil	Soybean Oil	Palm Oil	Lard	Tallow
Iodine Number	110 - 115	125 - 140	44 - 58	60 - 70	50 – 60
Cetane Number	58	53	65	65	75

*Data from Helber et al. (2006).

2.2.3. Feedstock Economic Considerations

Price, availability, origin, geography, and consistent quality generally dictate which feedstock biodiesel producers use. Because the cost of feedstock constitutes between 70 and 85% of the overall cost of biodiesel production (Knothe et al., 2005), there is a strong incentive to purchase the cheapest feedstock that is in close proximity to the production facility. Before development of infrastructure involving long-term dependence on a particular feedstock, it is important to consider if it is sustainable, has potential expansion for growth, and has consistent properties. Table 2.4 below summarizes properties typical of the different major kinds of feedstocks.

Table 2.4. Economic considerations of biodiesel feedstocks*.

Biodiesel Feedstock	Cost/Unit	Supply/Growth Flexibility^	Content/Quality Variability	Degree of Pretreatment Required
Virgin plant based feedstocks (e.g. soy, palm, canola, corn, cottonseed, sunflower, etc.)	Moderate to high	Supply can be expanded	Low variability	Modest
Virgin animal based feedstocks (e.g. lard, tallow, chicken fat, fish oil)	Moderate	Fixed (dependent on meat, poultry, fish, demand and processing)	Low to moderate variability	Modest to High
Recycled feedstock (e.g. yellow grease from frying or brown grease)	Low	Fixed (dependent on restaurant, fried activity)	High variability	High

*Data from Hilber et al. (2006).
^Ability to expand total supply in response to price increases from demand shifts

2.3. Biodiesel Standardization and Fuel Quality

Generally, the quality of a biodiesel fuel is dependent on the quality and fatty acid composition of the feedstock, the production process, and post-production parameters (Knothe et al., 2005). Pure biodiesel fuels, regardless of feedstock, must meet the ASTM D6751 standards (Table 2.5). Because there are so many varying factors in the production of biodiesel, it is critical that these specifications are met. When biodiesel meets the requirements, it can be used in most "modern

engines without modifications while maintaining the engine's durability and reliability" (Van Gerpen et al., 2004).

Thus, the fuels reviewed in this multimedia risk assessment will be B20 (20% ASTM D6751 biodiesel mixed with 80% ASTM D975 ultra low sulfur diesel). Our focus on B20 is designed to target the composition of fuel most frequently involved in on-site storage and distribution from fuel service stations. We will also consider transportation and storage of B100 as a distributed ingredient in on-site mixing.

Table 2.5. ASTM D6751-07a. Specifications for biodiesel (B100)*.

Property	ASTM Method	Limits	Units
Calcium & Magnesium, combined	EN 14538	5 max	ppm (ug/g)
Flash Point (closed cup)	**D 93**	**93 min.**	**Degrees C**
Alcohol Control (One of the following must be met)			
1. Methanol Content	EN14110	0.2 Max	% volume
2. Flash Point	D93	130 Min	Degrees C
Water & Sediment	**D 2709**	**0.05 max.**	**% vol.**
Kinematic Viscosity, 40 C	D 445	1.9 - 6.0	mm^2/sec.
Sulfated Ash	D 874	0.02 max.	% mass
Sulfur **S 15 Grade** **S 500 Grade**	 **D 5453** **D 5453**	 **0.0015 max. (15)** **0.05 max. (500)**	 **% mass (ppm)** **% mass (ppm)**
Copper Strip Corrosion	D 130	No. 3 max.	
Cetane	D 613	47 min.	
Cloud Point	**D 2500**	**Report**	**Degrees C**
Carbon Residue 100% sample	D 4530*	0.05 max.	% mass
Acid Number	**D 664**	**0.50 max.**	**mg KOH/g**
Free Glycerin	**D 6584**	**0.020 max.**	**% mass**
Total Glycerin	**D 6584**	**0.240 max.**	**% mass**
Phosphorus Content	D 4951	0.001 max.	% mass
Distillation, T90 AET	D 1160	360 max.	Degrees C
Sodium/Potassium, combined	EN 14538	5 max	ppm
Oxidation Stability	**EN 14112**	**3 min**	**hours**

*Data from NBB (2007).

To ensure compatibility with diesel engines, the transesterification reaction must be run to completion and without accumulation of byproducts. If there is any remaining glycerin, catalyst, alcohol, or FFAs in the biodiesel, operational problems can occur. The ASTM D6751 standard

"prescribes the required properties of biodiesel fuel at the time and place of delivery" unless other agreements were arranged between purchaser and supplier. (ASTM, 2007) All biodiesel produced for commercial sale must be registered with the United States Environmental Protection Agency under 40 CFR Part 79.

The ASTM D6751-07a "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels" identifies the parameters that pure "diesel (B100) Grades S15 and S500 for use as a blend component with middle distillate fuels" (ASTM, 2007). These specifications, shown below, prescribe the required properties of the fuel as existing at the time and place of the sale.

2.3.1. Biodiesel Fuel Energy Content

The energy content of a fuel can greatly influence fuel economy, torque, and horsepower. Compared to diesel, the energy content of biodiesel (measured in Btu/gal) is slightly lower. The EPA reported that the average energy content of biodiesel is dependent upon the type of feedstock. Testing revealed that "rapeseed and soybean-based biodiesels cannot be distinguished from one another, but that the animal-based biodiesels can be distinguished from plant-based biodiesels (at a 99% confidence level)" (USEPA, 2002). This is clearly indicated by the results shown below (Table 2.6).

Table 2.6. Average energy content of 100% biodiesel*.

	Average net Btu/gal
All biodiesels	118,296
Animal-based	115,720
Rapeseed/canola-based	119,208
Soybean-based	119,224
Rapeseed or soybean-based	119,216

*Table from EPA (2002).

The energy content of conventional diesel fuel is 129,500 Btu/gal. Animal based biodiesel and plant based biodiesel contain 10.6% and 7.9% less energy, respectively, than diesel.

2.4. Waste Generation and Waste Management

In evaluating the production of biodiesel (and other alternative diesel options) it is important for the multimedia assessment and the life-cycle assessment to identify where and what kind(s) of hazardous waste(s) may be generated. For example, sodium hydroxide and potassium hydroxide may be used as base catalysts for producing fatty acid methyl esters (FAME) from fats and oils. Acids are also used as catalysts for converting free fatty acids to methyl esters. In the process of using those catalysts, corrosive hazardous wastes may be generated. Some solvents are applied in the production process as well. Proper identification and management of the waste solvents are required to comply with hazardous waste laws and regulations. Although biodiesel formulations are less toxic than standard diesel formulations, the storage stability of biodiesel is less than the standard ultra low sulfur diesel (ULSD). Degradation could be caused by temperature, oxidation, and/or material incompatibility; and some toxic components may be produced in the biodiesel. Thus, further studies are required to determine:

a) if the leaked or spilled Biodiesel after oxidation and degradation contains any hazardous substances; and
b) if the Biodiesel product, stored beyond the recommended six-month term, becomes a hazardous waste.

These issues must be addressed in the Tier II and Tier III assessments.

Once the sources, composition, and magnitude of waste streams from biodiesel fuel production have been identified, there is a need to identify management approaches that could be applied to the identified hazardous waste streams. When generated hazardous wastes are identified, the appropriate waste management approach, such as treatment, storage, and disposal should be identified and described in the Tier II and Tier III reports. Among the waste management strategies considered, priority should be given to available alternatives for hazardous waste reduction and pollution prevention. To address these and other hazardous-waste issues, the Tier II and Tier III reports will include a section that provides a work plan to specify the hazardous waste storage, transportation, treatment, disposal, waste reduction, and emergency planning for the biodiesel life cycle.

3. Storage and Distribution of Biodiesel

3.1. Material Compatibility

Material compatibility is an important property to consider. Since biodiesel can react with some metals and polymers, it is critical that the material of tanks, hoses, gaskets, and other parts that may come in contact with biodiesel, are compatible with the fuel's properties. When biodiesel is exposed to incompatible materials, it can degrade, soften, or seep through them (USDOE, 2006). As discussed above, biodiesel is not compatible with brass, bronze, copper, lead, tin and zinc as these metals can initiate oxidation and sediment production. Biodiesel can also have compatibility issues with some polymers. Table 3.1 shows different polymer's compatibility relative to diesel. Nitrile rubber compounds, polypropylene, polyvinyl, and Tygon are particularly vulnerable to biodiesel.

Table 3.1. Biodiesel materials compatibility.

Biodiesel Material Compatibility Table

Polymer	Relative to Standard Diesel
Fluorosilicon	Hardness little change, swell +7%
Nitrile	Hardness –20%, swell +18%
Nylon 6/6	Little Change
Polypropylene	Hardness –10%, swell +8-15%
Polyurethane	Hardness little change, swell +6%
Polyvinyl	Much worse
Teflon	Little change
Tygon	Worse
Viton A401-C	Little change
Viton GFLT	Little change

Table from Van Gerpen, 2004

Vehicles manufactured before 1993 may have issues with incompatible seals, gaskets and adhesives as they were made from natural and nitrile rubber (Van Gerpen, 2004). Most engines produced after 1994 are compatible with biodiesel (B20); however, "the user should consult the equipment manufacturer or owner's manual regarding the suitability of using biodiesel (B100) or biodiesel blends in a particular engine" (ASTM, 2007). Since biodiesel is considered a "hazardous substance", UST owner/operators are required by state health and safety codes to demonstrate material compatibility prior to storage of biodiesel (SWRCB, 2008).

Materials such as "Teflon, Viton, and Nylon have very little reaction to biodiesel and can be used to update incompatible equipment" (NBB, 2007). However, some grades of these materials have shown compatibility issues with different blends of biodiesel and the manufacturer of the material should be contacted to determine the most suitable grade. Additional acceptable materials for non contaminated biodiesel (pure B100) storage tanks are: aluminum, steel, and fluorinated polyethylene or polypropylene. However there have been cases of biodiesel oxidizing to form peroxides that corroded steel tanks. Contamination by water or sulfur also has the potential to weaken materials commonly used in UST (Hodam, 2008).

Assuring materials compatibility requires the compilation of both comparative corrosion tests and elastomers tests. Comparative corrosion tests should include copper and steel strip tests for all samples. Elastomers should be tested for tensile strength, hardness, and swelling for at least 1000 hours of exposure at 60 F. The elastomer samples to be used will be determined in consultation with Cal-EPA staff as part of the Tier-II effort.

3.2. Biodiesel Solvency

Biodiesel has higher solvency properties than diesel fuel and can act as a mild solvent. It can dissolve the residual sediments in diesel storage tanks and engine fuel tanks. These dissolved sediments can harm fuel systems as they plug fuel filters. Solvency decreases with a decreasing percentage of biodiesel. Pure biodiesel (B100) exhibits the greatest solvency effects; whereas typically "20% or less blends of biodiesel in diesel will nearly completely dilute the solvency effect" (Van Gerpen, 2004).

To avoid such problems with solvency, the USDOE recommends that users "clean the tanks and anywhere in the fuel system where sediments or deposits may occur before filling with B100" (USDOE, 2006). After the cleaning process, it is important to remove all excess water, as this can affect fuel quality (as discussed previously). When switching a vehicle to biodiesel, it is recommended to change the fuel filters several times after the switch as some sediments could clog the filters causing operation problems.

3.3. Storage Stability

Biodiesel is susceptible to chemical changes during long-term storage. Fuel aging and oxidation by atmospheric oxygen can lead to increased acid numbers, increased fuel viscosity, and the formation of gums and sediments. Storage stability refers to the ability of the fuel to resist chemical changes during long-term storage. While storage stability is an important parameter, the ASTM biodiesel standards have not yet established "stability tests that ensure satisfactory long-term storage of biodiesel (B100)" (ASTM, 2007). There are data that suggest that common 100 hour fuel exposure tests may not be adequate as drastic changes in material properties can occur at times between 300 and 1000 hours of exposure with biodiesel (Hodam, 2008). Due to the lack of information on storage stability, the National Biodiesel Board recommends no longer than a six-month storage life for B100 biodiesel (NBB, 2007). As discussed below, the chemical reactivity of esters (biodiesel) depends on the fatty acid profile, fuel additives, temperature, metals, and the presence of water and natural antioxidants.

3.3.1. Biodiesel Oxidation

Biodiesel oxidative stability is affected by exposure to air, sunlight, and elevated temperatures. Sunlight will accelerate the oxidation of fatty esters through a photo-oxidation process "whereby oxygen directly attacks the olefinic (double-bonded) carbons" (Southwest Research Institute, 2005). This can cause fuel degradation, which consequently can alter the fuel's quality. High storage temperatures can also accelerate fuel degradation. Thus, ASTM D6751 recommends underground or isothermal storage to avoid extreme temperatures, with limited exposure of headspace to atmospheric oxygen. Fixed roof tanks should be kept full to limit oxygen supply and tank breathing (ASTM, 2007).

Much of the fuel's oxidation behavior can be characterized by its fatty acid profile. The lower the level of saturation in an ester, the more susceptible it will be to oxidation. The presence of

double bonds within a fatty acid leads to autoxidation; the rate at which autoxidation proceeds depends on the "number and position of the double bonds" (Knothe et al., 2005). Fatty acid compounds that are composed of adjacent allylic (double-bonded) carbons contain pi bonds, where the *p* orbitals overlap and electrons are shared throughout the carbon chain (Kemp and Vellacio, 1980). This electron sharing leads to greater atomic forces, creating a weak hydrogen bond. When hydrogen is removed "oxygen rapidly attacks and a hydroperoxide is ultimately formed" (SRI, 2005). Hydroperoxides then decompose and interact to form "numerous secondary oxidation products including aldehydes, alcohols, shorter chain carboxylic acids, and higher molecular weight oligomers often called polymers" (SRI, 2005). These secondary products of the oxidation process cause the fuel to eventually deteriorate.

Oils high in polyunsaturated fatty acids are most susceptible to autoxidation. As a rule, saturated fatty acids (such as 16:0 or 18:0) are stable; but as the presence of double bonds (between carbon atoms) increases (for example from 18:1 to 18:2 to 18:3), the oxidative stability decreases (these ratios describe the number of carbon atoms and double bonds in the fatty acid chain such that "18:2" refers to a fatty acid chain comprised of eighteen carbon atoms and that there exist two double bonds in the chain). This was verified in an early study that "measured the relative rate of oxidation for the methyl esters of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids to be 1:12:25" (SRI, 2005). Soybean oil and canola (rapeseed) are the feedstocks highest in linoleic and linolenic acid and most prone to oxidation.

Metals are known to catalyze oxidation reactions of biodiesel. Copper, iron, and other transition metals, "act as a Lewis acid to catalyze polymerization of polyunsaturated hydrocarbon molecules in biodiesel" (Kenreck, 2007). These metals may be present if corrosion occurs in the manufacturing process. Free fatty acids can also adversely affect the oxidative stability of biodiesel as they may degrade or cause corrosion and thermal instability. (Kenreck, 2007).

3.3.2. Residual Water

While biodiesel is generally considered to be insoluble in water, it can actually contain as much as 1500 ppm of dissolved water (Van Gerpen et al., 2004). Storage stability of biodiesel is also affected by the presence of water within the tank. Water can enter fuel tanks through vents and seals as humidity in the air where it either condenses or dissolves into the fuel. According to Van Gerpen et al. (1996), virtually all diesel fuel storage tanks can be assumed to contain some water. Further, blending biodiesel into ULSD reduces the water separation capability of the fuel and the formation of water/fuel mixtures (Quigley, 2007). Water can cause hydrolytic degradation of the fuel, contribute to microbial growth in the fuel, and can cause corrosion of fuel systems and tanks.

The presence of water within the biodiesel can cause corrosion of fuel tanks and engine fuel system components. The most direct form of corrosion is rust, "but water can become acidic with time and the resulting acid corrosion can attack storage tanks" (Wedel, 1999). Hydrolytic degradation can also occur if concentrations of water are present within the tank. Substances such as "mono- and diglycerides (intermediates in the transesterification reaction) or glycerol can emulsify water" (Knothe et al., 2005).

Condensed water in a fuel tank can support the growth of bacteria and mold that use the hydrocarbons in the biodiesel as a food source. These "hydrocarbon-degrading bacteria and molds will grow as a film or slime in the tank and accumulate as sediment" (Wedel, 1999).

The control of water is primarily a housekeeping issue (i.e. keeping storage tanks clean) and a problem frequently addressed by using fuel filters (Sunny Beaver of Yokayo Biofuels [B100 distributor], personal communications). Additives may also be used to address residual water problems.

3.4. Distribution and Blending of Biodiesel

Biodiesel is typically transported via rail cars, tank trucks and drums; the choice of vessel depends on the quantity of biodiesel being transferred and the cold flow properties of the fuel. Due to biodiesel's poor cold flow properties, it is recommended to ship the fuel by the following means in cold climates: hot biodiesel in tank cars that are rapidly delivered, solidified biodiesel in tank cars that are equipped with steam coils, 20% biodiesel blends with winterized diesel, or 50% biodiesel blends with diesel No. 1 (Van Gerpen, 2004).

Transportation vessels must be composed of materials that are compatible with biodiesel. Seals, gaskets, and adhesives present in the transfer system should also be compatible with biodiesel. If the vessels have been previously used to transport diesel, they should be cleaned and dried prior to biodiesel transport, due to biodiesel's high solvency properties (as mentioned previously). While biodiesel is considered non-hazardous, "it is recommended that PVC-coated gloves as well as safety glasses or goggles be used when handling biodiesel" (Van Gerpen, 2004).

There are various regulations in place for biodiesel transport and biodiesel plants. The Clean Water Act (CWA) and the Oil Pollution Act (OPA) "outline various requirements that must be met in order to comply with regulations" (Van Gerpen, 2004). Under these acts, there is no distinction between petroleum oils, vegetable oils, and animal fats, as they share common physical properties and produce similar environmental effects.

With the amendment of the OPA in 2002, the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) was introduced. This legislation requires "owners or operators of vessels and certain facilities that pose a serious threat to the environment to prepare facility response plans" (Van Gerpen, 2004). Greater contingency planning can reduce spills during transportation and at the plant.

In 2002, the EPA published a Spill Prevention Control and Countermeasure (SPCC) rule at Title 40 of the Code of Federal Regulations, Part 112 (40 CFR 112) to ensure that facilities put in place containment and other countermeasures that would prevent oil spills. While each SPCC is unique to the facility, all should clearly address: "operating procedures that prevent oil spills, control measures installed to prevent a spill from reaching navigable waters, and countermeasures to contain, clean up, and mitigate the effects of an oil spill that reaches navigable waters" (Van Gerpen, 2004).

4. Use of Biodiesel

4.1. Vehicle Operability Issues

There are a number of vehicle operability issues associated with the use of biodiesel blends. These include cold fuel flow, fuel foaming, water separation, and fuel oxidative stability (Taracha, 2006; Quigley, 2007). Cold flow can result in fuel system clogging. Fuel foaming can result in difficulty during tank filling and can potentially increase the possibility of fuel spills. Reduced water separation can result in water/fuel mixtures that can clog fuel systems and promote microbial growth that can also clog fuel systems. Oxidative degradation of biodiesel can result in injector deposits, and lacquer formation, and fuel systems corrosion. These impacts to the vehicle fuel system can result in reduced drive-ability, higher tailpipe emissions, and increased maintenance costs.

4.2. Biodiesel Cold Flow Characteristics

One of the greatest challenges associated with the use of biodiesel is cold flow behavior. In cold temperatures, biodiesel can start to freeze or gel. If the fuel begins to gel, "it can clog filters or can eventually become too thick to pump from the fuel tank to the engine" (USDOE, 2006). Biodiesel's behavior in cold climates can depend on the fatty acid profile and the amount and types of impurities within the fuel (Pradhan et al., 2007). Several cold flow properties are commonly used to classify cold flow performance: cloud point, pour point, and cold filter plugging point (CFPP).

The cloud point is the temperature at which crystals begin to precipitate from the fuel, giving it an appearance as if wax was forming. As the temperature decreases, the biodiesel reaches its pour point; this is the lowest temperature at which the fuel can still flow, before the crystals start to gel. To determine cold flow characteristics in a more precise and reliable manner, the cold filter plugging point can be evaluated. CFPP is the lowest temperature at which the fuel can pass through a standard test filter under standard conditions.

As the content of saturated fatty acids increases, so does the cold filter plugging point. Saturated fatty acids are comprised of single bonds and can easily form highly regular crystalline structures; this results in crystallization at high temperatures. Typical relationships between the content of saturated fatty acids in biodiesel (without additives) and the corresponding CFPP value are displayed in Figure 4.1.

4.3. Use of Additives

Chemical additives are commercially available to address the oxidative stability, cold-flow properties, microbial contamination, increased water affinity and increased NO_x emissions of biodiesel. The varying properties of the fuel, based on the feedstock variety and fragmented nature of the new industry, result in a lack of consistency in the current use of additives. However, as larger companies enter the market and standards are further developed, more uniform practices regarding the use of additives can be expected.

Figure 4.1. Relation between content of saturated fatty acids in biodiesel (without additives) and its CFPP value*.

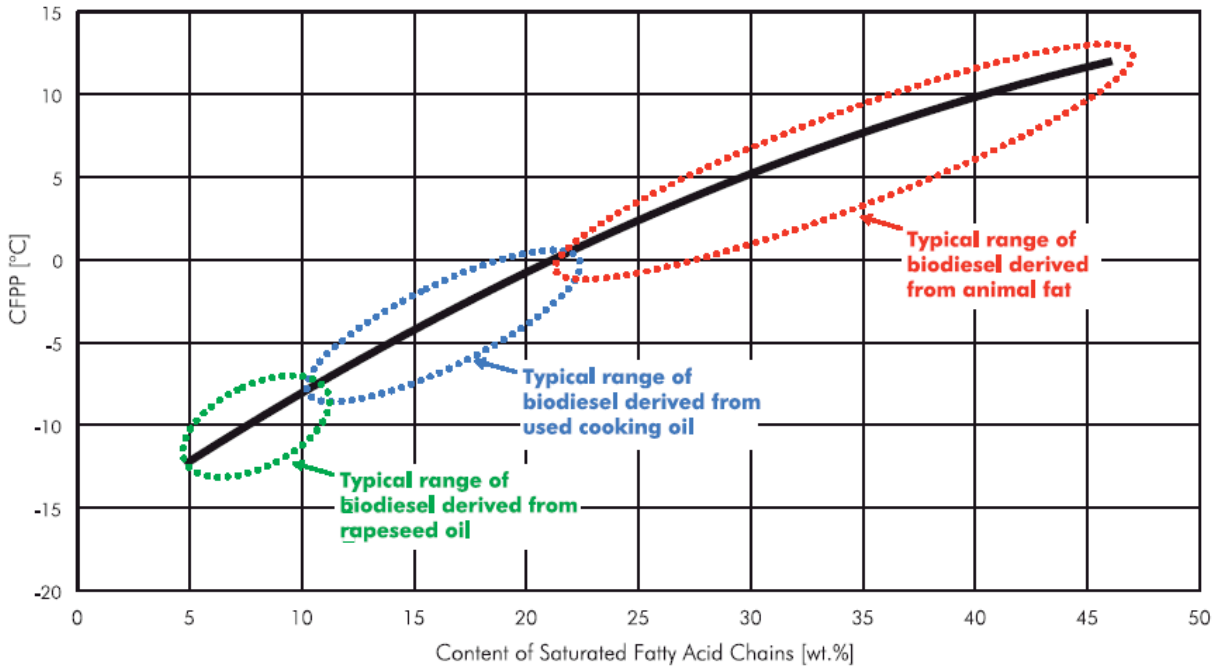


*Figure from Hilber et al. (2006).

4.3.1. Antioxidants

Oxidation of biodiesel results in the formation of hydroperoxides, which in turn induce free-radical chain reactions that lead to decomposition into low-molecular weight, highly oxidized species including aldehydes, ketones, formic acids and acetic acids (Albermarle Corp., 2005).

Vegetable oils (such as soybean oil) typically contain naturally occurring antioxidants (tocopherols, i.e., vitamin E) and provide some protection against oxidation. Antioxidants contain a highly-labile hydrogen that is easily extracted, acting as a free radical. This resulting antioxidant free radical is "either stable or further reacts to form a stable molecule that does not contribute to the chain oxidation process" (SRI, 2005).

Natural antioxidants can be added to biodiesel to improve the fuel's antioxidant behavior. However, during the feedstock processing for biodiesel derived from plant oil (where the seeds are bleached, deodorized and the oil is distilled) the natural antioxidants may be removed. Recent studies have shown that synthetic antioxidants may actually be more effective than natural antioxidants (SRI, 2005). The efficiency and necessary quantity of antioxidants are strongly dependent on the feedstock and biodiesel production technology (Lacoste et al., 2003). These additives have different effects on biodiesel, depending on the feedstock; however, fuel properties such as viscosity, cold-filter plugging point, density, and others, are not affected by the antioxidants (Knothe et al., 2005).

A category of compounds referred to as "hindered phenols" are frequently employed, which react very rapidly with free radicals because of the low energy required to remove the hydrogen

located alpha to the double bonds. The free radical generated does not initiate oxidation because of resonance stabilization.

Several antioxidants consisting of hindered phenols are commonly referenced in biodiesel lab tests and used in commercial products (Ribiero et al., 2007). These include:

- Tertiary butylhydroquinone (TBHQ)
- Butylated hydroxyanisole (BHA)
- Butylated hydroxytoluene (BHT; 2,6-di-tert-butyl-4-mehylphenol)
- Pyrogallol (PY; 1,2,3-trihydroxybenzene)
- n-Propyl gallate (PG; 3,4,5-trihydroxybenzoic acid propyl ester)

In recent antioxidant "evaluations involving biodiesel methyl esters, TBHQ was frequently found to be the best overall performer" (SRI, 2005).

The additive manufacturers' Material Safety Data Sheets (MSDSs) and product literature list several of these and other hindered phenols as components in a number of commercial biodiesel antioxidant products (Appendix C). Given that the biodiesel oxidation process begins immediately, additive manufacturers recommend to biodiesel suppliers to blend in antioxidants as far upstream in the delivery process as possible (ASTM, 2007; Bill Silzle of Lubrizol Corp., personal communication).

4.3.2. Cold-Flow Enhancement

The traditional cold weather treatment method for diesel is to blend in kerosene, a practice that is followed by some in the biodiesel industry (Sunny Beaver of Yokayo Biofuels [B100 distributor], personal communications). Commercial cold flow additives on the market contain proprietary components that are typically copolymers of ethylene and vinyl acetate or other olefin-ester copolymers (University of Idaho, 2005). A commonly used chemical for soybean feedstock biodiesel is Milan styrene ester, with Polymethacrylate and Ethylene vinyl acetate used for other feedstocks, such as rapeseed (Bill Silzle of Lubrizol Corp., personal communication). A review of manufacturer MSDSs listed in table 2 of Appendix C reveals instances of esters, but also components such as naphtha and toluene.

Currently cold-flow additives apparently provide unsatisfactory results with B100 in the United States. According to a Department of Energy Biodiesel Handling and Use Guideline document (D.O.E., 2006): "B100 in the United States cannot be effectively managed with current cold flow additives like some petro-diesel fuels or European rapeseed oil based biodiesel. The U.S. biodiesel oils and fats contain concentrations of saturated compounds that are too high for most additives to be effective. Cold flow additive effectiveness can also change dramatically depending on the exact type of biodiesel and the processing it has undergone."

4.3.3. Biocides

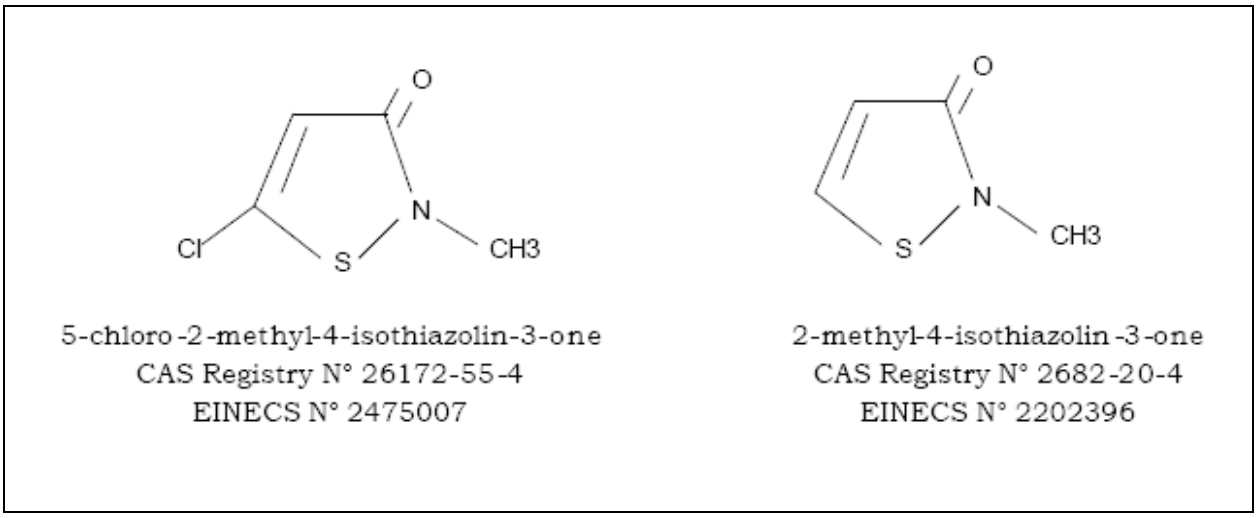
Fuel additives such as biocides can be added to the fuel to "destroy or inhibit the growth of fungi and bacteria which can grow at fuel-water interfaces to give high particulate concentrations in the fuel" (ASTM, 2007).

Additives used to control microbes are generally water-soluble and migrate into any water found in the fuel storage tank. Given the biocides mix with the water, the same biocides used in petroleum based diesel fuel systems are used with biodiesel. Biocides are too expensive to be

widely deployed upstream in the distribution process, and there is an added concern of creating microbial resistance, so biocides are typically used on an "as-needed" basis in the distribution chain wherever and whenever microbial contamination is detected as a problem (Howard Cheznow, Fuel Quality Systems Corp., personal communication).

The market-leading biocide is manufactured by the large chemical company Rohm and Haas Corporation and is sold under the product name of Kathon FP 1.5. The active ingredients in the Kathon product, isothiazols, are shown in Figure 4.2 and listed in Appendix C, Table C-4.

Figure 4.2. Rohm and Haas Kathon FP 1.5 Biocide*.



*Source: Rohm and Haas (1999).

Other common fuel biocide chemicals are methylene bisthiocyanate (MBT) and nitromorphalines (Howard Cheznow, Fuel Quality Systems Corp., personal communications). MBT is often used as a biocide in water treatment plants, paper mills, and other industrial processes involving water. Carbamates also appear in MSDSs of some commercial biocides listed in table 4 of Appendix C.

An environmental issue for biocides involves the treatment and disposal of biocide-containing effluent drained from the storage tanks. The Rohm Haas literature discusses this process and proper deactivation, which involves the use of sodium metabisulphate or sodium bisulphate (Rohm and Haas, 1999).

4.3.4. Cetane Enhancers and NOx Reduction Additives

A frequently used indicator of diesel fuel quality is its cetane number. This number is a measure of a fuel's ignition delay. It measures the time period between the start of injection and start of combustion (ignition) of the fuel. The cetane numbers for biodiesel are generally higher than for standard diesel, ranging from 48-65 and 40-55 respectively (D.O.E., 2006). Increases in cetane numbers reduce NO_x emissions, so there remains a motivation to maximize this value in biodiesel fuels (Ribiero et al., 2007).

Cetane enhancers are commonly based on 2-ethylhexyl nitrates (Bill Silzle of Lubrizol Corp., personal communication). It is also a component in the Oryx Energy International's NO_x

reduction additive, which passed an official emissions testing required by the Texas Commission on Environmental Quality for entry into the market (Irwin, 2007). Another product passing the Texas requirements for biodiesel blends was Viscon, which lists on its MSDS a Polyisolbutylene polymer, describe the company's website as a "high molecular weight pure hydrocarbon polymer," (Viscon, 2008). According to a Brazilian report, Oleochemical carbonates are finding increasing interest in commercial biodiesel applications as cetane number enhancers (Ribiera et al. 2007).

Clean Diesel Technologies in Connecticut provides a NO_x reduction solution consisting of a urea-injection system, which injects urea (or ammonia) into the exhaust gas of the operating engine, reducing NO_x to elemental nitrogen and water vapor. They claim that at typical exhaust temperatures, the reduction of NO_x emissions is between 70% and 90% (Clean Diesel Technologies, 2008).

A report was issued in 2007 by McMinnville Energy System on the results of a stationary biodiesel test involving a large bore Caterpillar power generator in a grid-connected electricity generating application. Funded by the Department of Energy, the American Public Power Association, the National Biodiesel Board, and The Tennessee Soybean Promotion Association, it demonstrated a 96.6% reduction in NO_x emissions from a B100-powered Caterpillar generator using a catalytic converter process that required no ammonia or urea (McMinnville Energy System, 2007).

4.3.5. Water Dispersants

There are two general categories of additives used to deal with water in the tanks of vehicles. A *demulsifying* agent extracts water out of suspension within fuel, which allows it to be separated from the fuel by the fuel filter. An *emulsifying* agent works by surrounding water molecules with additive molecules, holding them in suspension and making them small enough that they pass harmlessly through the fuel system.

Little information is available specifically on the chemical composition of commercial demulsifiers/emulsifiers, as they tend to be components of multi-purpose additives. A research paper from the Russian Research Institute of Oilfield Chemistry claims that current demulsifiers primarily consist of "non-ionic surfactants, such as alkylene oxide block copolymers" (Solodov et al., 2005). This corresponds to the Biofuels Systems Group FTG Fuel Treatment product, which lists a "non-ionic surfactant" (Alcohol Ethoxylate) as an ingredient in its MSDS.

4.3.6. Anti-Foaming Agents

Although an issue with biodiesel blends, foaming does not appear to be a serious issue with B100 biodiesel (Quigley, 2007). Anti-foaming agents are typically silicon based (Bill Silzle of Lubrizol Corp., personal communication). The German additive manufacturer, Degussa, states in a 2007 product brochure that its diesel (and B5 biodiesel blend) anti-foaming product contains "organosilicone technology" (Degusa, 2008).

4.4. Potential Impacts During Fuel Use

In the fuel-use stage of the biodiesel life cycle, the releases of greatest concern are emissions to air, but there are also potential releases to water and soil from atmospheric deposition and from

leaks and spills during fueling and vehicle use. The primary releases to air occur during the actual combustion process. There are also vapor emissions during fueling and liquid fuel spills.

4.4.1. Biodiesel Impact on Air Quality

Because of the importance of the combustion emissions, the focus below is on air-quality impacts of biodiesel relative to extant diesel fuels. Several studies have determined that use of biodiesel (as a neat fuel or as a blend with petroleum-derived fuel) instead of conventional diesel may be expected to exhibit large reductions in hydrocarbons (HC), particulate matter (PM) and carbon monoxide (CO) emissions. Fuel properties, such as cetane number and oxygen content, are attributed to biodiesel's emission advantages. Since biodiesel (B100) contains approximately 11% oxygen by weight (Graboski et al., 2003), the fuel is able to burn more completely, resulting in fewer unburned fuel emissions.

But studies to date indicate that biodiesel use may have little impact on reducing emissions of NO_x and some toxic air pollutants and could lead to increasing emissions of these pollutants. Because NO_x emissions have a large impact on ambient ozone concentrations, an effective control strategy for reducing ozone is to decrease NO_x emissions. Since there are very few ways of reducing NO_x emissions from a broad range of combustion sources, any small increase in NO_x from biodiesel could affect the California State Implementation Plan. This means that the significance of any increases of NO_x emissions must be discussed and evaluated in some detail in both the Tier II and Tier III multimedia impact reports. In addition, the question of whether the health benefits of decreases in CO, PAHs, and PM are out-weighed by the increases in NOx, ozone, and volatiles should be addressed in the Tier II or Tier III report.

4.4.2. Exhaust Emissions

The US Environmental Protection Agency (USEPA) conducted a comprehensive analysis of the emission impacts of biodiesel fuel (EPA, 2002). Previous studies were reviewed and data from 39 out of 80 studies were retained for the EPA analysis. It is important to note that the available data only included tests on heavy-duty diesel vehicles (HDDV) designed for highway use. No predictions could be made concerning the impacts of biodiesel emissions from light-duty vehicles or diesel-powered off-road equipment. The database was also limited in that 98% of the tests were performed on engines with a model year of 1997 or earlier. These engines were not equipped with exhaust gas recirculation (EGR), NO_x absorbers, or PM traps. However, the EPA has "no reason to believe that biodiesel will have substantially different impacts on emissions" for engines lacking this equipment (USEPA, 2002).

The USEPA 2002 investigation "made use of statistical regression analysis to correlate the concentration of biodiesel in conventional diesel fuel with changes in regulated and unregulated pollutants" (USEPA, 2002). The results from the USEPA 2002 study are shown below (Figure 4.3). Particulate matter (PM), carbon monoxide (CO), and hydrocarbons (HC) were significantly reduced with increasing concentrations of biodiesel.

Similar emission results for HDDV were estimated in a study entitled "Impacts of biodiesel fuels on air quality and human health" conducted by ENVIRON International Corporation (Morris et al., 2003). These results are summarized in Table 4.1.

Figure 4.3. Average emission impacts of biodiesel for heavy-duty highway engines*.

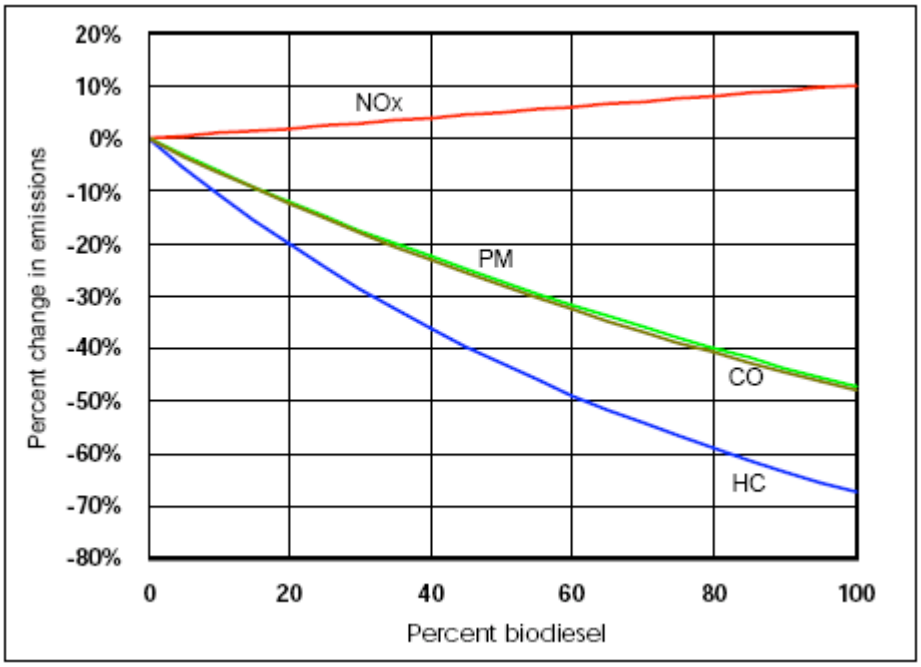


*Figure from USEPA (2002).

Table 4.1. Overall average change in mass emission effects due to use of biodiesel fuels in heavy-duty highway vehicles compared to standard diesel fuel*.

Biodiesel Fuel	NOx	PM	CO	VOC	SO_2
B20	+2.4%	-8.9%	-13.1%	-17.9%	-20%
B100	+13.2%	-55.3%	-42.7%	-63.2%	-100%

*Table from Morris et al. (2003a).

Both studies reveal that the use of biodiesel reduces the emissions of four pollutants regulated by the EPA—PM, CO, HC, and sulfur dioxide (SO_2)—but increases slightly nitrogen oxides emissions.

The USEPA 2002 analysis indicates that various components of biodiesel fuel can influence the pollutant emissions. While the engine model year did not impact emissions, the type of feedstock and the type of conventional diesel used for blending did influence the emission. The feedstocks used within the study were divided into three categories: soybean, rapeseed/canola, and animal fat. Type of feedstock affected NO_x, PM, and CO emissions but not hydrocarbons emissions.

Carbon monoxide is generated from a variety of combustion processes including industrial sources, household heating, and motor vehicles. Typically 90% of CO emissions in urban areas come from on-road motor vehicles (Mansell et al., 2003). The CO emissions are dependent on feedstocks, as can be seen in Figure 4.4; however, the USEPA 2002 and other similar reports provided no explanation for this trend.

Figure 4.4. Biodiesel feedstock effect on CO emissions.

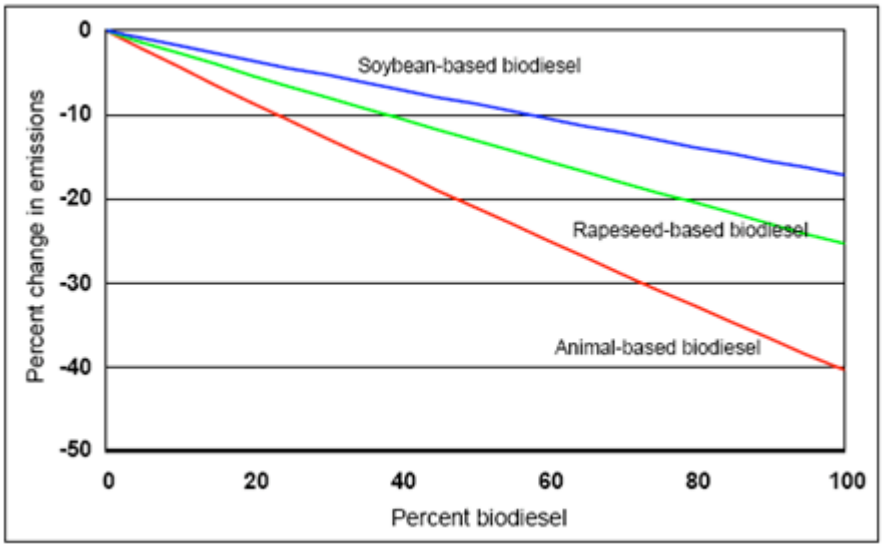


*Figure from USEPA (2002).

The NO_x emissions from biodiesel fuels increased with percent biodiesel in the fuel mix and varied considerably with biodiesel feedstock because the fuel's chemistry can greatly affect emissions. For a fixed percent of biodiesel, biodiesel containing feedstocks high in polyunsaturated fatty acids emit a greater percentage of NO_x than biodiesel high in saturated fatty acids. As illustrated in Figure 4.5, highly unsaturated fuels, such as soybean-based and rapeseed-based biodiesel, produce higher NO_x emissions than do saturated animal-based fuels.

Figure 4.5. Biodiesel feedstock effect on NO_x emissions*.

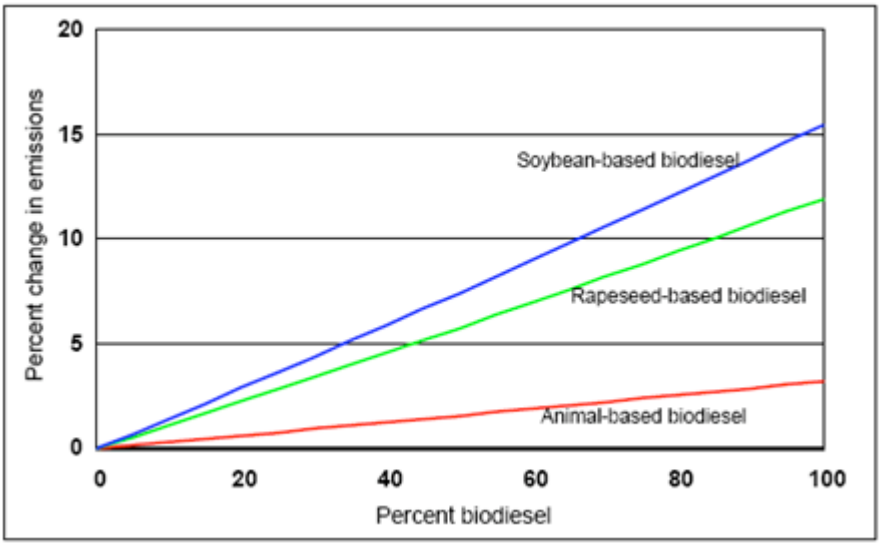


*Figure from USEPA (2002).

Since fuels with few double bonds exhibit high iodine numbers (recall the iodine number is a measure of the degree of saturation), these fuels will also have low cetane numbers (because iodine number is inversely proportional to cetane number). Thus, a fuel with a low cetane number, can cause excessive ignition delay and poor combustion performance, resulting in high NO_x emissions (Graboski et al., 2003). A study conducted by Colorado Institute for Fuels and Engine Research determined that biodiesels with cetane numbers greater than about 68 are expected to produce NO_x emissions equal to or less than diesel (Graboski et al., 2003).

The length of the fatty-acid carbon chain can also affect NO_x emissions. The shorter chain hydrocarbons, those below C12, have densities greater than longer chain esters and produce higher NO_x emissions. The mechanism(s) by which NO_x emissions increase with the shortening of hydrocarbon chain lengths remains unknown (Graboski et al., 2003).

As can be seen in Figure 4.6, PM emissions are reduced significantly with the use of biodiesel. Unlike for NO_x, particulate matter emissions are dependent not on the molecular structure of the biodiesel, but also on the sulfur and oxygen content of the fuel. Lower sulfur content reduces PM emissions. A higher oxygen content generally allows a fuel to burn more completely, resulting in fewer unburned or partially burned PM emissions (Graboski et al., 2003). Thus the more oxygen contained within a fuel, the lower the PM emissions released.

The study conducted by Graboski et al. (2003) at the Colorado Institute for Fuels and Engine Research confirms this relationship, as indicated in Figure 4.7. In the USEPA 2002 study, the lower PM emissions from animal-based biodiesel relative to plant-based biodiesel is attributable to slightly more oxygen in the animal-based formulation.

Figure 4.6. Biodiesel feedstock effect on PM emissions*.

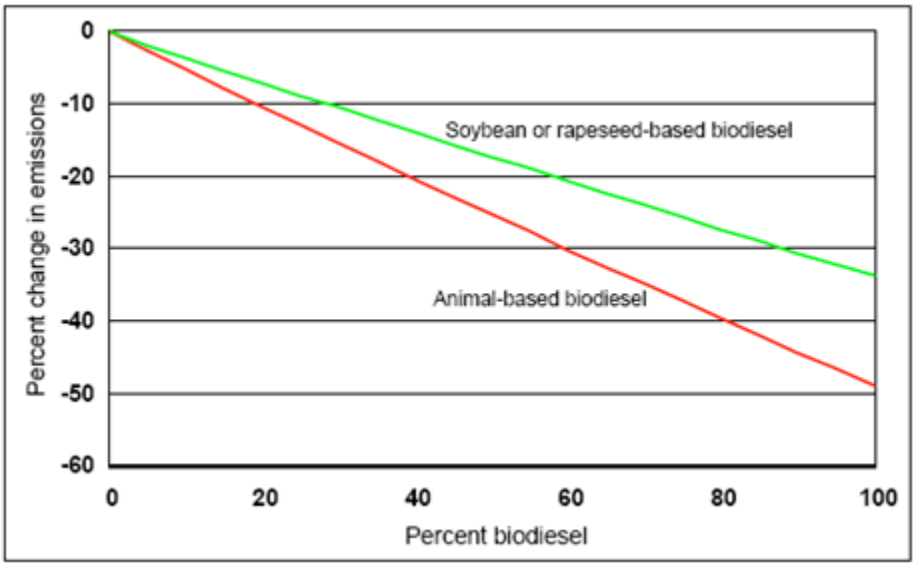


*Figure from USEPA (2002).

Figure 4.7. Regression model showing effect of oxygen on particulate matter*.

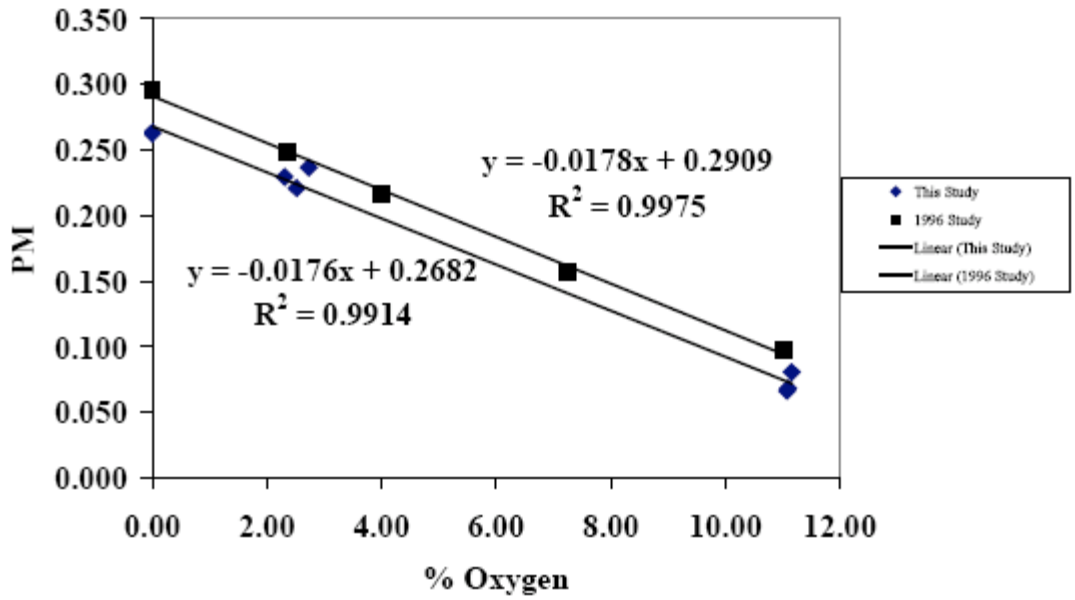


*Figure from Graboski et al. (2003).

4.4.3. Effects on Ambient CO and PM Concentrations

CO and PM are criteria air pollutants that are regulated under the 1990 Clean AIR Act. The Clean Air Act specifies that all regions of the US comply with EPA-specified National Ambient Air Quality Standards (NAAQS), which specify threshold concentrations that CO and PM.

While some studies have focused specifically on how biodiesel use impacts exhaust emissions from HDDV, researchers at the ENVIRON International Corporation considered more generally how biodiesel use can impact ambient air quality (Mansell et al., 2003). Two NAAQS have been established for CO: a one-hour standard of 35 ppm and an eight-hour standard of 9 ppm. Typically 90% of "area-wide CO emissions in congested urban areas come from on-road motor vehicles" (Mansell et al., 2003). One-hour and eight-hour CO concentrations were estimated in the Las Vegas Valley for standard diesel and B20 with scenarios of 50% and 100% penetration in the HDDV. The results (Table 4.2) indicate that biodiesel does reduce peak CO concentrations; however, these reductions are quite small, ranging from 0.01 to 0.03 ppm (< 0.2%).

Table 4.2. Peak estimated 1-hour and 8-hour carbon monoxide (CO) concentrations in the Las Vegas Valley, 100% B20, and 50% B20 emission scenarios and the differences in CO concentrations between the biodiesel fuel scenarios and the standard diesel base case*.

	Std. Diesel	50% B20		100% B20	
Episode	Peak (ppm)	Peak (ppm)	Difference (ppm)	Peak (ppm)	Difference (ppm)
1-Hour CO Dec 8-9	17.90	17.89	-0.01	17.87	-0.02
8-Hour CO Dec 8-9	9.39	9.38	-0.01	9.37	-0.02
1-Hour CO Dec 19-20	18.38	18.36	-0.02	18.35	-0.03
8-Hour CO Dec 19-20	13.73	13.72	-0.01	13.71	-0.02

*Table from Mansell et al. (2003).

Biodiesel effects on ambient concentrations of PM in the South Coast (Los Angles regions) Air Basin (SoCAB) have also been investigated. The NAAQS for PM_{10} (particulate matter of 10 µm or less) consists of an annual standard of 50 µg/m^3 and a 24-hour average standard of 150 µg/m^3 (Morris and Jia, 2003a). Additionally, $PM_{2.5}$, a new fine particulate matter standard, should not exceed annual and 24-hour average thresholds of 15 and 65 µg/m^3, respectively.

Morris and Jia (2003a) assessed separately the effects of biodiesel for particulate sulfate, nitrate, ammonium, elemental carbon (EC), organic carbon (OC), other fine particulate, course matter, total PM_{10} mass, total $PM_{2.5}$ mass, and exposure to PM_{10} and $PM_{2.5}$. The maximum increases and decreases in PM concentrations for each of the PM species listed above are shown in Table 4.3.

Table 4.3. Estimated maximum increases and decreases in particulate matter (PM) concentrations (µg/m^3) in the Southern California air basin due to a 100% penetration of B20 biodiesel in the heavy-duty diesel vehicle fleet*.

	Annual Average		Maximum 24-Hour Average	
PM Species	Maximum Increase	Maximum Decrease	Maximum Increase	Maximum Decrease
Sulfate	0.00	-0.03	0.00	-0.07
Nitrate	+0.04	-0.09	+0.58	-1.12
Ammonium	+0.01	-0.03	+0.15	-0.34
EC	0.00	-0.06	0.00	-0.10
OC	0.00	-0.15	0.00	-0.27
Other PFIN	0.00	-0.01	0.00	-0.01
Other PCRS	0.00	-0.01	0.00	-0.01
PM_{10} Mass	+0.04	-0.31	+0.62	-1.61
$PM_{2.5}$ Mass	+0.04	-0.30	+0.62	-1.61

*Table from Morris and Jia (2003a).

Nitrate and ammonium exhibit both increases and decreases associated with use of B20 fuel. Since the SoCAB is already high in NO_x, a precursor to ammonium nitrate, these species can act as major contributors to PM. The decrease in nitrate occurred in "more populated portions of SoCAB, whereas the increases occurred east of the SoCAB in the desert" (Morris et al., 2003a). Despite these small increases, the results indicate that the PM_{10} for annual and 24-hour exceedances are reduced 4% and 7%, respectively, in biodiesel compared to standard diesel fuel.

4.4.4. Effect on Ozone

Ozone is formed in the atmosphere through "complex reactions involving Volatile Organic Compounds (VOC) and oxides of Nitrogen (NO_x) in the presence of sunlight" (Morris et al., 2003a). Since the largest impacts on ambient ozone concentrations are due to NO_x, the most effective control strategy for reducing ozone would be to decrease NO_x emissions.

The threshold values for NAAQS 1-hour and 8-hour ozone concentrations are 0.12 ppm (124 ppb) and 0.08 ppm (84 ppb), respectively. An ozone air quality modeling study for biodiesel was conducted by ENVIRON International Corporation (Morris et al., 2003b). The effect of biodiesel fuel use on urban and regional ozone air quality was evaluated in Southern California (SoCAB), Lake Michigan, and the Northeast Corridor. The results revealed small increases and decreases in peak daily maximum 1-hour and 8-hour ozone concentrations for B20 with 100% and 50% penetration in the HDDV (Table 4.4 and Table 4.5). Because increasing NO_x is expected to increase ozone levels, these results seem inconsistent with the relatively large increase of NO_x from B20. But ozone formation depends on both VOC and NO_x levels. It appears that ozone levels remain low in Morris et al. (2003) results due to reductions of VOC (see Table 4.1) that compensate for increases in NO_x emissions.

Since the maximum ozone increase is well below 1 ppb, "the use of biodiesel fuel is estimated to have no measurable adverse impact on 1-hour and 8-hour ozone attainment in Southern California and the Eastern United States" (Morris et al., 2003b). In fact, based on the results from the SoCAB region, the use of biodiesel can result in small but potentially measurable beneficial impacts on ozone attainment, because the daily maximum ozone concentrations were reduced by approximately 1 ppb.

Table 4.4. Maximum increases and decreases in daily maximum 1-hour ozone concentrations in three air basins*.

Date	50% B20 Biodiesel (ppb)		100% B20 Biodiesel (ppb)	
	Max Increase	Max Decrease	Max Increase	Max Decrease
2007 Lake Michigan Domain				
July 11, 1995	+0.03	-0.16	+0.05	-0.33
July 12, 1995	+0.07	-0.10	+0.09	-0.19
July 13, 1995	+0.05	-0.12	+0.09	-0.24
July 14, 1995	+0.07	-0.09	+0.09	-0.18
July 15, 1995	+0.04	-0.26	+0.08	-0.53
2007 Northeast Corridor Domain				
July 11, 1995	+0.06	-0.08	+0.11	-0.14
July 12, 1995	+0.07	-0.12	+0.13	-0.25
July 13, 1995	+0.12	-0.06	+0.15	-0.07
July 14, 1995	+0.15	-0.04	+0.20	-0.09
July 15, 1995	+0.10	-0.10	+0.18	-0.20
1997 South Coast Air Basin Domain				
August 4, 1997	+0.09	-0.48	+0.17	-0.95
August 5, 1997	+0.10	-0.56	+0.19	-1.11
August 6, 1995	+0.11	-0.60	+0.22	-1.20
August 7, 1995	+0.13	-0.49	+0.26	-0.98

*Table from Morris et al. (2003b).

Table 4.5. Maximum increases and decreases in daily maximum 8-hour ozone concentrations in three air basins*.

Date	50% B20 Biodiesel (ppb)		100% B20 Biodiesel (ppb)	
	Max Increase	Max Decrease	Max Increase	Max Decrease
2007 Lake Michigan Domain				
July 11, 1995	+0.02	-0.14	+0.04	-0.28
July 12, 1995	+0.03	-0.09	+0.07	-0.17
July 13, 1995	+0.04	-0.11	+0.09	-0.21
July 14, 1995	+0.03	-0.09	+0.07	-0.18
July 15, 1995	+0.03	-0.20	+0.07	-0.40
2007 Northeast Corridor Domain				
July 11, 1995	+0.05	-0.07	+0.10	-0.13
July 12, 1995	+0.05	-0.10	+0.11	-0.20
July 13, 1995	+0.07	-0.04	+0.12	-0.07
July 14, 1995	+0.07	-0.04	+0.14	-0.07
July 15, 1995	+0.06	-0.04	+0.15	-0.08
1997 South Coast Air Basin Domain				
August 4, 1997	+0.06	-0.34	+0.12	-0.68
August 5, 1997	+0.07	-0.39	+0.15	-0.77
August 6, 1995	+0.08	-0.48	+0.15	-0.96
August 7, 1995	+0.08	-0.42	+0.15	-0.83

*Table from Morris et al. (2003b).

4.4.5. Effect on Toxic Air Pollutants

The class of air contaminants referred to as toxic air pollutants or "air toxics" contains numerous chemical compounds with widely varying sources, environmental fate, exposure pathways, and health outcomes. Over 40 chemical compounds in diesel exhaust have been listed as toxic air pollutants based on carcinogenicity and exhaust from diesel engines account for a significant fraction of the total added cancer risk in outdoor air from all hazardous air pollutants combined (Morris and Jia, 2003). There have been a number of studies comparing toxic air pollutant emissions, particularly polycyclic aromatic hydrocarbons (PAHs), from conventional diesel and biodiesel. In the paragraphs below we review key issues that can be drawn from these studies.

In the early 1990s, Kado et al. (1996) in collaboration with the University of Idaho, the Montana Department of Environmental Quality, and the U.S. Department of Energy, investigated the concentrations of PAHs in the exhaust from four different fuels tested in a 1995 Dodge 3/4 ton pickup truck with a Cummins B (5.9 L, Turbo diesel). The four tested fuels include: 1) 100% ethyl ester of rapeseed oil (REE), 2) 100% diesel 2-D low sulfur fuel, 3) 20% REE + 80% diesel, and 4) 50% REE + 50% diesel. For a catalyst-equipped engine, they found volatile PAHs such as phenanthrene, fluoranthene, and pyrene remained at an approximately equivalent emission rate (g/mile) independent of the REE content in the fuel (ranging from 100% diesel to 100% REE). In addition, the more chemically reactive PAHs [for example, benzo(a)pyrene] were emitted at greater levels for the pure REE and some of the blended REE fuels than in emissions from 100% diesel fuel.

Turrio-Baldassarri et al. (2004) compared the chemical (and toxicological) characteristics of emissions from an urban bus engine fueled with standard diesel and a biodiesel blend. Exhaust gases were produced by a turbocharged EURO 2 heavy-duty diesel engine, operating in steady-

state conditions on the European test 13 mode cycle (ECE R49). They studied both regulated and unregulated pollutants, including PAHs and nitrated derivatives of PAHs (nitro-PAHs), carbonyl compounds, and light aromatic hydrocarbons. The also evaluated the size distribution of PM. They found that the use of biodiesel blend seems to result in small reductions of emissions of most of the aromatic and PAH compounds. But they noted that these differences were not statistically significant. They found formaldehyde to have a statistically significant increase (18%) in emissions from the biodiesel blend. Their electron microscopy analysis indicated that PM for both fuels has the same chemical composition, morphology, shape and granulometric spectrum, with most of the particles in the range 0.06–0.3 μm.

Lin et al. (2006) investigated PAH and regulated pollutant emissions from heavy-duty diesel engines (HDDEs) fueled with premium diesel fuel (PDF), palm-biodiesel–PDF blends and paraffinic–palm-biodiesel blends in brand-new (zero mileage) engines as the engines accumulated miles. Their results indicate that while the emissions of THC and CO increased with operation time, the emissions of NO_x and PAHs decreased with operation time between 0 and 300 h (18,000 km). They also found that palm-biodiesel–PDF blends or paraffinic–palm-biodiesel blends in place of PDF in HDDEs reduced the emissions of PM by 6.11to 26.8%, total PAHs by 43.0 to 90.2% and total benzo(a)pyrene toxic equivalents (BaPeq) by 63.1 to 89.6%.

Yang et al. (2007) carried out an 80,000-km durability test on two engines using diesel and biodiesel (methyl ester of waste cooking oil) blend (B20) to evaluate emissions resulting from the use of biodiesel. They measured emissions of regulated air pollutants, including CO, HC, NO_x, and PM, and PAHs at 20,000-km intervals. At 0 km, HC, CO and PM emission levels were lower for the B20 engine than those for diesel. After running for 20,000 km and longer, emissions of these pollutants were higher. However, the deterioration coefficients for these regulated air pollutants were not statistically higher than 1.0, implying that the emission factors do not increase significantly after 80,000 km of driving. Yang et al. (2007) also found that total (gaseous+particulate phase) PAH emission levels for both B20 and diesel decreased as the driving mileage accumulated. However, for the engine using B20 fuel, particulate PAH emissions increased as engine mileage increased. The average total PAH emission factors were 1097 and 1437 mg (bhp h)$^{-1}$ [bhp h = brake horsepower hour] for B20 and diesel, respectively. For B20, the benzo[a]pyrene equivalent emission factors were 0.77, 0.24, 0.20, 7.48, 5.43 and 14.1 mg (bhp h)$^{-1}$ for 2-, 3-, 4-, 5-, 6-ringed and total PAHs.

The studies cited above do not confirm that the use of biodiesel will reduce the emissions of both PM and toxic air pollutants, but they reveal that the use of biodiesel is not likely to increase these emissions. There is a need for more controlled combustion studies to assess how the spectrum of toxic air pollutants, in particular the spectrum of PAHs, will shift both in terms of volatile and particle-bound fraction but also in terms of any changes in toxic equivalency.

4.4.6. Summary Points on Biodiesel Emissions

Based on the discussions above, we note that, relative to petroleum diesel emissions from engine combustion, biodiesel emissions have been shown to contain less particulate matter, hydrocarbons, carbon monoxide, and polycyclic aromatic hydrocarbons (PAHs). However, available measurements indicate that the combustion of biodiesel in a diesel engine can increase the release in nitrogen oxides, which, in addition to their association with potential health effects, have been identified as an ozone precursor. Despite the reduction in a total mass of particulate matter, it is not clear whether or by how much the shift in PM and toxic air pollutant composition changes in terms of chemistry and toxicity potential. It should be noted that approximately 80-

95% of diesel exhaust particulate matter (DEPM) mass consists of PM2.5, and within that is a subgroup of ultrafine particles (UFPs) with an aerodynamic diameter of less than or equal to 0.1 micron. UFPs account for ~1-20% of the DEPM mass and 50-90% of the total number of particles. It should be noted that the neither the data presented in Figures 4.3 and 4.6 nor the data from the corresponding references address the changes, if any, in UFP levels. Given the current literature demonstrating the health effects of UFPs, we note that there is a need to consider measuring UFP levels as part of the toxicity assessment for biodiesel. Such measurements can address the concern that that a drop in total PM mass does not necessarily equate to a drop in UFP number. Finally, the observation that formaldehyde increases significantly with biodiesel combustion indicates a need to address this issue in the Tier-II report. At a minimum, modeling should be used to assess how expected formaldehyde emissions relate to air-basin exposures. This will determine if formaldehyde emissions from biodiesel will become an issue in light of the current chronic California recommended exposure limit (REL) for formaldehyde of 2 ppb.

Although considerable data are available on the effect of biodiesel on EPA-regulated pollutants (i.e., HC, CO, NO_x, and particulates), most of these data were generated using older technology engines. Further, very little detailed exhaust characterization data on biodiesel exists beyond a small number regulated pollutants. This raises a concern about the relevance of these data to newer engines. But recent studies with newer engines tend to confirm these earlier results and make clear factors that increase NO_x emissions. McCormick et al. (2006) for example tested emissions from entire vehicles (rather than engines) on a heavy-duty chassis dynamometer and found that the NO_x impact of B20 varied with engine/vehicle technology and test cycle over the range -5.8% to +6.2%. Sze et al., (2007) used a series of paired (standard diesel/soy methyl-ester biodiesel blends) with transient cycles on a 2006 model year Cummins ISB compression ignition engine equipped with exhaust gas recirculation. Their results show statistically-significant differences in NO_x emission for all fuel pairs with average NO_x emissions due to biodiesel increased over each cycle, ranging from 0.9 to 6.6% and from 2.2 to 17.2% for the B20/B0 and B50/B0 fuel pairs, respectively. They also observed reductions in CO and PM in these tests. Eckerle et al. (2008) used a precisely-controlled single-cylinder diesel engine experiment to determine the impact of a 20% blend of soy methyl-ester biodiesel (B20) on NO_x emissions and found that the magnitude and even direction of NOx effect changes with engine load, with higher duty cycle average power corresponding to a larger NO_x increases.

Given the wide variety of oils and fats the might be used to make biodiesel fuel, the actual emissions of PMs and toxic air pollutants should be considered for each proposed formulation of biodiesel fuel to be used in California. This situation requires a systematic and ongoing effort to assess emissions from diesel engines. But it should be recognized that, due to the large number of fuel formulations along with the resources and cost required to evaluate each formulation, it is not feasible to assess all combinations of engine types and fuel formulations. This is especially the case with additives, since the number of additive and feedstock combinations could be very large. So it will be important in the Tier-II and Tier-III assessments to target a smaller set of archetypal and informative combinations of engines and fuel formulations. For example, because the life-cycle impact assessment of biodiesel is a comparative evaluation between CARB diesel and biodiesel, the emissions assessment can be simplified if both CARB diesel and additives currently used in CARB are considered the baseline rather than just the CARB diesel alone.

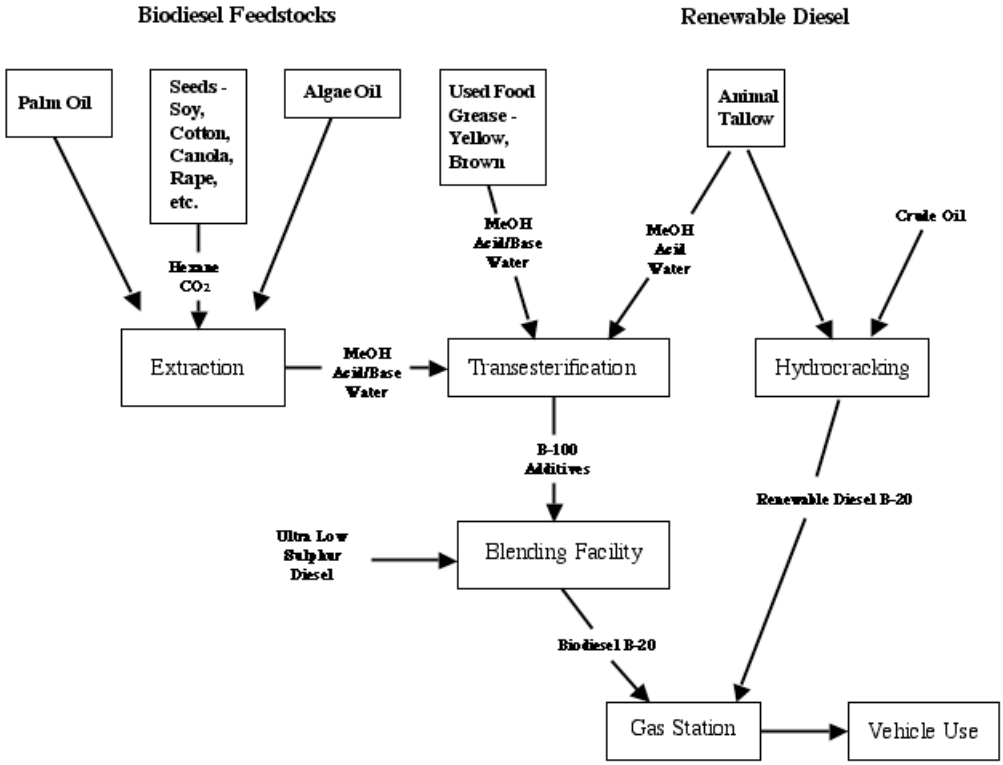
5. Release Scenarios

5.1. Defining Release Scenarios

One of big challenges in evaluating potential release scenarios associated with the use of biodiesel in California is the wide variety of feedstocks and different production processes that may be used. For the Tier I evaluation of release scenarios, our main focus is to identify releases that could have the greatest impact on the environment, human health, and important resources such as surface and groundwaters.

As indicated previously in Section 2.2, production feedstocks can range from palm oil, to seed oils, to yellow or brown used greases, to animal tallow, to algae oil (Figure 5.1). Different groups of feedstocks use different catalysts depending on the amount of FFAs. Biodiesel from seed feedstocks require extraction using hexane or other chemical processes such as super-critical carbon dioxide. To address fuel stabilization and performance issues such as fuel oxidation, biodegradation, NO_x, residual water and sediments, and fuel pour point, a variety of additives may be required and stored in bulk at either a production facility or a blending facility. The storage of bulk feedstocks, processing chemicals, additives, and finished B100 and B20 will likely be accomplished using above ground storage tanks of various sizes.

Figure 5.1. Biodiesel and Renewable Diesel process flow chart.



Further, the feedstocks will be widely distributed geographically and will use a variety of transportation means. Palm oil will likely arrive from distant global sources via tanker ship. Soy oil will likely arrive via rail tank car from the Midwestern United States. Yellow grease will be collected from a variety of sources within a city or region and transported by truck to a processing facility.

The higher density of fatty acid methyl esters compared to ULSD can cause heterogeneous biodiesel blends. Since many blenders rely on "splash blending" to mix B100 with ULSD there can be a tendency to form higher levels of pure diesel in the bottom of a tank than at the top. This, along with the fact that many distributors do not check the biodiesel content of the blends they receive from the blenders, can result in the distribution of biodiesel blends with B100 contents far from the advertised percentage (NREL 2005). One survey of B100 content in B20 blends found B100 levels ranging from 10% to 74%. In fact, only 10% of the samples taken for the survey met the standards of the US Department of Defense, a significant end-user of biofuels in the US (Reddy 2008).

It is also unclear where the final blending of the B100 with ULSD to make B20 will occur. It may occur at the B100 production facility or a centralized blending facility that collects B100 from a variety of feedstocks. The blending of a variety of feedstock B100 may be needed to create a standardized, fungible product. As the volume of biodiesel used increases, centralized blending facilities may need to locate near existing fuel pipelines that can import bulk ULSD and export B20 easily.

5.2. Normal Releases

Releases associated with the production, storage and distribution, and use of biodiesel can be regarded as normal (routine) or off-normal (unplanned but not necessarily unlikely). Different feedstocks and production processes may have different normal and off-normal releases and may affect different environmental media and human populations depending on geographic location.

Normal or routine releases during the production of B100 include:

- Hexane or CO_2 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 the use of biodiesel include combustion tailpipe emissions, both to the air and to surface waters in the case of marine use. The magnitude of these normal production and use releases within California is not clear yet.

5.3. Off-Normal Releases

Off-normal releases or unanticipated releases can occur primarily during the production, distribution and storage of B100 and B20. These off-normal releases may include spills or leaks of bulk feedstock oil, production chemicals, such as methanol, hexane, acid, base, or blending stocks such as ULSD or B100, or finished B20 fuel. These off-normal releases may be the result of leak or rupture of:

- an above ground or below ground storage tank and associated piping,

- a liquid transportation vehicle such as rail tank car, tanker truck, or tanker ship.
- a bulk fuel transport pipeline

Even if releases of B100 or B20 would not cause significantly greater impacts to the environment, human health, or water resources when compared to ULSD, the impact of releases of associated additives and production chemicals is of concern. For example, small releases of normal diesel fuel typically naturally biodegrade in the environment. If a biocide additive in B100 or B20 inhibits this natural process, then environmental and resource impacts and costs of cleanup could increase significantly. Releases of CO_2 can impact both the environment and humans nearby. Releases of methanol into subsurface environments which are also contaminated with either or both biomass derived and petroleum based fuel oils may cause increased contamination to groundwater.

6. Environmental Transport and Fate of Biodiesel

6.1. A Multimedia Framework for Fate, Transport, and Exposure

A multimedia transport, fate and exposure assessment synthesizes information about partitioning, reaction, and multimedia-transport properties of a chemical in a representative or generic environment with information about exposed humans or wildlife to assess impacts, such as health risk. The multimedia impact characterization approach is illustrated in Figure 6.1. This assessment is typically carried out using models supplemented with limited sampling analyses. In the modeling approach for characterizing potential impacts, the environment is treated as a set of compartments that are homogeneous subsystems exchanging water, nutrients, and chemical contaminants with other adjacent compartments. A cumulative multi-pathway exposure assessment for humans relates contaminant concentrations in multiple environmental media to concentrations in the media with which a human population has contact (for example; personal air, tap water, foods, household dusts, and soils). The potential for harm is assessed either as the average daily intake or uptake rate or as time-averaged contact concentration.

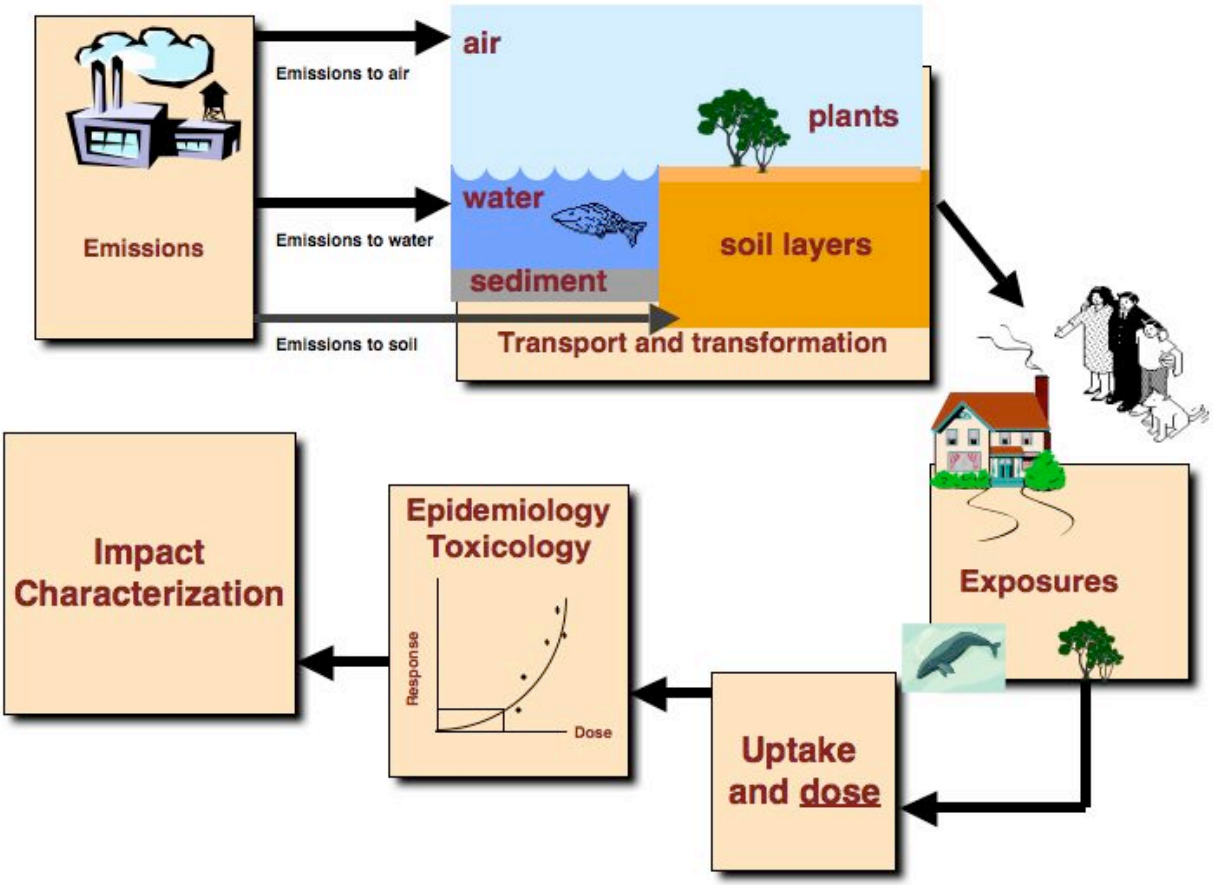


Figure 6.1. A conceptual illustration how pollutant emissions from each life-stage of biodiesel enter air, water, and or soil, undergo multimedia transport into exposure media, followed by contact with humans and ecosystems.

Multimedia contaminant fate and exposure models have been useful to decision makers because these models provide an appropriate quantitative framework to evaluate our understanding of the complex interactions between chemicals and the environment. The greatest challenge for multimedia models is to provide useful information without creating overwhelming demands for input data and producing outputs that cannot be evaluated. The multimedia modeler must struggle to avoid making a model that has more detail than can be accommodated by existing theory and data while also including sufficient fidelity to the real system to make reliable classifications about the source-to-dose relationships of environmental chemicals. In the early 1990s, the California Environmental Protection Agency adopted a multimedia approach for setting clean-soil goals through its CalTOX program (McKone, 1993), and the European Union adopted a multimedia multipathway framework for chemical risk assessment (RIVM, 1994.

Deploying a multimedia assessment framework requires basic chemical properties information about the substances under consideration. These properties include multiphase partitioning properties that describe how a substance will distribute itself among the major components of the environment—air, water, and organic phases such as lipids and organic materials in soil.

In the sections below, we identify the important multiphase transport properties needed for the multimedia impact assessment and summarize available information and information gaps. Where there are information gaps we consider how these gaps contribute to overall uncertainty and suggest approaches for increasing available information.

The greatest difficulty we can anticipate with determining the chemical properties of biodiesel fuels is that biodiesel fuel is not a defined chemical formulation or a defined mixture of components, but can be formulated from of any of a very large number of feedstocks with different chemical components.

6.2. Data Needs for Multimedia Transport

Multimedia transport and transformation models require three different types of input data. First they require chemical properties data. Next they require data describing the climate, soil, and hydrologic properties of the environment or landscape receiving the contaminants, and finally, information on emissions patterns and mode of entry (air, soil, water, groundwater). In this section we focus on data needs for the first of these, chemical properties.

The basic chemical properties needed to describe the environmental fate of a chemical, are those that define equilibrium distribution among the key environmental phases and those describing removal rates by biological or chemical degradation in air, water, and soil. Partitioning involves following media pairs:

- Air-Water
- Air-Atmospheric particulates (aerosols)
- Air-Soil
- Water-Solids (suspended solids, sediments and soil).
- Non-aqueous phase liquid (NAPL) and
- Pure phase

Degradation in air, water, and soil involve one or more of the following processes:

- Biodegradation
- Hydrolysis
- Photolysis
- Oxidation

For non-polar, non-ionizing organic substances a number of assumptions have been found to be reasonable for establishing partitioning among the primary environmental media. These are the air-water, K_{AW}; octanol-water, K_{OW} and octanol-air, K_{OA} partition coefficients. Other phase distributions can be derived from this basic set. For example, sorption to solids in air, water, soil, and sediments is dominated by partitioning or absorption into the organic fractions of these solids. K_{OW} and K_{OA} have been useful proxies for these solid-phase partition factors. These three partition coefficients, as well as those partition coefficients involving the pure substance phase (vapor pressure, solubility in water and solubility in octanol) are interrelated as shown in Figure 6.2 (Wania, 2001).

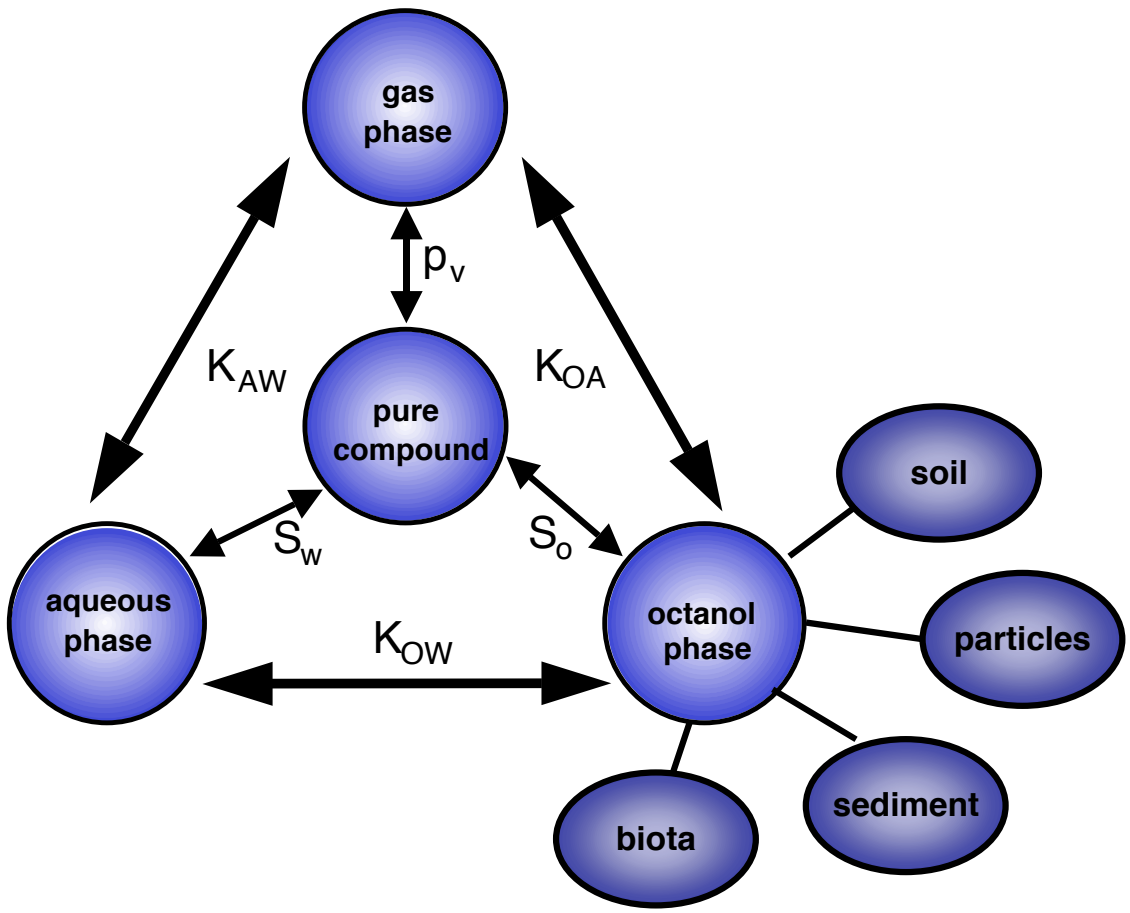


Figure 6.2. Phase distribution equilibria involving pure phase partition coefficients (water solubility S_W, solubility in octanol S_O and vapor pressure p_V) showing the links for describing environmental phase partitioning (K_{AW} air/water partition coefficient, K_{OW} octanol/water partition coefficient, K_{OA} octanol/air partition coefficient). The octanol phase is used for soil, sediment, particles and biota).

Figure 6.2 shows that the minimum data requirements for describing phase partitioning of non-polar organic substances are:

- Any two of the three partition coefficients K_{AW}, K_{OW}, and K_{OA}. The third can be estimated from the other two or:

- Any three of the six properties listed in the above figure as long as they do not form a triangle. (For example, if vapor pressure, water solubility and log K_{OW} are known, the remaining partition coefficients can be deduced from these. However, if only vapor pressure, water solubility and log K_{AW} are known, partitioning into organic solids cannot be established).

The approach outlined above for the non-polar substances may also be applicable to polar substances. Compounds that ionize in the aqueous phase can be treated as non-electrolytes by multiplying the partition coefficients K_{AW} and K_{OW} for the neutral species by the fraction that is undissociated, which in turn can be calculated from the dissociation constant of the compound pKA and the pH of ambient water. This approach assumes that the dissociated form does not volatilize and does not sorb to solids. This approach neglects, however, that the dissociated form might associate with the non-organic part of soil materials such as minerals. For many other compound classes, such as metals, surface active substances, extremely water insoluble or involatile substances, polymers, or biological macromolecules the environmental phase distribution can not be estimated using the octanol-based approach outlined for non-ionizing chemicals. For example, their sorption to solids is not necessarily dominated by simple phase partitioning into the organic fraction, but other mechanisms, such as specific surface sorption may become important. It may still be possible to describe them with the help of multimedia models, if the relevant environmental phase distributions can be quantified directly or if different estimation methods exist that allow the estimation of these phase distributions. However, it should be noted that multimedia models are meant to describe the environmental fate of chemicals that distribute into more than one environmental phase. For chemicals that occur predominantly in one medium of the environment, multimedia models help guide us to which components of the environment require the most detail in making an impact assessment. For example, a multimedia model will show that there we do not gain insight when estimating a characteristic atmospheric travel distance for a polymer or a biological macromolecule.

Reactivity information (i.e. degradation rates) for the various environmental compartments is required to carry out a multimedia assessment. The reaction rates in the various media can either be measured or estimated. Experimentally obtained rate data are preferred over estimated data. Accurate degradation rates are only needed for those compartments in which a significant part of the total chemical mass in the system resides. Because the question of how much of a chemical can be found in which environmental compartment strongly depends on the partitioning properties of the chemical, one way to estimate the presence of a chemical in the different compartments is based on its partition coefficients. It has been suggested that for compartments with less than 5% of the chemical mass present, as estimated from partitioning coefficients, a rough estimate of the degradation rate is sufficient (Woodfine et al. 2001).

6.3. Chemical Composition and Multimedia Transport Properties

The fate and transport of a fuel and its component chemicals in the environment depend on the properties of these constituent chemicals. The most important properties for established partition and transport in water and air phases are water solubility, vapor pressure, K_{OW} and distributions coefficients. Component partitioning depends in turn on source product infiltration, redistribution, and lens formation on water tables in the subsurface. These multiphase transport processes are governed by viscosities, densities, and interfacial tensions of the aqueous and pure product phases. These properties may also depend on dissolved compounds. Both diesel and

biodiesel can contain tens and even hundreds of different compounds, each with different properties affecting their multimedia partitioning, mobility, and persistence.

6.3.1. Chemical Makeup of Biodiesel and Diesel

Unless we are considering B100, biodiesel fuels will consist of a mixture of standard diesel and biodiesel. Petroleum-based diesel fuel oils are mixtures of aliphatic (open chain and cyclic compounds that are similar to open chain compounds) and aromatic (benzene and compounds similar to benzene) petroleum hydrocarbons. In addition, they may contain small amounts of nitrogen, sulfur, and other elements as additives. The exact chemical composition (i.e., precise percentage of each constituent) of any particular diesel oil type can vary somewhat, depending on the petroleum source and other factors. Petroleum-based diesel fuels are distinguished from each other primarily by their boiling point ranges, and chemical additives. Bio-based diesel fuel consist of short chain alkyl (methyl or ethyl) esters along with performance and stability additives along with some aromatic hydrocarbons. Table 6.1 provides a summary of chemical properties data ranges for constituents of petroleum-based diesel (ATSDR, 1993). This table also illustrates the types of data that must be obtained for the ethyl and methyl esters and additives in different biodiesel formulations.

Table 6.1 Physical and Chemical Properties of Fuel Oils (ATSDR, 1995)

Characteristic	Fuel oil no. 1	Fuel oil no. 1-D	Fuel oil no. 2	Fuel oil no. 2-D
Molecular weight	No data	No data	No data	No data
Color	Pale yellow[b]; Colorless to brown[c,d]	Colorless to brown[c]	Colorless to brown[c]	Colorless to brown[c]
Physical state	Liquid[c]	Liquid[c]	Liquid[c]	Liquid[c]
Melting point	-45.6°C[d]	-34°C[d]	-29°C[d]	18°C[d]
Boiling point	175–325°C[b]; 200–260°C[d]	193–293°C[d]	160–360°C[f] 282–338°C[d]	282–338°C[d]
Density:				
At 15°C	0.810–0.9360 g/mL[c]	0.810–0.9360 g/mL[c]	No data	No data
At 20°C	0.80 g/mL[e,f]	No data	0.8700–0.9500[c]	0.8700–0.9500 g/mL[c]
Odor	Kerosene-like[c]	Kerosene-like[c]	Kerosene-like[c]	Kerosene-like[c]
Odor threshold (ppm)	0.082[f]; 1[d]	0.7[d]	No data	No data
Solubility				
Water at 20°C	≈5 mg/L[c]	≈5 mg/L[c]	≈5 mg/L[c]	≈5 mg/L[c]
Organic solvent(s)	Miscible with other petroleum solvents[b]	No data	No data	No data
Partition coefficients:				
Log K_{ow}	3.3–7.06[c]	3.3–7.06[c]	3.3–7.06[c]	3.3–7.06[c]
Log K_{oc}	3.0–6.7[c]	3.0–6.7[c]	3.0–5.7[c]	3.0–6.7[c]
Vapor pressure at 21°C	2.12–26.4 mmHg[c]	2.12–26.4 mmHg[c]	2.12–26.4 mmHg[c]	2.12–26.4 mmHg[c]
Henry's law constant at 20°C - atm-m^3/mol	5.9 x 10^{-5}–7.4[c]	5.9 x 10^{-5}–7.4[c]	5.9 x 10^{-5}–7.4[c]	5.9 x 10^{-5}–7.4[c]

6.3.2. Solubility in Water

The solubility of biodiesel in water is an important characteristic as it can affect fuel quality and the environment (in the event of a fuel spill). Because biodiesel is a mixture of several chemicals, the solubility of biodiesel in water is compound specific, and will involve partitioning between multiple phases. One can also express an average solubility for biodiesel in water in terms of its

ability to absorb moisture. Due to biodiesel's unique oxygen-containing polar chemical structure of carboxyl groups, it is on average 15 to 25 times more soluble in water than diesel (He et al., 2007). Biodiesel absorbs 1,000 to 1,700 ppm (0.10 to 0.17%) moisture at temperatures of 4° to 35^oC. Tests have determined that the moisture content of biodiesel is not dependent on feedstock but is affected by temperature. As the temperature increases, "the moisture content increases at a rate of 22.2 ppm/^oC which is more than 9 times higher than that of D-2 diesel" (He et al., 2007). The moisture absorbance is also affected by the level of blending (biodiesel/ D-2 diesel). Blending "creates a mixture with a lower capacity for moisture absorption." As can be seen in Figure 6.3, increasing concentrations of biodiesel within a mixture result in a greater level of moisture content.

Figure 6.3. Statistical significance of temperature and level of blending on moisture content (MC)*.

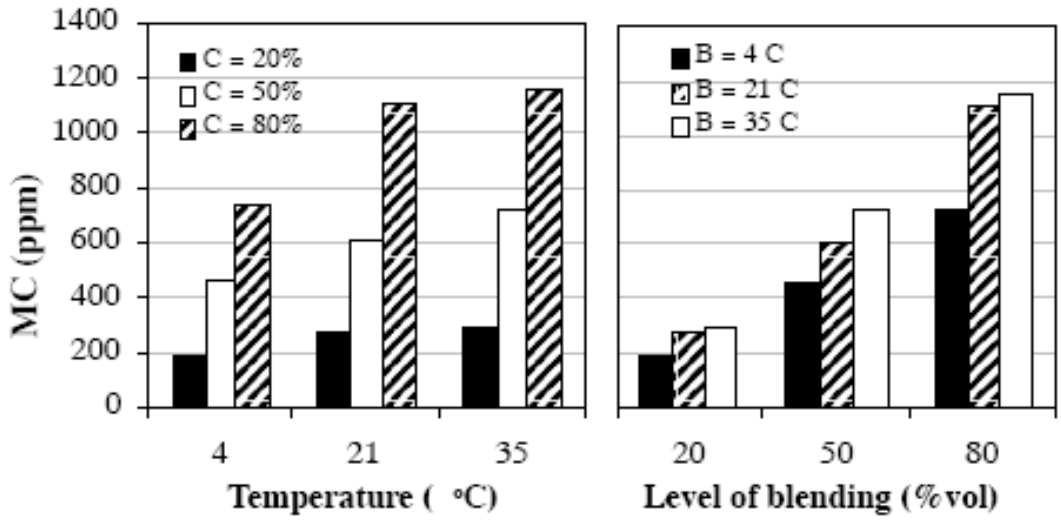


*Figure from He et al. (2007)

The high moisture content of biodiesel can cause problems because it makes the fuel susceptible to water accumulation and microbial growth. This can result in fuel deterioration during fuel handling, storage and transportation. In the event of a fuel spill, biodiesel will diffuse within natural water bodies (e.g., lakes, rivers and groundwater aquifers) faster on the average than diesel. This type of environmental dispersion will be a challenge to evaluate because it is ultimately compound specific and involves partitioning between multiple phases. This behavior will be problematic for cleaning up spills because it can be more difficult to remove the fuel from these water bodies.

6.3.3. Sorption to Solids

There are no reported measurements of the K_{OW} of biodiesel fuel. There are few measurements of the air-particle, water-soil, or water-sediment partition coefficients. Because biodiesel is a mixture of several chemicals it may be necessary to assess the partition properties of each of the individual components to make an accurate assessment of the multimedia behavior of the different biodiesel formulations. In many cases it may be necessary to obtain direct measurements of the effective distribution coefficient (water-solid partitioning factor K_D) in sediments, soils, and aquifers.

6.3.4. Vapor Pressure

There are no reported measurements of the vapor pressure for biodiesel fuels, however there are some available data on individual chemicals in biofuels. Similarly, there are also no measurements of the air-water partition coefficient K_{AW} for biodiesel. However, for the diesel component of B20 and other mixtures that include petroleum-based diesel, there are vapor pressure and K_{AW} data available for the petroleum-based diesel components. Because biodiesel is a mixture of several chemicals it will be necessary to assess the vapor pressure and K_{AW} of each of the individual components to make an accurate assessment of the multimedia behavior of the different biodiesel formulations.

6.4. Biodegradation of Biodiesel Components

As biodiesel becomes increasingly commercialized, its potential for persistence in the environment is an area of growing concern. Since petroleum spills have contributed significantly to environmental contamination in the past, it is essential to examine biodiesel's potential for biodegradation. The long-term persistence of the fuel in freshwater and marine aquatic environments, or in porous media such as soil and sediment, may be harmful to biota in these ecosystems.

Biodegradation of hydrocarbons by microorganisms "represent[s] one of the primary mechanisms by which petroleum and diesel products are removed from the environment" (Stolz et al., 1995). The simple chemical structures of biodiesel constituents make it more readily degradable than diesel. Microorganisms can easily break down the straight carbon chain structures of biodiesel under aerobic conditions via the beta-oxidation pathway. "Fatty acids are oxidized at the β carbon and degrade to acetic acid and a fatty acid with two fewer carbons" (Zhang et. al., 1998).. Diesel, in comparison, is not as readily biodegradable because of its chemical complexity. "Many components of [the fuel] are recalcitrant to microbial degradation" (Stolz, et al., 1995). The complex structure of diesel contains a mixture of "aliphatic cyclic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and alkylbenzenes, as well as their derivatives such as toluene, xylenes, PCBs (phenyl and biphenyls), and so on" (Zhang et. al., 1998). Hydrocarbons are less susceptible to microbial degradation when oxygen is not available as a terminal electron acceptor.

6.4.1. Biodegradability in Aquatic Environments

The biodegradation potential of biodiesel and various biodiesel/diesel blends was investigated in aerobic shaker flask systems by Zhang et. al. (1998) at the University of Idaho. Mineral media were amended with a mixed microbial inoculum from soil, activated sewage and raw sewage. Carbon dioxide evolution was measured and compared to measurements by gas chromatography of the disappearance of biodiesel components. Six biodiesel fuels including neat rapeseed oil (NR), neat soybean oil (NS), rapeseed methyl ester (RME), rapeseed ethyl ester (REE), soybean methyl ester (SME), and soybean ethyl ester (SEE) were tested and the results were compared to those of Phillips 2-D reference diesel. The most common biodiesel used was REE, a biodiesel that is produced using ethanol as a catalyst and rapeseed as feedstock. Negligible differences between feedstocks were detected through statistical analysis, as they all degraded between 85.54 – 88.49% in 28 days. This percentage degradation is particularly high compared to diesel's 26.24% degradation (Zhang et al., 1998). The biodegradation rate of biodiesel was equivalent to that of dextrose (sugar).

Biodiesel can promote and accelerate the biodegradation of diesel through a process called cometabolism. Zhang et al. (1998) determined that diesel in a mixture degraded three times faster (56%) than diesel alone (16%) under aerobic conditions (as shown in Table 6.2). This "suggests that in the presence of REE, microorganisms use the fatty acids as an energy source to promote the degradation of diesel" (Zhang et. al., 1998).

Table 6.2. Biodegradation of fuel in biodiesel mixture and diesel alone*.

Days	Diesel in mixture	Diesel Alone
0	0	0
1	56.49%	16.27%
4	94.79%	53.54%

*Data from Zhang et al. (1998).

Differences in degradation patterns were also noted between pure biodiesel and biodiesel/diesel blends. After one day, REE 100 degraded 61.81% while in the same period of time a biodiesel/diesel mixture degraded 56.4%. This relatively small difference in degradation suggest that "microorganisms attacked the fatty acids in REE and alkane chains in the diesel at the same time and at the same rates instead of favoring the fatty acids only" (Zhang et. al., 1998).

Since microorganisms metabolize biodiesel and diesel at roughly the same rates, the more biodiesel present in a biodiesel/diesel mixture, the greater the rate of degradation. This can be seen in Table 6.3 below.

Table 6.3. Percent degradation in different rapeseed ethyl ester (REE)/diesel mixtures*.

days	CO_2 evolution (%)				
	REE100	R80/d20	R50/d50	R20/d80	d100
0	0%	0%	0%	0%	0%
7	64.09%	52.33%	37.85%	25.24%	1 2.08%
14	77.51%	61.26%	45.74%	31.59%	14.96%
28	84.37%	67.82%	51.90%	35.67%	18.18%

*Table from Zhang et al. (1998).

Because the presence of vegetable fatty acids increases the degradation rate of diesel, new biosolvents, based on vegetable methyl esters (similar to biodiesel), can be used as cleaning agents after a diesel spill. The California Department of Fish and Game recently licensed *CytoSol Biosolvent* (an oil similar to biodiesel) "as a shoreline cleaning agent to extract crude oil from shorelines and marshes after a spill" (Wedel, 1999).

6.4.2. Biodegradation in Soil

Five biodiesel fuels were also tested via gas chromatography for biodegradability in soil samples. Information on the type of soil and its associated physical and chemical properties was not indicated. In 28 days, the biodiesel fuels degraded 83 to 95%, with an average of 88%, while diesel (Phillips 2-D low sulfur diesel) only degraded 52%.

Seed germination is also used as an indicator of biodegradability and itself is an important criterion to consider in soils contaminated by fuels. The University of Idaho's study included an investigation of the seed germination rates in soil treated with diesel and the five biodiesel samples. In soil exposed to diesel, it took seven days longer for seeds to germinate than in the biodiesel treatments. The germination rate for biodiesel was initially slow; however, in week 3, after the biodiesel began to degrade, the seed germination rate increased (Knothe et al., 2005). After the sixth week, the germination rates reached 92 to 98%. These results demonstrate that "biodegradation can restore a biodiesel fuel-contaminated soil in 4 to 6 weeks to such a degree that it can support plant germination" (Knothe et al., 2005).

6.4.3. Biodegradation Under Aerobic and Anaerobic Conditions

Stolz et al. (1995) from Duquesne University studied the biodegradability of soy biodiesel under aerobic and anaerobic conditions (adding nitrate as an electron acceptor) in microcosms simulating freshwater and soil environments. The biodiesel completely degraded within 7 days under aerobic conditions and 14 days under anaerobic conditions. (No distinctions between degradation within aquatic and soil environments were specified). The presence of oxygen was a significant contributing factor to the rapid aerobic biodegradation. Biodiesel degraded at a slower rate under anaerobic conditions using alternative terminal electron acceptors to oxygen, such as nitrate, iron (Fe(III)), or sulfate (Stolz et al., 1995).

Lapinskiene and Martinkus (2007) measured the anaerobic biodegradation of fats, biodiesel fuel and diesel fuel in flooded soil samples under an argon atmosphere. Propionic acid fermentation was the major pathway for biodegradation of biodiesel fuel and fats, whereas butyric acid fermentation was important in diesel fuel samples. After 60 days of incubation, 47.9% of diesel fuel, 81.2 % of, biodiesel fuel, 78.6% of sunflower oil and 80% of beef grease was degraded.

6.4.4. Biological and Chemical Oxygen Demand

Biological oxygen demand (BOD_5) is a standardized method that can be used as a means to estimate the biodegradability of a chemical. It serves as a "relative measure of the amount of organic matter subject to microbially mediated oxidative processes present in biodiesel fuel" (Knothe et al., 2005). Chemical oxygen demand (COD) is a measure of the total oxidizable organic matter present in a sample. A study conducted by the University of Idaho measured BOD_5 and COD of biodiesel (Knothe et al., 2005).

While the biological oxygen demand of the six biodiesel fuels (same as listed above) did vary considerably, the magnitude of differences among the fuels was less than 10%. The biodegradability of all six biodiesel fuels are considered to be equivalent, relative to the difference in BOD between diesel and the biodiesel fuels which was substantially different (average 122% difference). The low BOD_5 values for Phillips 2-D diesel "indicates the presence of a much smaller amount of microbial biodegradable organic matter" (Knothe et al., 2005). It may also reflect the toxicity of this diesel fuel to microbes (Figure 6.4).

Since COD is a measure of oxidizable organic matter, it was expected that there would not be a significant difference between COD values for biodiesel or diesel. This was in fact the case and the results can be seen in Figure 6.5.

Figure 6.4. BOD_5 values for biodiesel and diesel*.

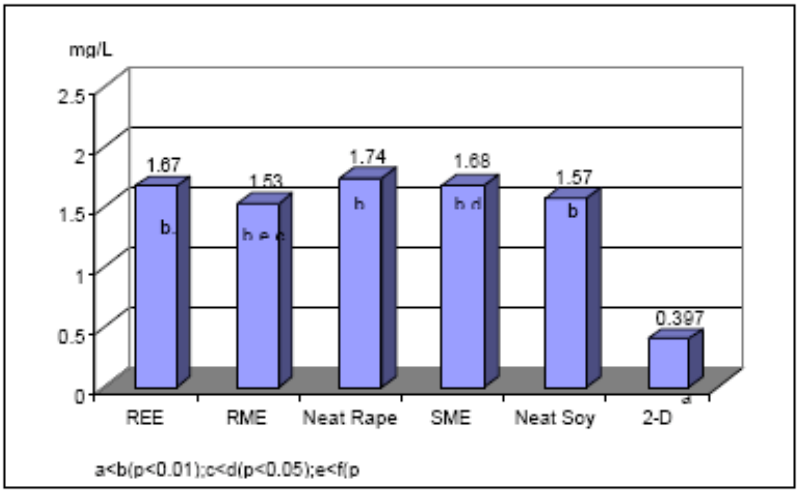


*Figure from Knothe et al. (2005)

Figure 6.5. COD values for biodiesel and diesel*.

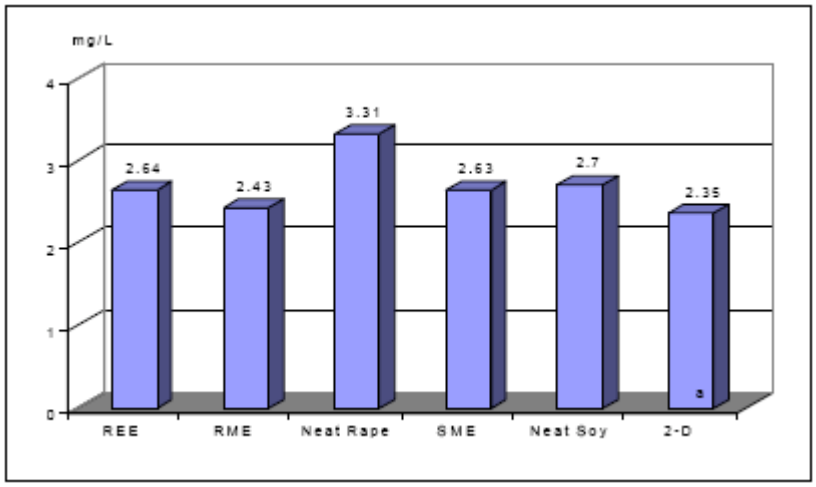


*Figure from Knothe et al. (2005).

7. Biodiesel Toxicity

7.1. Human and Ecological Risk Assessment

As with any new fuel formulation being introduced into California commerce in large quantities, we are concerned with the potential toxicity to humans and to the environment of biodiesel fuels. Estimating the toxicity requires that we follow a standard paradigm for risk assessment:

1. Hazard identification
2. Toxicity assessment
3. Evaluation of the potential for human and ecological exposure
4. Are there specific sensitive populations at risk of exposure to biodiesel fuel components?

The greatest difficulty we can anticipate with determining the human and ecological toxicity of biodiesel fuels is that biodiesel fuel is not a defined chemical formulation or a defined mixture of components, but can be formulated from of any of a very large number of feedstocks with different chemical components. It is beyond the scope of this study to attempt to consider all of these possibilities; we will analyze the toxicity of biodiesel formulations from one or two typical feedstocks in detail and then try to generalize when generalization is possible. Manufacture of biodiesel fuel may well occur, at least in part, in California, so we will have to consider potential releases of chemicals involved in synthesis and use of biodiesel during their transport and use, as well as their appropriate disposal, their combustion, and their degradation products. Extraction of oils from plants will generally require the use of organic solvents such as hexane, or saponification with alkaline methanol. Thus, we must consider potential adverse health effects and ecological damage related to release scenarios for organic solvents as well. Finally, there may be significant amounts of fuel additives added to biodiesel formulations; the toxicity of these compounds and their potential release products will also have to be considered. Significant routes of exposure that must be considered include oral, dermal, and inhalation. We anticipate that we will encounter significant data gaps at every stage of this process.

In general, tests show that pure biodiesel is considerably less toxic than pure diesel fuel. Formulations of mixed biodiesel-diesel fuel such as B20 or B50 have shown results consistent with the calculated diluent effect of the percentage of biodiesel fuel on the total toxicity of the mixture.

7.2. Acute Oral and Acute Dermal Toxicity

Acute oral toxicity tests were conducted on albino rats and acute dermal toxicity tests were conducted on albino rabbits at the WIL Research Laboratories in Ashland, Ohio. Samples of biodiesel, biodiesel/diesel blends, and diesel (100% RME, 100% REE, 50% RME/50% 2-D, 50% REE/50% 2-D, 20% RME/80% 2-D, 20% REE/80% 2-D, and 100% 2-D) were administered (once) to rats via gastric intubation. No deaths were reported; however, the "occurrences of clinical observations increased as the ratio of diesel fuel increased" (Knothe et al., 2005). The LD50 of each test substance was greater than 5 g/kg.

Biodiesel and diesel (100% RME, 100% REE, and 100% 2-D) were administered (once) dermally at a dose of 2 g/kg to the clipped, intact skin of albino rats. The rats were monitored for mortality, clinical observations, dermal findings, body weights and gross necropsy findings. It

was reported that the 2 g/kg dose was a "No Observable Effect Level (NOEL) for systemic toxicity [via the dermal exposure route] under the conditions of this study for the three fuels tested" (Knothe et al., 2005). It was also noted that 100% REE was the least severe skin toxicant in the acute dermal toxicity study.

7.3. Toxic Air Pollutants and Human Health

The PM and HC emissions from diesel fuel combustion are suspected of causing cancer and other life threatening illnesses in exposed populations. The State of California and the U.S. EPA have identified diesel PM as a toxic compound. The use of biodiesel fuel has been reported to reduce total emissions of PM and associated toxics (Morris and Jia, 2003b). A review of the broader literature suggests that reduced emissions of PM10, PAHs, and nitro-PAHs can be anticipated with biodiesel formulations in comparison to diesel fuels (see section 4.4). However, as noted in section 4.4, the wide variety of oils and fats that might be used to make biodiesel fuel, makes the actual emissions of PM and toxic air contaminants uncertain. Moreover, the toxic profiles of the altered emissions also remain uncertain. Given this issue of different formulations of biodiesel probably having different emissions and toxicity profiles, it is not appropriate to accept any common wisdom or popular literature that suggests that biodiesel fuel has been thoroughly tested by the EPA and is "safe". Such issues can only be resolved with continued emissions and toxicity testing.

A number of recent studies have addressed some of the potential health impacts of emissions from biodiesel combustion. Bünger et al. (2000a, 2000b) compared the toxicity and mutagenicity of diesel exhaust particles (DEP) from standard diesel fuel (DF) with low-sulfur diesel fuel (LS-DF) rapeseed methyl esters (RME), and soybean methyl esters (SME). They found lower mutagenic potency of DEP from LS-DF, RME, and SME compared to DEP from DF but a higher toxicity from RME relative to DF. They estimate that the higher mutagenicity of DEP from DF is probably due to lower emissions of polycyclic aromatic compounds and that the higher toxicity of RME is probably caused by carbonyl compounds and unburned fuel. Finch et al. (2002) have measured the effects of subchronic inhalation exposure of rats to emissions from a diesel engine burning biodiesel fuel derived from soybean oil and found statistically significant, but minor and not consistently exposure-related, differences in body weight, nonpulmonary organ weights, serum chemistry, and glial fibrillary acidic protein in the brain. They found no significant exposure-related effects on survival, clinical signs, feed consumption, ocular toxicity, hematology, neurohistology, micronuclei in bone marrow, sister chromatid exchanges in peripheral blood lymphocytes, fertility, reproductive toxicity, or teratology. Finch et al. (2002) concluded that there are modest adverse effects at the highest exposure level, and none other than the expected physiological macrophage response to repeated particle exposure at the intermediate level. Ackland et al. (2007) compared the cellular effects of biodiesel emissions particulate matter (BDEP) and petroleum diesel emissions particulate matter (PDEP) using a human airway cell line. They found a lower induction of multinucleate cells for BDEP. Swanson et al., (2007) report that although the use of biodiesel fuel is favorably viewed, and there are suggestions that its exhaust emissions are less likely to present any risk to human health relative to petroleum diesel emissions, the speculative nature of a reduction in health effects based on chemical composition of biodiesel exhaust needs to be followed up with more investigations in biologic systems.

According to the multiple air toxics exposure study (MATES-II) (SCAQMD, 2000), there are six compounds among currently identified toxic air contaminants (TACs) (diesel PM, four organic

TACs—benzene, 1,3-butadiene, formaldehyde, and acetaldehyde—and hexavalent chromium) that account for over 90 percent of the risk associated with exposure to TACs in the South Coast Air Basin (SoCAB). Based on unit risk factors for these six compounds obtained from the Cal-EPA Office of Environmental Health Hazard Assessment's (OEHHA's) input to the toxic air contaminants identification process, Morris et al. (2003b) compared these TACs with B20 diesel particles by estimating the concentration leading to a one in a million risk of premature death due to long-term exposure. These concentrations are as follows:

- Benzene: 2.9×10^{-5} $(\mu g/m^3)^{-1}$
- 1,3-Butadiene: 1.7×10^{-4} $(\mu g/m^3)^{-1}$
- Acetaldehyde: 2.7×10^{-6} $(\mu g/m^3)^{-1}$
- Formaldehyde: 6.0×10^{-6} $(\mu g/m^3)^{-1}$
- Standard Diesel Particles: 3.0×10^{-4} $(\mu g/m^3)^{-1}$
- B20 Diesel Particles: 2.85×10^{-4} $(\mu g/m^3)^{-1}$

Based on the unit risk factors for these compounds, Morris et al. (2003b) estimated the unit risk factor if B20 diesel as being 0.95 that of standard diesel. They then estimated that the use of B20 fuel for the 50% and 100% HDDV fleet penetration scenarios would reduce the estimated risk of premature death due to air toxics in the SoCAB by approximately 2% and 5%, respectively.

Emissions of unregulated hazardous air pollutants (toxics) were investigated in an EPA study, "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions." The study focused on 11 mobile source air toxics that are significant contributors to toxic emission inventories. However, due to the limited nature of the data, the EPA considered the "conclusions regarding the effects of biodiesel on toxics as preliminary and only potentially indicative of the true effects" (EPA, 2002).

The Cal-EPA recognizes that risk ranking for biodiesel relative to other fuels requires consideration of toxic air pollutants that may be emitted from biodiesel beyond the six risk drivers listed above. In order to address this, a broader set of toxic air pollutants are considered here. Among the potential toxic air pollutants that should be considered in biodiesel risk comparison are polycyclic aromatic compounds (PAHs) and nitro-PAHs.

Semi-volatile organic compounds (SVOCs) such as PAHs are released to urban air from motor vehicles and from other combustion sources. In addition, these compounds may derive a large amount of their exposure from non-inhalation pathways, particularly ingestion through food. In a risk-ranking analysis for toxic air pollutants in indoor air, outdoor air and food, Loh (2005) estimated risks for a subset of key SVOCs based on total personal exposure. She divided this set of PAHs into two groups based on the EPA's weight-of-evidence classification for carcinogenic effects and the amount of available data from field studies. The first group includes benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene—compounds that are B2 carcinogens meaning there is sufficient animal evidence of carcinogenicity, but inadequate human evidence. The second group includes anthracene, benzo[g,h,i]perylene, phenanthrene, pyrene, fluoranthene, and naphthalene—compounds that are classified as C or D carcinogens with limited information on potential carcinogenicity. Loh (2005) also provided toxic equivalency factors (TEFs) obtained from Cal-EPA and other sources. The TEF expresses the cancer potency of a given PAH relative to benzo[a]pyrene, which has a unit risk factor of 1.1×10^{-3} $(\mu g/m^3)^{-1}$ (ARB-OEHHA), 1994).

Group 1 compounds and TEF	
benzo[a] anthracene	0.1
benzo[b] fluoranthene	0.1
benzo[a] pyrene	1
chrysene/ iso-chrysene	0.001
dibenz[a,h] anthracene	1
indeno (1,2,3-cd) pyrene	0.1

Group 2 compounds and TEF	
anthracene	0.0005
benzo[ghi] perylene	0.02
phenanthrene	0.0005
pyrene	0.001
fluoranthene	0.05
naphthalene	0.03

In general, the effects of biodiesel on toxic air pollutants appear to be favorable. But the current absence of industry standards for feedstocks, fuel formulation, and additives makes it problematic to assess the potential toxicity of biodiesel as a generic fuel. As a prerequisite to Tier II, it will be necessary to provide the criteria used to select and define biodiesel formulations to be studied in depth.

7.4. Previous Toxicity Testing of Biodiesel Fuel Exhaust Emissions

A comprehensive toxicity study of the exhaust from a biodiesel fuel formulation, consisting of a 13-week subchronic inhalation study in F344 rats and additional tests, was reported by The Lovelace Respiratory Research Institute (LRRI, 2000). This report states that

> "No effects of biodiesel-exhaust-emission exposure were observed in a variety of endpoints including mortality, toxicity as revealed by detailed clinical observations, feed consumption, toxicity to the eyes, neurohistopathology, formation of micronuclei (MN) in bone marrow cells, sister chromatid exchanges (SCEs), fertility, reproductive toxicity, and teratology. Endpoints in which effects were caused by biodiesel-exhaust-emission exposure, with minor changes not deemed as biologically significant, included group mean body weights, non-pulmonary organ weights at necropsy, clinical chemistry, and glial fibrillary acidic protein (GFAP) in the brain. Weak mutagenicity in a bacterial mutagenicity assay was observed from extracts of both particulate and semi-volatile fractions of biodiesel-exhaust-emission fractions. Relative to total body weights, lung weights were increased in female rats in the high-level group compared to controls (0.52 vs. 0.49% of total body weight), and histopathological evaluation of a number of tissues revealed exposure-induced changes only in the lungs. Findings included the presence of particles in macrophages and macrophage hyperplasia; these findings were judged to be a normal physiologic response to exposure and not a toxic reaction. Lesions included alveolar bronchiolarization, which was found only in rats in the high-level group, and alveolar histiocytosis, which was found in three of the four groups, but at slightly higher incidence in the high-level group. Based on these results, rats were adversely affected by exposure to high-level biodiesel exhaust emissions, the effect was

greater in female rats than in males, and the no-adverse-effect-level for this study of inhaled biodiesel exhaust emissions was the intermediate level."

It should be noted that the exhaust from the biodiesel fuel tested was potentially harmful at high doses, and therefore that some testing of exhaust emissions will be required for different formulations of biodiesel fuel. At lower doses, hazard tests used to assess biofuels impact should be expanded, where feasible, to include endpoints that may presage asthma or other adverse effects on lung function--for example hyperreactive airways or changes in forced expiratory volume (FEV).

7.5. Aquatic Toxicity

Tests used to measure toxicity include measurements of LC50 (median lethal concentration), EC50 (median effective concentration), and IC50 (inhibition concentration). Comparative tests of all the fuel samples conducted for marine and freshwater conditions will also be used to determine the relative no observed adverse effects concentrations (NOAECs).

The University of Idaho exposed *Daphnia magna* to biodiesel fuels (and to the reference 2-D diesel) for 48 hours in static and flow-through environments. The mortality rates were measured at 24 and 48 hours and LC50s were calculated. In both static and flow through tests, "the rapeseed based fuels, REE and RME, displayed the highest EC50 values, signifying them to be less toxic than the other substances" (Knothe et al., 2005). Interestingly, soybean methyl esters (SME) were significantly more toxic than rapeseed biodiesel; however, the reasons for the differences are unknown. The biodiesel/diesel blends (REE 20/2-D 80 and REE 50/2-D 50) followed similar trends: the blend with the highest biodiesel percentage displayed characteristics similar to pure biodiesel. The blend with the least biodiesel (REE 20/2-D 80) produced results similar to diesel. Under static conditions, REE 20/2-D 80 was determined to be more toxic than 2-D diesel. These results can be seen below in Figure 7.1 and Figure 7.2.

The phytotoxicity of biodiesel oil was also studied at the Centre for Aquatic Plant Management. Birchall et al. (1995) examined the "comparative toxicity of diesel and biodiesel fuels to a range of aquatic species at doses which might result from spillages from boats." Single-species toxicity tests were used to assess the toxicity of biodiesel to algae, macrophytes and invertebrates.

Growth of all species of algae tested was reduced due to the impact of both diesel and biodiesel fuels. However, biodiesel was determined to be considerably less toxic than diesel to a diverse range of freshwater algal species at all doses. Macrophytes, such as *Myriophyllum spicatum* (water milfoil) and *Elodea canadensis* (Canadian pondweed), were also more susceptible to diesel. However, the floating plant, *Lemna minor* (duckweed) was equally affected by diesel and biodiesel; its growth rate was reduced 65% at the highest doses of both fuels. The growth of *Lemna minuta* was reduced by 60% from the highest dosage of biodiesel and the plant was killed by the same dosage of diesel.

Figure 7.1. 48 hour static, non-renewal, *Daphnia magna* EC_{50}*.

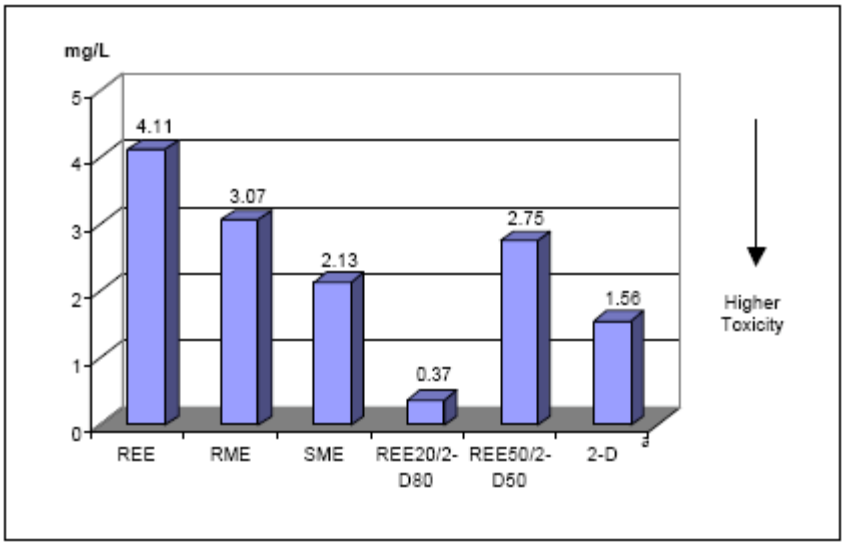


*Figure from Knothe et al. (2005).

Figure 7.2. 48 hour flow-through, *Daphnia magna* EC_{50}*.

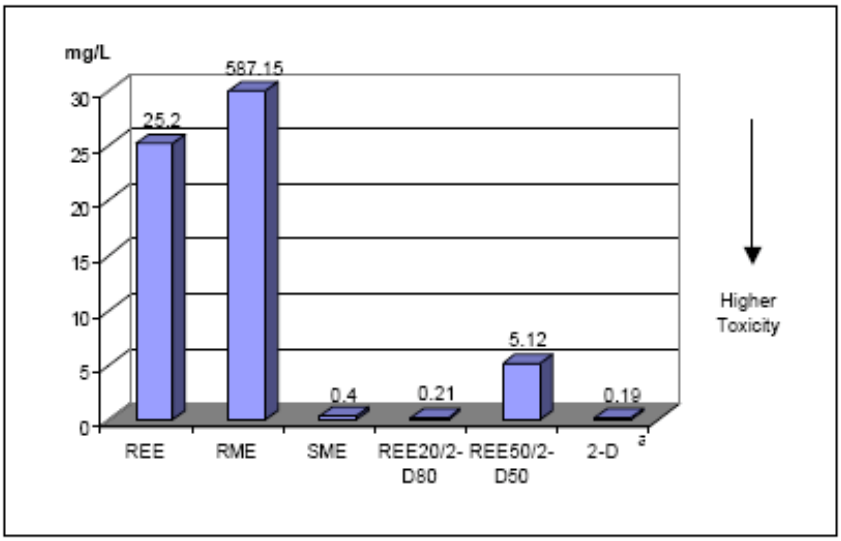


*Figure from Knothe et al. (2005).

The invertebrates tested were highly sensitive to diesel as they were "killed relatively quickly at all doses." *Daphnia magna* (water flea) and *Lymnea peregra* (water snail) were more tolerant to biodiesel with severe effects exhibited only at high doses. *Gammarus pulex* (water louse) was more sensitive with a mortality rate at relatively low biodiesel doses. Toxicity tests conducted on rainbow trout indicated that rainbow trout were more susceptible to diesel than biodiesel based on observations that the fish exposed to diesel exhibited greater weight loss, "more severe behavioral symptoms, loss of balance, muscular spasms and erratic fish and gill movements" (Birchall et al., 1995).

An indirect effect of biodiesel, through its behavior at the water surface, was also noted by Birchall et al. (1995). Biodiesel forms discrete globules on the water surface that "result in less interference with oxygen diffusion into the water, and with surface breathing or moving invertebrates" than would continuous distribution of the material. This globular distribution of the oil is much less harmful than the uniform "slicks" of diesel that cover the water's surface. The globules also aid in degradation as they allow biodiesel to "enter the water body more quickly than diesel."

While biodiesel is significantly less toxic than petroleum diesel, it can still cause harm to the environment in the event of a spill. Birds, mammals and fish can become coated with the oil, causing hypothermia, illness, or even death (Wedel, 1999). Biodiesel can also indirectly harm aquatic life as it can deplete oxygen during biodegradation.

7.6. Toxicity in Aerated Soil

Based on the results of a study conducted by Lapinskiene et. al. (2005), biodiesel is less toxic than diesel to soil microbial communities. The toxicity was evaluated by measuring the respiration of microorganisms and the activity of dehydrogenases in soil over a period of six days. Five concentrations (1, 3, 6, 9 and 12%) of diesel and biodiesel fuels were evaluated in the soil. The maximum material concentration of "12% was chosen because previous research established that at 24% of soil moisture, which corresponds to 60% of the soil's full water retention capacity, the maximum retention of diesel fuels and biodiesel fuels was 12% for both fuels" (Lapinskiene et al., 2005). Results of both assays indicated that "biodiesel fuel is non toxic at concentrations up to 12% (by weight) whereas that diesel exhibits toxic properties at concentrations higher than 3% (by weight)" (Lapinskiene et al., 2005).

8. Biodiesel Life Cycle Impacts

8.1. Life Cycle Assessment

The purpose of the life-cycle assessment (LCA) is to quantify and compare environmental flows resources and pollutants (to and from the environment) associated with both biodiesel and petroleum-based diesel, over the entire life cycle of the product. The flows of resources and pollutants provide framework for assessing human health, environmental systems and resource impacts. LCA evaluates a broad range of requirements and impacts for technologies, industrial processes and products in order to determine their propensity to consume natural resources or generate pollution. The term "life cycle" refers to the need to include all stages of a process—raw material extraction, manufacturing, distribution, use and disposal including all intervening transportation steps—so as to provide a balanced and objective assessment of alternatives. An LCA includes three types of activities: (1) collecting life cycle inventory data on materials and energy flows and processes; (2) conducting a life-cycle impact assessment (LCIA) that provides characterization factors to compare the impacts of different product components; and (3) life-cycle management, which is the integration of all this information into a form that supports decision-making. A comprehensive LCA for biodiesel must address cumulative impacts to human health and the environment from all stages, impacts from alternative materials, and impacts from obtaining feedstocks and raw materials. Figure 8.1 illustrates our approach for biodiesel LCA.

The focus of the Tier-II and Tier-III efforts is on the direct health and environmental impacts associated with pollutant emissions from biodiesel production and use. There are many other life-cycle issues that are of interest—including green-house-gas (GHG) emissions, water use, energy balance, land conversion, and competing uses for food crops. These are outside of the scope of this effort and are being addressed in great detail by other California programs—particularly the low-carbon fuel standard program. A list of reports currently available from this program is available at: http://www.energy.ca.gov/low_carbon_fuel_standard/

The life-cycle of biodiesel fuels include the following stages

- Biomass production and preparation (for biodiesel derived from plant biomass)
- Oil extraction processes (for biodiesel derived from plant biomass)
- Collection of recycled oils and greases
- Biodiesel production (preparation and esterification)
- Refining the final product, B10, B20, B100 etc.
- Transportation, storage and distribution of biodiesel product
- End-use combustion

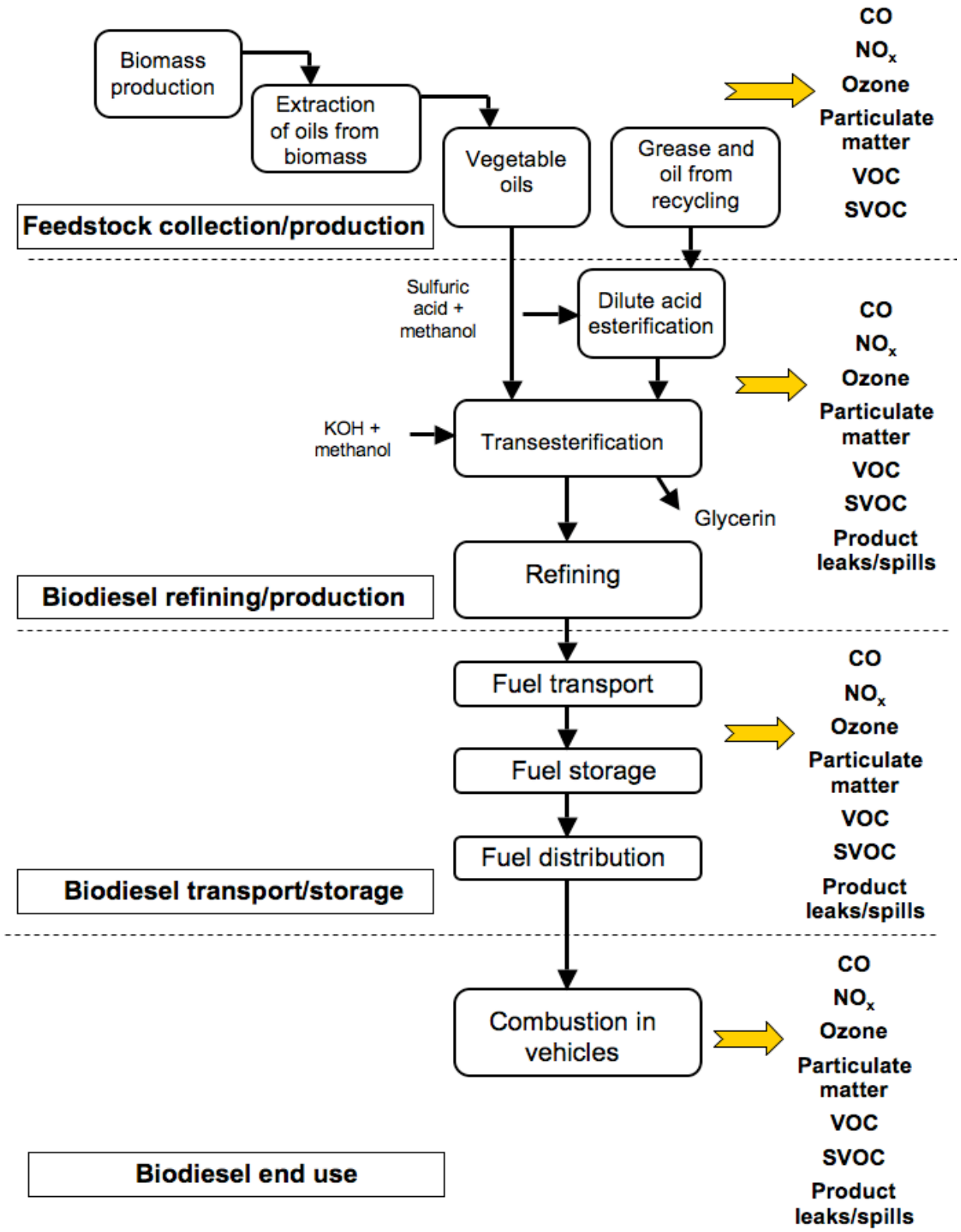


Figure 8.1. An illustration of life stages and life-cycle impacts for biodiesel fuels.

For each of these stages we must address emissions to the environment for the following pollutant categories

- Carbon monoxide (CO)
- Nitrogen oxides (NO_x)
- Ozone
- Particulate matter
- Volatile organic compounds (VOCs) such as benzene, formaldehyde, etc.
- Semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons
- Metals
- Fuel product leaks and spills
- Hazardous wastes

In 1998, the U.S. Department of Agriculture and the U.S. Department of Energy sponsored a study on the life cycle of biodiesel and diesel fuels. life cycle inventories (LCIs) of both fuels allow a side-by-side comparison (USDA and USDOE, 1998). The biodiesel used in this case study was produced from soybeans and the diesel was characterized as "on-highway" low-sulfur diesel made from crude oil. The life cycles of both fuels were compared with the same "functional unit" that is based on the work (brake-horsepower hour (bhp-h)) the fuel provided to a bus engine.

In this study the LCIs quantified the total energy demands and the overall energy efficiencies of the process and products. Two types of energy efficiencies were determined: the fossil energy ratio and the life cycle energy ratio. The fossil energy ratio determines the degree to which a fuel is renewable. It is the ratio of the final fuel product energy to the amount of fossil energy required to make the fuel. While the life cycle energy is the ratio of fuel product energy to total primary energy.

The study determined that the life cycle energy demands of both fuels are essentially equivalent. The life cycle energy efficiencies of biodiesel and diesel are 80.55% and 83.28%, respectively. Lower biodiesel efficiency "reflect a slightly higher demand for process energy across the life cycle" (USDA and USDOE, 1998).

The production process of converting raw energy resources (petroleum or soybean oil) into fuels was almost equal in its efficiency for both fuels. However, since soy oil is biodiesel's largest raw resource and it is renewable, less fossil fuel (only 0.31 units) is required to make 1 unit of fuel. In contrast, diesel requires 1.2 units of fossil resources to produce 1 unit of fuel. Overall, "biodiesel yields 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle" (USDA and USDOE, 1998). The fossil energy ratio of B20, however, is less than B100 with a ratio of 0.98 units.

8.2. Emissions of Pollutants to Air

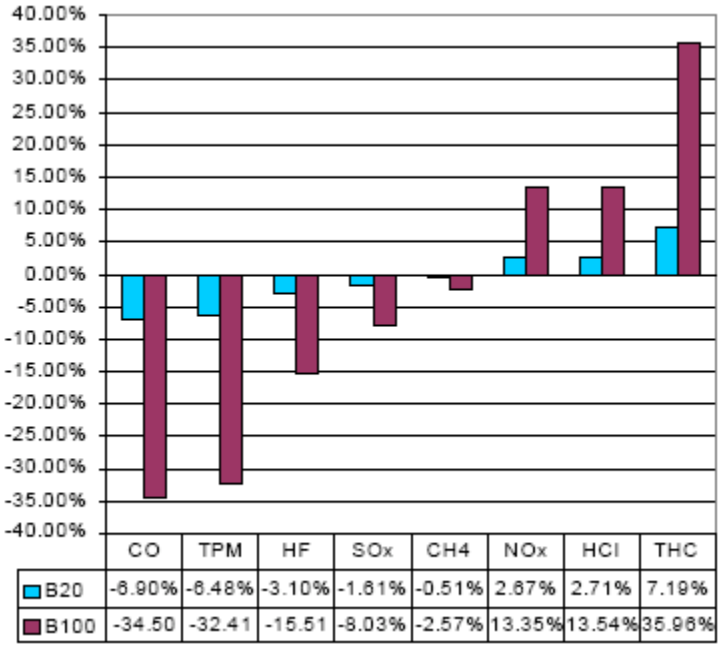
The LCI also included air pollutants: carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM), sulfur oxides (SO_x), and non-methane hydrocarbons (NMHC). All tested pollutants,

other than NO_x, hydrochloric acid (HCl), and total hydrocarbons (THC), showed decreased emissions relative to diesel (Figure 8.2).

Biodiesel produces 32% less total particulate matter (TPM) and 35% less CO than does petroleum diesel in its typical life cycle. Of the TPM, the "PM10 emissions from an urban bus operating on biodiesel are 68% lower than those from an urban bus operating on petroleum diesel" (USDA and USDOE, 1998). SO_x emissions also decreased 8.03% and 1.61% for B100 and B20 respectively. The amount of sulfur oxides emitted is a function of the sulfur content in the diesel fuel.

Both HCl and HF emissions occur as a result of coal combustion and electric power generation. These emissions are tracked because they may contribute to acidification in the environment. Since "HF levels drop with biodiesel in proportion to the amount of electricity consumed over the life cycle," a 15.51% reduction in emissions occurs (USDA and USDOE, 1998). The HCl biodiesel emissions, however, increase 13.54%. This is because there are "additional sources of HCl associated with the production and use of inorganic acids and bases used in the conversion step" (USDA and USDOE, 1998).

Figure 8.2. Life cycle air emissions for B100 and B20 compared to petroleum diesel life cycle air emissions*.



	CO	TPM	HF	SOx	CH4	NOx	HCl	THC
B20	-6.90%	-6.48%	-3.10%	-1.61%	-0.51%	2.67%	2.71%	7.19%
B100	-34.50	-32.41	-15.51	-8.03%	-2.57%	13.35%	13.54%	35.96%

*Figure from USDA and USDOE (1998).

Biodiesel's life cycle produces 35% more THC than does the diesel life cycle. Most of these emissions are produced during agricultural operations and soybean crushing. However, biodiesel's tailpipe emissions are 37% lower than diesel's emissions (these reductions were similar to those in the EPA study, discussed in Section V, Part A). Methane, CH_4, a greenhouse gas and a subset of THC emissions, produces 25% of the life cycle emissions of THC. For B100, CH_4 emissions were reduced by 2.57% relative to those from diesel.

8.3. Solid Waste and Emissions to Water

The USDA/USDOE study estimated biodiesel life cycle wastewater flows as almost 80% lower than petroleum diesel. The extraction of crude oil accounts for 78% of the total wastewater flow in diesel's life cycle, while only 12% is associated with the refinery process. The largest contributor to the wastewater flows of biodiesel come from soybean and oil processing (66%).

The life cycle assessments also include two classifications of solid waste: hazardous and nonhazardous. Biodiesel produces less hazardous waste than does diesel because it does not require a crude oil refining process. In contrast, almost all of diesel's hazardous solid waste is derived from the refining process. Agriculture accounts for 70% of biodiesel's hazardous waste, "but these flows are indirect charges against agriculture for hazardous waste flows associated with the production of diesel fuel and gasoline used on the farm" (USDA and USDOE, 1998). The total hazardous waste generation of diesel is 0.41g/bhp-h of engine work compared to 0.018g/bhp-h for biodiesel.

The nonhazardous waste generated within biodiesel's life cycle is 12.7g/bhp-h of engine work; this is largely attributed to the trash and trap metals that are removed from the soybeans after the crushing stage. Diesel's nonhazardous waste is significantly lower with only 2.8g/bhp-h of engine work. This waste is primarily generated in diesel's crude oil refining and extraction steps.

8.4. Life Cycle Inventory Information Gaps

The USDA/USDOE study provides a useful starting point of a biodiesel life-cycle impacts, but there are a number of limitations that must be addressed. First of all, the USDA/USDOE study considered only one type of biodiesel—that derived from soybeans. So there is a need to consider other types of biodiesel feedstock. The study considered only differences in emissions inventories, but did not address the differences in health and environmental impacts associated with these differences. There are computer models and databases that make this possible. The USDA/USDOE also did not address leaks and spills of fuel product during transport, storage, and distribution—an important issue for California.

9. Tier I Conclusions

Through a detailed review of the current knowledge on biodiesel use and impacts, this report provides a foundation for proceeding to a more detailed impact assessment for biodiesel use in California. A key focus of our review is identification of key knowledge gaps about physical, chemical, and toxicological properties of biodiesel governing environmental fate and transport and ecosystem and human health impacts. During this review, we discovered that there is a lack of information available on additives and their associated properties, both in mixture with biodiesel and alone. Therefore consideration of additive impacts leads the list of knowledge gaps by virtue of both the intrinsic impacts of the additives themselves, such as aquatic toxicity, and the coupled effects of additives on other properties of biodiesel fuels such as fate and transport and biodegradation. In the paragraphs below we summarize our key findings and conclusions. These issues set priorities for Tier II efforts.

1. Additives impacts. To provide a stable, useful, and reliable fuel, additive chemicals will need to be introduced into almost all biodiesel blends. These additives will be required to control oxidation, corrosion, foaming, cold temperature flow properties, biodegradation, water separation, and NO_x formation. The specific chemicals and amounts used have not been well-defined for the emerging industry in California. A careful evaluation of the possible chemicals would be beneficial to California and may lead to a "recommended list" or "acceptable list" that would minimize the uncertainty of future impacts as industry standards are developed.

The impact of various additives that may be used with biodiesel blends needs to be considered for releases to the air, water, and soils. Additives may affect fuel quality or storage stability in unintended ways. Because the properties of additives can potentially alter the characteristics of biodiesel, increasing its environmental and health risks, there is a need for additional tests on biodiesel with specific concentrations of additives. In particular it is necessary to assess the impact of

- cold flow property controllers on surface water- biodiesel interaction and on subsurface multiphase transport of biodiesel (see number 2 below).
- biocides and anti-oxidants on biodegradation (see number 3 below).
- all priority additives on human and ecosystem toxicity.

2. Subsurface fate and transport properties. The impacts of leaks and spills of biodiesel fuel product during transport, storage, and distribution have not been addressed. This is an important issue for California. Because the chemical composition of biodiesel differs significantly from that of petroleum diesel, it is expected that infiltration, redistribution, and lens formation on water tables will differ for the two fuels, leading potentially to significant differences in relative impacts to groundwater quality. Properties governing these processes are density, viscosity, and interfacial tensions. Component (including additive) solubility into the water phase ultimately governs water quality and so inter-phase solubilization of individual components also needs to be identified. To address these issues requires experiments with conventional soil column tests that will establish relative transport behaviors among different fuel compositions and for site-specific analyses. But the relevance of these results for state-wide assessments should be considered along with the value of full-scale comparative field tests with releases into the groundwater, or into the vadose zone just above the groundwater table.

3. Biodegradation in soils and aquifers. The anticipated use of biocides in B20 fuels may affect the biodegradation potential for biodiesel released into the environment. The impact of biocides added to blended biodiesel may reduce the biodegradation of biodiesel and other petroleum-based fuels leaked or spilled into the subsurface. Since subsurface biodegradation can play an important role in the remediation of fuel spills and leaks, an understanding of the fate of biodiesel with biocide additive is needed.

Not all biodiesel or renewable-diesel fuel blends have been tested for degradation under aerobic and especially anaerobic conditions. To our knowledge, only one alternate electron acceptor, nitrate, has been tested; others such as sulfate and methanogenic conditions should be explored, because these are the primary available electron acceptors expected in the reducing environments expected in deeper soil contamination and in aquifers.

Pure biodiesel (B100) without additives may be more biodegradable than ULSD and may be preferentially metabolized by subsurface microbes. The interaction of B100 with existing gasoline or conventional diesel previously released into the subsurface needs to be examined more closely.

4. Production and storage releases. In addition to impacts from released B100 or blended B20 biodiesel, increased production and associated feedstock processing may involve impacts from released reactants and by-products. There are potential impacts to California's air and water during the large-scale industrial operations use to extract seed oils. These impacts may result from air emissions of solvents used to extract the seed oil (e.g., hexane) and from leaking tanks containing chemicals to process the plant oils into biodiesel. There is also the issue of occupational exposures. Finally, UST material compatibility must be addressed: owner/operators are required by state health and safety codes to demonstrate material compatibility prior to storage of biodiesel. The impacts during seed extraction will be become more of an issue for California as in-state production of plant-derived oils increases and may require further study. Currently, the possible impacts during seed extraction will be minimal in California since it is anticipated that most of the seed oils will be derived from soy grown and extracted out-of-state.

Among the most important current production reactants are: methanol, generic acid or base catalysts, feedstock oils, and post-processing water. As the biodiesel industry matures, release scenarios developed in this report need to be refined and prioritized.

5. Additional air-emission studies. There are not yet sufficient data to assert that the use of biodiesel will reduce the emissions of criteria and toxic air pollutants. Although considerable data are available on the effect of biodiesel on EPA-regulated pollutants (i.e., HC, CO, NO_x, and particulates), most of these data were generated using older technology engines. Further, very little detailed exhaust characterization data on biodiesel exist beyond a small number of regulated pollutants. Planned emission testing is based on newly blended B20 fuel stocks with only an anti-oxidant added and purged with nitrogen. B5, B50 and B100 will also be tested. The anti-oxidant and nitrogen purge are needed because the fuel used for the planned testing will be at least six month old-which is at the maximum recommended storage time for biodiesel. We note that these fuel mixes may not necessarily represent the general storage conditions expected throughout California. It is well established that fuel-handling practices have an important influence on engine performance and combustion emission. Additionally, the impact of various additives on combustion air emissions needs to be evaluated. Given the wide variety of oils and fats that might be used to make biodiesel fuel and the potential additives, the actual emissions of PMs and toxic air pollutants will have to be determined for each proposed formulation of

biodiesel fuel to be used in California. This situation demands a systematic and ongoing effort to assess emissions from diesel engines. In particular, there is a need for more controlled combustion studies to assess how the spectrum of toxic air pollutants, such as the spectrum of PAHs, will shift both in terms of volatile and particle-bound fraction but also in terms of any changes in toxic equivalency.

6. Tier II Sampling Plan. Many of the data gaps identified above will be addressed in the sampling plan developed for the Tier II study and report. In preparing this report, we had a number of discussions with Cal-EPA staff that provide important insight for developing the Tier-II sampling plan. First there is the issue of differences in emissions from different vehicle/engine classes such as on and off road vehicles. Where possible, this information should be included in the Tier two assessment. Next there are a number of issues of coordination among samples for different media and different objects. Samples used to test fate, transport, and toxicity should come from the same batch and be stored (aged) under the same conditions. When making comparisons of ULSD and biodiesel, all fuels should be subjected to the same tests. One example includes efforts to assure that fuel samples tested for water quality should include the same types of fuel samples used by CARB for air emissions tests to evaluate the effects and toxicity of the antioxidant additive. A second example is that the biodiesel formulation used to approve underground storage tank components for material compatibility should be the same formulation used in material compatibility tests. (The quantity of biodiesel required for this test at B20, B50, and B100 is probably on the order of one liter.) Fatty-acid-methyl-ester-derived biodiesel samples used in fate, transport, and toxicity testing should represent the vegetable oil feedstock most widely found in biodiesel marketed in California and the animal fat feedstock most widely found in biodiesel marketed in California. If the budget allows, we should also include the second most prevalent vegetable oil feedstock found in biodiesel marketed in California. Finally, samples used in fate studies should, where possible, represent both ideal conditions of biodiesel that meets ASTM D6751-07a specifications, as well as a more real-world example of fuel stored in an underground storage tank. These latter samples should contain 1.0% water at 100 ppm Cl salinity, peroxide levels of 150-200 ppm, and a total ammonia nitrogen (TAN) of 0.5 or greater. The peroxide and TAN levels should be attainable through natural aging of biodiesel without antioxidants. There will be a need to calculate quantities of each fuel, feedstock, blend, additive and water content, necessary to conduct all the planned sampling tests.

7. Life Cycle Impacts. Only differences in emissions inventories were considered during recent studies comparing life cycle inventories (LCI) of biodiesel to petroleum diesel. Differences in health and environmental impacts associated with these LCI differences needs to be evaluated. Additionally, current LCI studies have been limited to only soybean oil feedstocks. It is well established that different feedstocks can have an important influence on life cycle emissions. Information is needed for other feedstocks as well as for renewable diesel.

8. Priority list of biodiesel formulations. Because the number of potential feedstocks, the number of fuel blends, and the number of additive choices and mixes makes for an unmanageable suite of permutations of cases for consideration, it is critical to identify the priority feedstocks, fuel blends, and additives requiring study for our impacts assessment. Not specifically addressed in this Tier I evaluation are the environmental impacts from the increased use of fertilizers and water and land resources as the production of plant oils increases in the State. These factors may be some of the most important eventual impacts to California as the biofuels industry expands. More sustainable sources of biodiesel such as yellow or brown grease may be preferable and should be encouraged.

Finally, a key goal of encouraging fuels such as biodiesel is to reduce California's carbon "footprint" as part of a global strategy. To consider only the environmental impacts to California and disregard the impacts that may be occurring nationally or internationally during the production of the biofuels feedstock that is used in California is short-sighted.

10. References

Ackland ML, Zou L, Freestone D, van de Waasenburg S, Michalczyk AA. 2007. Diesel exhaust particulate matter induces multinucleate cells and zinc transporter-dependent apoptosis in human airway cells. *Immunol Cell Biol*. 85(8): 617-622.

Albermarle Corporation. 2006. Solutions for improved biodiesel: Antioxidants for sustainable fuels. Product literature, 2006.

ARB-OEHHA. 1994. "Benzo[a]pyrene as a Toxic Air Contaminant." prepared by the staffs of the California Air Resources Board and the Office of Environmental Health Hazard-Assessment.

ASTM (American Society for Testing and Materials). 2007. Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, D 6751-07a, ASTM International.

ATSDR (Agency for Toxic Substances and Disease Registry). 1995. Toxicological profile for fuel oils. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Beaver, Sunny. 2008. Personal communication. Yokayo Biofuels, Ukiah, CA.

Birchall, C., J. Newman, and M. Greaves. 1995. Degradation and Phytotoxicity of Biodiesel oil, Institute of Arable Crops Research, 1995.

Biodiesel Magazine. 2006. "NREL, Chevron Consider Renewable Diesel Research", *Biodiesel Magazine*. December 2006.

Bünger J, Krahl J, Baum K, Schröder O, Müller M, Westphal G, Ruhnau P, Schulz TG, Hallier E. 2000a. Cytotoxic and mutagenic effects, particle size and concentration analysis of diesel engine emissions using biodiesel and petrol diesel as fuel. *Arch Toxicol*. 74(8): 490-498.

Bünger J, Müller MM, Krahl J, Baum K, Weigel A, Hallier E, Schulz TG. 2000b. Mutagenicity of diesel exhaust particles from two fossil and two plant oil fuels. Mutagenesis 15(5): 391-397.

CalEPA (California Environmental Protection Agency). 2008. Guidance Document and Recommendations on the Types of Scientific Information to be Submitted by Applicants for California Fuels Environmental Multimedia Evaluations.

Canakci, M. and J. Van Gerpen, 2001. A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks, Proceedings, Amer. Soc. Agric. Engineers, 2001, paper number 016049, 2001.

Chesnow, Howard. 2008. Personal communication. Fuel Quality Systems Group. Corporation.

Chor H and D. Wilson. 2000. Improving the cold flow properties of biodiesel. A technical presentation given at the 91st American Oil Chemists' Society (AOCS) annual meeting, San Diego, CA, April 26, 2000. Lubrizol Corporation.

Clean Diesel Technologies. 2008.

Clark N. 2008. Virgin Atlantic Plans a Biofuel Flight, The New York Times, January 15, 2008.

Cox, C. 2006. "Is algae the new oil?", *Ode Magazine*, December 2006.

Degussa Corp. 2008. www.degusa.com

Fargione J, J. Hill, D. Tilman, S. Polasky, and P. Hawthorne. 2008. Land Clearing and the Biofuel Carbon Debt, *Science*, February 2008

Federal Record. 2005. One Hundred and Ninth Congress of the United States of America. Energy Policy Act of 2005,. City of Washington 2005. http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=109_cong_bills&docid=f:h6enr.txt.pdf

Finch GL, Hobbs CH, Blair LF, Barr EB, Hahn FF, Jaramillo RJ, Kubatko JE, March TH, White RK, Krone JR, Ménache MG, Nikula KJ, Mauderly JL, Van Gerpen J, Merceica MD, Zielinska B, Stankowski L, Burling K, Howell S. 2002. Effects of subchronic inhalation exposure of rats to emissions from a diesel engine burning soybean oil derived biodiesel fuel. *Inhal Toxicol*. 14(10): 1017-1048.

Graboski, M., R. McCormick, T. Alleman, and A. Herring. 2003. The Effect of Biodiesel Composition on Engine Composition on Engine Emissions from a DDC Series 60 Diesel Engine. Final Report, National Renewable Energy Laboratory, NREL/SR-510-31461, February, 2003.

He, B., J. Thompson, D. Routt, and J. Van Gerpen 2007. Moisture Absorption in Biodiesel and its Petro-Diesel Blends, *Applied Engineering in Agriculture*. 23(1): 71 – 76.

Hilber, T., E. AHN, M. Mittelbach, and E. Schmidt. 2007. "Animal Fats Perform Well in Biodiesel.", *Render Magazine*, February 2007.

Hodam R, 2008. Alternative Fuels: Ethanol and Biodiesel Compatibility: A Framework for Decision Making. California CUPA Forum, February, 2008.

Irwin, L. 2007. Additive Adjustment. Biodiesel Magazine, May 2007. www.biodieselmagazine.com

Jessen, H.. 2007. Waving the Palm Branch, *Biodiesel Magazine*, February 2007. http://www.biodieselmagazine.com/article.jsp?article_id=1433

Johnson, B. 2007. Increasing Use of Biodiesel could Fuel Canola Explosion, *SeedQuest News*, California Farm Bureau Federation. March 2007.

Kado, NY, Okamoto, RA, Kuzmicky, PA (1996) Chemical and Bioassay Analyses of Diesel and Biodiesel Particulate Matter: Pilot Study, Final Report. Prepared for The Montana Department of Environmental Quality and the US Department of Energy by the Department of Environmental Toxicology, University of California, Davis, California 95616.

Kaffka, Stephen. 2007. Oral Communication. July 17, 2007.

Kantor J, 2008. Europe May Ban Imports of Some Biofuel Crops, The New York Times, January 15, 2008.

Kemp, D. and Frank V. 1980. Organic Chemistry, Worth Publishers, Inc. New York. 1980

Kemp, William. 2006. Biodiesel Basics and Beyond, Aztext Press, Ontario 2006.

California Senate Bill 140. 2007. Christine Kehoe. 2007 Senate Rules Committee. http://info.sen.ca.gov/pub/07-08/bill/sen/sb_0101-0150/sb_140_cfa_20070601_154941_sen_floor.html

Kenreck, G. 2007. Improving Biodiesel Stability with Fuel Additives, *Biodiesel Magazine,* February, 2007.

Knothe, G., J.V. Gerpen, and J. Krahl. 2005. The Biodiesel Handbook, AOCS Press, Champaign, Illinois, 2005.

Kotrba, Ron. 2007. Budding Opportunities in Canola, *Biodiesel Magazine*, February 2007.

Kram, Jerry. 2007. Algae on the Edge, *Biodiesel Magazine*, March 2007.

Krauter, Bob. 2006. Biodiesel Use Gaining more Converts in California, *Capital Press*, August 2006.

Lacoste, F., P. Bondioli, M. Mittelbach, J. Blassnegger, T. Brehmer, A. Frohlich, B. Dufrenoy, J. Fischer. 2003. Stability of Biodiesel, Summary Report, BLT, August, 2003

Lapinskiene, A., P. Martinkus, and V. Rebzdaite. 2005. Exo-toxicological studies of diesel and biodiesel fuels in aerated soil, *Environmental Pollution*, 142: 432 – 437.

Lapinskiene, Asta, and Povilas Martinkus. 2007.Research on Anaerobic Biodegradation of Fats, Biodiesel Fuel and Diesel Fuel in Soil Medium**.** Environmental Research, Engineering and Management, 2007.No.1(39), P. 30-37.

Leung, D., B. Koo, and Y. Guo, 2005. Degradation of biodiesel under different storage conditions, *Bioresource Technology*, 97: 250-256.

Lin, YC, Lee, WJ, Wu, TS, Wang, CT. 2006. Comparison of PAH and regulated harmful matter emissions from biodiesel blends and paraffinic fuel blends on engine accumulated mileage test, *Fuel*, **85**:2516–2523.

Loh, M. 2005. "Assessing Personal Exposures and Risks to Organic Hazardous Air Pollutants," PhD Dissertation, Harvard University School of Public Health.

LRRI (Lovelace Respiratory Research Institute). 2000. Final Report, Tier 2 Testing of Biodiesel Exhaust Emissions, Study Report Number FY98-056, May, 2000.

Mansell, G., R. Morris, and G. Wilson. 2003. Impact of Biodiesel Fuels on Air Quality and Human Health: Task 3 Report, Impact of Biodiesel Fuels on Ambient Carbon Monoxide Levels in the Las Vegas Nonattainment Area, National Renewable Energy Laboratory, NREL/SR-540-33796, May, 2003

Max, Arthur.2007. Palm Oil's Luster Fades on Biofuel Scene, *USA Today*. http://www.usatoday.com/tech/science/2007-04-01-palmoil_N.htm

McKone TE. 1993. CalTOX, a Multimedia Total-Exposure Model for Hazardous-Wastes Sites Part I: Executive Summary. Rep. UCRL-CR-111456PtI, Lawrence Livermore National Laboratory, Livermore, CA.

McMinnville Energy Systems. 2007. Project Report: Agricultural biofueled generation of electricity and the development of durable and efficient NO_x reduction. www.mesystem.net

Mittelbach, M. and C. Remschmidt. 2004. Biodiesel: The Comprehensive Handbook, Martin Mittelbach, Austria.

Morris, R., A. Pollack, G. Mansell, C. Lindhjem, Y. Jia, and G. Wilson. 2003a. Impact of Biodiesel Fuels on Air Quality and Human Health, Summary Report, National Renewable Energy Laboratory, NREL/SR-540-33793, May, 2003.

Morris, R., G. Mansell, Y. Jia, and G. Wilson 2003b. Impact of Biodiesel on Air Quality and Human Health: Task 2 Report, The Impact of Biodiesel Fuels on Ozone Concentrations, National Renewable Energy Laboratory, NREL/SR-540-33795, May 2003.

Morris, R., and Y. Jia. 2003a. Impact of Biodiesel Fuels on Air Quality and Human Health: Task 4 Report, Impact of Biodiesel Fuel Use on PM, National Renewable Energy Laboratory, NREL/SR-540-33797, May, 2003.

Morris, R., and Y. Jia. 2003b. Impact of Biodiesel Fuels on Air Quality and Human Health: Task 5 Report, Air Toxics Modeling of the Effects of Biodiesel Fuel Use on Human Health in the South Coast Air Basin Region of Southern California, National Renewable Energy Laboratory, NREL/SR-540-33798, May, 2003.

Natl. Inst. Public Health Environ. Prot. 1994. Uniform system for the evaluation of substances (USES), version 1.0. Rep. VROM Distrib. 11144/150, RIVM; Minist. Hous., Spat. Plan. Environ. (VROM); Minist. Welf., Health, Cult. Aff. (WVC), The Hague, Netherlands.

NBB (National Biodiesel Board). 2007. Biodiesel Production and Quality. 2007 Fact Sheet12. http://www.biodiesel.org/pdf_files/fuelfactsheets/prod_quality.pdf

NREL (National Renewable Energy Laboratory). 2005. Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004; Technical report NREL/TP-540-38836; National Renewable Energy Laboratory, 2005.

Pradhan, A., and D.S. Shrestha. 2007. Impacts of Some Common Impurities on Biodiesel Cloud Point, American Society of Agricultural and Biological Engineers, Michigan. http://asae.frymulti.com/abstract.asp?aid=23434&t=2

Quigley R. 2007. Biodiesel: The good, the bad, and the additives. Biofuels International, February 2007, pp. 70-72.

Reddy M, DeMello J, Carmichael C, Emily P, Li X, Arey JS, 2008. Determination of Biodiesel Blending Percentages Using Natural Abundance Radiocarbon Analysis: Testing the Accuracy of Retail Biodiesel Blends. Environmental Science and Technology, February 2008. http://pubs.acs.org/cgi-bin/sample.cgi/esthag/asap/html/es071814j.html

Ribiero, NM, AC Pinto, CM Quintella, GO da Rocha, LSG Teixeira, LN Guariero, MC Rangel, MCC Veloso, MJC Rezende, RS Cruz, AM Oliviera, EA Torres, and JB Andrade. 2007. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: A review. Energy and Fuels 21:2433-2445.

RIVM. 1994. *Uniform System for the Evaluation of Substances (Uses), Version 1.0. Rep. VROM Distribution No. 11144/150*, National Institute of Public Health and Environmental Protection (RIVM); Ministry of Housing, Spatial Planning and Environment (VROM); Ministry of Welfare, Health, and Cultural Affairs (WVC), The Hague, the Netherlands.

Rohm and Haas. 1999. Product literature, Publication number BIO.KFPI.5GENECAL.TB.

Rosenthal E, 2007. Once a Dream Fuel, Palm Oil May Be an Eco-Nightmare, The New York Times, January 31, 2007. http://www.nytimes.com/2007/01/31/business/worldbusiness/31biofuel.html?pagewanted=1

Searchinger T, Heimlich R, Houghton RA, Dong F, Elobeid A, Fabiosa J, Tokgoz S, Hayes D, Yu T, 2008. Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land Use Change, Science, February 7, 2008.

Sheehan, J., T. Dunahay, J. Benemann, and P. Roessler. 1998. A Look Back at the U.S. Department of Energy's Aquatic Species Program – Biodiesel from Algae, National Renewable Energy Laboratory. http://www.nrel.gov/docs/legosti/fy98/24190.pdf

Sioux City Journal. 2007. Soybean Oil Prices put Squeeze on Biodiesel, June 12, 2007. http://www.siouxcityjournal.com/articles/2007/06/12/news/iowa/881238934ec50219862572f8000765ae.txt#

Sizle, Bill. 2008. Personal communication. Lubrizol Corporation.

Solodov VA, OA Varnavskaya, LK Khvatova, BR Kakruthdinov, NA Lebedev, IN Diyarov. 2005. Sorbitol-based demulsifying agents and their surfactant properties. Russian Journal of Applied Chemistry 78 (6): 944-949.

South Coast Air Quality Management District (SCAQMD) 2000. Multiple air toxics exposure study (MATES-II) Final Report. March 2000. (2nd printing - July, 2000).

SRI (Southwest Research Institute). 2005. Characterization of Biodiesel Oxidation and Oxidation Products, National Renewable Energy Laboratory, NREL/TP-540-39096, November 2005.

Stolz, J., P. Follis, G. Floro, R. Donofrio, J. Buzzelli, and W. Griffin. 1995. Aerobic and Anaerobic biodegradation of the methyl esterified fatty acids of soy diesel in freshwater and soil environments. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19950101_gen-273.pdf

Swanson KJ, Madden MC, Ghio AJ. 2007. Biodiesel exhaust: the need for health effects research. *Environ Health Perspect.* 115(4): 496-499.

SWRCB, 2008. Memo to Local UST Regulatory Agencies and Interested Parties. State Water Resources Control Board, California Environmental Protection Agency, February 28th, 2008.

Taracha, J. 2006. Technology Issues and Trends: Biodiesel. ASPA Spring Meeting, June 2006. Lubrizol Corp.

Turrio-Baldassarria, L, Battistellia, CL, Contia, L, Crebellia, R., De Berardisa, B, Iamicelia, AL, Gambinob, M, Iannacconeb, S (2004) Emission comparison of urban bus engine fueled with diesel oil and 'biodiesel' blend, *Science of the Total Environment,* **327**:147–162.

The Wall Street Journal, 2008. Greenhouse Affect. February, 2008.

University of Idaho Department of Biological and Agricultural Engineering. 2005. Tech Note: Impact of additives on cold flow properties of biodiesel Fall/Winter 2005, volume 2, issue 2.

US (United States) DA (Department of Agriculture) and U.S. DOE (Department of Energy). 1998. An Overview of Biodiesel and Petroleum Diesel Life Cycles, National Renewable Energy Laboratory, NREL/TP-580-24772, May, 1998.

US EPA (United States Environmental Protection Agency). 2002. A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions, Draft Technical Report EPA420-P-02-001, October 2002.

U.S. DOE (Department of Energy). 2006. Biodiesel handling and use guidelines, third edition, DOE/G0-102008-2358, September, 2006.

Van Gerpen, J. Biodiesel Production and Fuel Quality. University of Idaho. http://www.uidaho.edu/bioenergy/biodieselED/publication/01.pdf

Van Gerpen, J., B. Shanks, R. Pruszko, D. Clements, and G. Knothe. 2004. Biodiesel Analytical Methods, National Renewable Energy Laboratory, NREL/SR-510-36240, July, 2004. http://www.nrel.gov/docs/fy04osti/36240.pdf

Van Gerpen, J., E. Hammond, L. Johnson, S. Marley, L. Yu, I. Lee, and A. Monyem. 1996. Determining the Influence of Contaminants on Biodiesel Properties, Iowa State University.

Van Gerpen, Jon. 2004. Business Management for Biodiesel Producers, National Renewable Energy Laboratory, NREL/SR-510-36242, July, 2004. http://www1.eere.energy.gov/biomass/pdfs/36242.pdf

Viscom. 2008. www.viscomusa.com

Wang M, Haq Z, 2008. Response to February 7, 2008 Sciencexpress Article, Argonne National Laboratory, Transportation Technology R&D Center. http://www.transportation.anl.gov/media_center/news_stories/20080214_response.html

Wania F, Fate and Transport of Chemicals in the Environment. In: *Encylopedia of Physical Science and Technology*, Academic Press, San Diego CA, 2001.

Wedel, Randall. 1999. Technical Handbook for Marine Biodiesel, National Renewable Energy Laboratory, DE-AC36-83CH10093, April, 1999.

Woodfine DG, MacLeod M, Mackay D, Brimacombe JR. 2001. Development of Continental Scale Multimedia Contaminant Fate Models: Integrating Gis. Environmental Science and Pollution Research 8: 164-72.

Yang, HH, Chien, SM, Lo, MY, Lan, JCW, Lu, WC, Ku, YY (2007) Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing, *Atmospheric Environment* **41**:7232–7240.

Zhang, X., C. Peterson, D. Reece, G. Moller, and R. Haws. 1998. Biodegradability of Biodiesel in the Aquatic Environment, *ASAE*, 41(5): 1423 – 1430.

Zhang, Y., M.A. Dube, D.D. McLean, and M. Kates. 2003. Biodiesel Production From Waste Cooking Oil:1. Process Design and Technological Assessment. Bioresource Technology 89:1-16.

11. Appendices

11.1. Appendix A: ASTM D6751-07a Standard Property Descriptions for Biodiesel

The significance of the ASTM D6751-07a standard properties (described below) are based primarily on the commercial use of biodiesel in on-road and off-road diesel engine applications (ASTM, 2007).

Calcium and Magnesium

Biodiesel can contain small amounts of calcium and magnesium in the form of abrasive solids or soluble metallic soaps. "Abrasive solids can contribute to injector, fuel pump, piston, and ring wear, as well as engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits" (ASTM, 2007).

Flash Point

This is the minimum temperature at which the fuel ignites on application of an ignition source; it has no direct relationship to engine performance but instead indicates the level of fire safety. The minimum flash point of biodiesel is much higher than diesel fuel and it "falls under the non-hazardous category under National Fire Protection Association codes" (ASTM, 2007).

Alcohol Control

The levels of unreacted alcohol remaining in the biodiesel must be controlled. This can be done in one of two ways: measuring the volume percent alcohol directly or through a high flash point value. The flash point varies indirectly with the fuel's volatility, which depends upon alcohol content. A flash point of the 100°C corresponds to 0.2 vol % alcohol standard. To ensure that the 0.2 vol % alcohol is met, ASTM specified a higher minimum flash point of 130°C.

Water and Sediment

These are primarily considered as post-production parameters. While excess water can be contained in the biodiesel after production, the fuel most commonly comes into contact with water and sediment during storage.

Sediment "may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation" (Van Gerpen et al., 2004). These sediments can cause fuel filter plugging problems.

Kinetic Viscosity

It is important to designate a minimum viscosity as there can be issues of power loss due to injection pump and injector leakage when fuels with low viscosity are used. Likewise, a maximum viscosity must be met for considerations involved in engine design, size, and characteristics of the injection system (ASTM, 2007). Because blended biodiesel/diesel fuel can exhibit relatively high viscosities, the maximum viscosity for biodiesel (6.0 mm^2/s at 40°C) is higher than the maximum for Grade 2-D and 2-D low sulfur.

Sulfated Ash

The ash content describes the amount of inorganic contaminants such as abrasive solids, soluble metallic soaps, and residual catalysts. These can contribute to injector, fuel pump, piston and ring wear, engine deposits, and filter plugging.

Sulfur

Limits have been placed on sulfur content for environmental reasons. B100 essentially contains no sulfur; the sulfur content in biodiesel blends is due to the diesel fuel. The limits for Grade S15 and Grade S500 indicate a limit of 15 ppm and 500 ppm of sulfur content, respectively. It is important to note that "other sulfur limits can apply in selected areas in the United States and in other countries" (ASTM, 2007). In California, sulfur content for diesel fuels 15 ppm or less.

Copper Strip Corrosion

This is a test to measure the presence of acids or sulfur-containing compounds in the fuel. A copper strip is immersed in the fuel to determine the level of corrosion that would occur if biodiesel came in contact with metals such as copper or brass.

Cetane Number (CN)

The cetane number (CN) is a primary indicator of the quality of biodiesel. It relates the ignition delay time of the fuel upon injection into the combustion chamber. The higher the CN, the shorter the ignition delay time; this suggests the fuel will exhibit a low idle noise and an easy cold start.

Cloud Point

This is an important property as it "defines the temperature at which a cloud or haze of crystals appears in the fuel… [and] relates to the temperature at which crystals begin to precipitate from the fuel" (ASTM, 2007). Petroleum based diesel fuel generally has a lower cloud point than biodiesel as it is not as susceptible to cold temperatures. There is currently no cloud point specification for biodiesel, although it does play a major role in cold weather operability.

Carbon Residue

Carbon residue is the "amount of carbonaceous material left after evaporation and pyrolysis of an oil." This is a measure of the carbon-depositing tendency of a fuel and is an approximation of the tendency for carbon deposits to form in an engine.

Acid Number

The level of FFAs within the biodiesel can be determined by the acid number; one unit of acid number corresponds to 0.503% FFAs. "Biodiesel with a high acid number has been shown to increase fueling system deposits and may increase the likelihood for corrosion" (ASTM, 2007).

Free Glycerin

Within the finished biodiesel, trace amounts of free glycerin can remain in small quantities as suspended droplets or dissolved into the fuel. If concentrations are high, the free glycerin can cause injector deposits and can clog fueling systems.

Total Glycerin

If the transesterification reaction is incomplete, excess triglycerides, diglycerides, and monoglycerides remain in the fuel. All three of these compounds still contain a glycerol molecule, referred to as a bound glycerin. The free glycerin and bound glycerin are summed together to describe the total glycerin within the biodiesel.

Phosphorus Content

With stricter emission controls, catalytic converters are becoming more common for diesel-powered equipment. Phosphorus content must be limited as it can cause great damage to catalytic converters.

Distillation Temperature

This specification is incorporated in the ASTM standards not because the boiling point of biodiesel is problematic, but rather as a "precaution to ensure the fuel has not been adulterated with high boiling contaminants" (ASTM, 2007).

Sodium and Potassium

While most of the excess catalyst is removed with the glycerol, some sodium and potassium may be present in the biodiesel as abrasive solids or soluble metallic soaps.

Oxidation Stability

Products of oxidation in biodiesel can cause fuel system malfunctions, deposits, and can lead to filter clogging. "Additives designed to retard the formation of acids and polymers can significantly improve the oxidation stability performance of biodiesel" (ASTM, 2007).

Free Fatty Acids (FFAs)

Free fatty acids are "any saturated or unsaturated monocarboxylic acids that occur naturally (as fats, oils or greases) but are not attached to glycerol backbones" (DOE, 2006). The greatest difference among feedstocks is the amount of free fatty acids associated with the triglycerides. The FFA content "affects the amount and extent of feedstock preparation necessary to use a particular reaction chemistry" (Van Gerpen et al., 2004).

Saturation

A fatty acid is saturated if it only contains single bonds. Unsaturated compounds can have double or triple bonds. (Discussed further in Section II, Part C).

11.2. Appendix B: Biodiesel Additive Chemicals

Figure B-1: Common Antioxidants

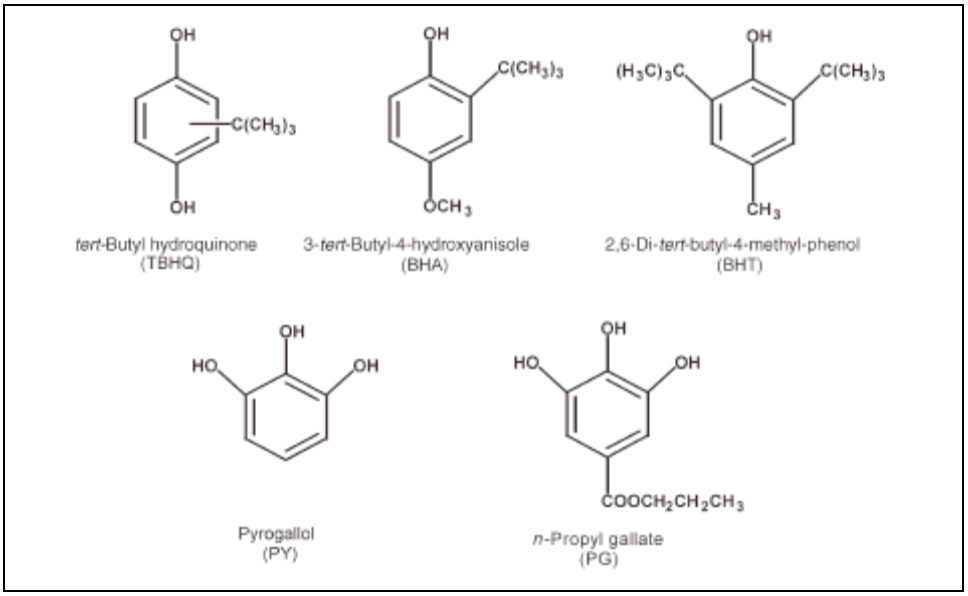
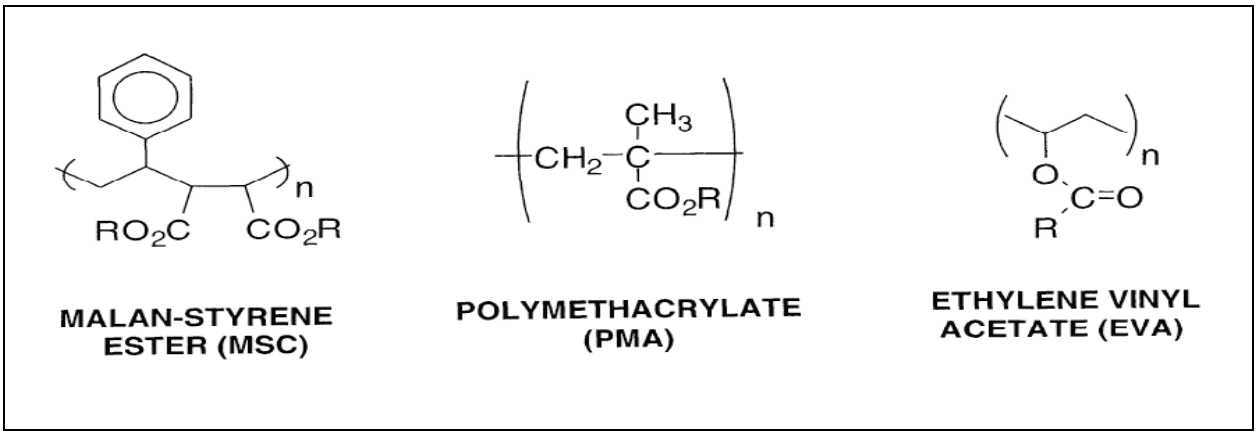


Table B-1. Commercial Biodiesel Antioxidants*

Manufacturer	Product Name	Chemical Components	%
Albemarle	Ethanox 4737	2,6 di-t-butylphenol 2,4,6 tri-tert butylphenol 2-tert-butylphenol Phenol Naptha Petroleum	52.5% 10.5% 7% 1.1% 25-30% 2%
Biofuel Systems	Baynox	2,6 di-tert-butyl-4-methylphenol	20%
Chemiphase	AllClear	Methyl Alcohol	18-24%
Eastman Chemical	Bioextend30	2-tert-butylhydroquinone Butyle acetate Diethylene glycol monobutyl ether	20% 30% 30%
Eastman Chemical	Tenox 21	Tertiary butylhydroquinone	20%
Lubrizol	8471U	Butylated phenol	70-79%

*Source: Company MSDSs and Product Data Sheets

Figure B-2. Lubrizol Corporation Cold Flow Additive Chemicals*



*Data from Chor et al. (2000). Lubrizol cold-flow additives are formulated for all diesel fuels and can be used with standard diesel and biodiesel formulations.

Table B-2. Commercial Cold Flow Additives*.

Manufacturer	Product Name	Chemical Components	%
Biofuel Systems	Wintron XC30	Toluene	2%
Chemiphase	Coldflow 350	Toluene	2%
Hammonds	ColdFlo	Vinyl copolymer in hydrocarbon solvent Naptha	N/A 40-70%
Lubrizol	FloZol502	Copolymer Ester Toluene	N/A 2%
Lubrizol	FlowZol503	Naptha Napthalene Trimetheyl Benzene Ethylbenzene Alkylphenol Xylene	40-49% 4.4% 1.4.9% 1.6% 5-9.9% 6.4%

*Source: Company MSDSs and Product Data Sheets

Table B-3. Commercial Biocides.

Manufacturer	Product Name	Chemical Components	%
Chemiphase	AllKlear, FilterClear	Sodium dodecyclbenzene sulfonate	2-32%
FPPF Chemical	Kill-Em	Disodium ethylenebisdithiocarbamate Sodium dimethyldithiocarbamate Ethylene thiourea	15% 15% 1%
Hammonds	Biobor JF	Naptha 2,2-(1-methyltrimethylenedioxy)bis-(4-methyl-1,3,2 dioxyborinane; 2,2,oxybis(4,4,6-trimethyl-1,3,2-dioxaborinane) [Substituted dioxaborinanes]	4.5% 95%
Power Serve Products	Bio-Kleen	4-(2-nitrobutyl)-morpholine 4,4, (2-ethyl-2-nitrotrimethylene)-dimorpholine Methylene dimorpholine Morpholine 1-Nitropropane	76-85% 2-7% 3.9-6.5% 3-6% .3-5.3%
Rohm and Haas	Kathon FP 1.5	Magnesium nitrate 5-chloro-2-methyl-4-isothiazol-3-one 2-methyl-4-isothiazol-3-one	1-2.5% 1-2.5% To 1 mix
Star Brite Corp	Biodiesel Biocide	Sodium dimethyldithiocarbamate Ethylenedimine Dimethylamine Ethylene thiourea Nabam	15-20.2% 0.0-0.75% 0.0-0.75 0-1.0% 15-20%

Table C-4. NOx Reduction.

Manufacturer	Product Name	Chemical Components	%
Clean Diesel Technologies	Aris2000 Injection system	Urea or Ammonia injected into exhaust	N/A
Oryxe	LED for biodiesel (and diesel)	2-ethylhexyl nitrate Toluene	45% w/w 45-55 w/w
Viscon USA	Viscon	Polyisobutylene (Polyalphaolefin) Polymer	5%

11.3. Appendix C: Biodiesel Web Links

Water Solubility

- Moisture Absorption in Biodiesel and its Petro-Diesel Blends. http://www.webpages.uidaho.edu/~bhe/pdfs/MC.pdf
- Determining the Influence of Contaminants of Biodiesel Properties (has specific section on water solubility). http://www.nbb.org/resources/reportsdatabase/reports/gen/19960731_gen014.pdf
- Moisture Distribution in Biodiesel and its Fossil Diesel Blends. http://asae.frymulti.com/request.asp?JID=5&AID=21513&CID=por2006&T=2

Toxicity

- Acute Oral Toxicity Study of 100% REE in Albino Rats. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19960110_gen-220.pdf
- Acute Dermal Toxicity Study of 100% REE in Albino Rats. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19960110_gen-229.pdf
- Eco-toxicological Studies of Diesel and Biodiesel Fuels in Aerated Soil. http://www.sciencedirect.com/science?_ob=MImg&_imagekey=B6VB5-4HS3C1J-7-C&_cdi=5917&_user=4421&_orig=search&_coverDate=08%2F31%2F2006&_sk=998579996&view=c&wchp=dGLbVlb-zSkzk&md5=25221a1dcb50d96ee2131ef572acc00f&ie=/sdarticle.pdf
- Inhalation Toxicology: Effects of Subchronic Inhalation Exposure of Rats to Emissions From a Diesel Engine Burning Soy-oil Derived Biodiesel Fuel. http://www.informaworld.com/smpp/content~content=a713857050
- Mutagenic and Cytotoxic Effects of Exhaust Particulate Matter of Biodiesel Compared to Fossil Diesel Fuel. http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6T2D-3TDR7MP-2&_user=4421&_coverDate=07%2F08%2F1998&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000059598&_version=1&_urlVersion=0&_userid=4421&md5=556346ff8d6a7443b14cb75173ea45dc

Aquatic Toxicity

- Degradation and Phytotoxicity of Biodiesel Oil. http://www.biodiesel.org/resources/reportsdatabase/reports/mar/19950801_mar-008.pdf

Air Quality and Human Health

- A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions, 2002. http://www.epa.gov/OMS/models/analysis/biodsl/p02001.pdf
- Impact of Biodiesel Fuels on Air Quality and Human Health: Summary Report Sept. 99 – Jan 2003. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20030501_gen-365.pdf
- Impact of Biodiesel Fuels on Air Quality and Human Health: Task 2. Impact of Biodiesel fuels on Ozone Concentrations. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20030501_gen-364.pdf
- Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine. http://www.nrel.gov/docs/fy03osti/31461.pdf (by NREL 2003)

- Effect of Biodiesel Composition on NO_x and PM from a DDC Series 60 Diesel Engine. http://www.biodiesel.com/images/emissions.pdf (by NREL 1999)
- Regulated Emissions from Biodiesel Tested in Heavy Duty Engines Meeting 2004 Emission Standards. http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/37508.pdf
- Impact of Biodiesel Fuels on Air Quality and Human Health: Task 5 Report. Air Toxic modeling of the effects of biodiesel fuel use on human health in the south coast air basin region of Southern California 2003. http://www.nrel.gov/docs/fy03osti/33798.pdf
- Impact of Biodiesel Fuel on Air Quality and Human Health: Task 4 Report. Impact of Biodiesel fuel use on PM 2003. http://www.nrel.gov/docs/fy03osti/33797.pdf
- Impact of Biodiesel Fuel on Air Quality and Human Health: Task 3 Report. Impact of Biodiesel Fuels on Ambient Carbon Monoxide Levels in the Las Vegas Nonattainment Area 2003. http://www.nrel.gov/docs/fy03osti/33796.pdf
- NO_x Solutions for Biodiesel. Final Report: Report 6 in Series of 6, 2003. http://www.nrel.gov/docs/fy03osti/31465.pdf
- Effects of Biodiesel Blends on Vehicle Emissions 2006. http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/40554.pdf
- Bioassay Analysis of Particulate Matter from a Diesel Bus Engine Using Various Biodiesel Feedstock Fuels. Report 3 in a series of 6. http://www.nrel.gov/docs/fy03osti/31463.pdf
- NO_x Reduction from Biodiesel Fuels. http://pubs.acs.org/cgi-bin/article.cgi/enfuem/2006/20/i01/pdf/ef050202m.pdf

Biodegradability

- Biodegradability of Biodiesel in the Aquatic Environment. http://www.canadianbioenergy.com/resources/Degradability_of_biodiesel_in_marine_environment.pdf
- Aerobic an Anaerobic Biodegradation of the Methyl Esterified Fatty Acids of Soy Diesel in Freshwater and Soil Environments. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19950101_gen-273.pdf
- Toxicity, Biodegradability, and Environmental Benefits of Biodiesel. http://www.biodiesel.org/resources/reportsdatabase/reports/mar/19940101_mar-002.pdf
- Biodegradability of Biodiesel fuel of Animal and Vegetable Origin. http://www3.interscience.wiley.com/cgi-bin/fulltext/114265170/PDFSTART
- The Effect of biodiesel on the rate of removal and weathering characteristics of crude oil within artificial sand columns. http://www.sciencedirect.com/science?_ob=MImg&_imagekey=B6VH4-3TB5W4J-3-1&_cdi=6056&_user=4421&_orig=search&_coverDate=12%2F31%2F1997&_sk=999959998&view=c&wchp=dGLzVlz-zSkWW&md5=d2bd2d70ff67724abadb0aac1f5407c6&ie=/sdarticle.pdf
- Biodegradability, BOD_5, COD, and Toxicity of Biodiesel Fuels. http://www.uidaho.edu/bioenergy/BiodieselEd/publication/04.pdf

Storage/ Stability

- Stability of Biodiesel: Used as a Fuel for Diesel Engines and Heating Systems. http://www.blt.bmlfuw.gv.at/BIOSTAB/download/BIOSTAB_Proceedings.pdf
- Stability of Biodiesel and Biodiesel Blends: Interim Report (by NREL 2006). http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/39721.pdf
- Quantification and Improvements of the long term storage stability of biodiesel and biodiesel blends. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19971201_gen-022.pdf
- Oxidation Stability of Fatty Acid Methyl Esters. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19980611_gen-160.pdf
- Determination of Biodiesel Oxidation and Thermal Stability. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19970212_gen-230.pdf
- Characterization of Biodiesel Oxidation and Oxidation Products, 2005. http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/39096.pdf
- Biodiesel Fuels: The Use of Soy Oil as a Blending Stock for Middle Distillate Petroleum Fuels (has section on storage). http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20000701_gen-289.pdf
- Degradation of Biodiesel Under Different Storage Conditions http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V24-4FWKM8F-2&_user=4421&_coverDate=01%2F31%2F2006&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000059598&_version=1&_urlVersion=0&_userid=4421&md5=7c2863e00abd845ca5cedf7bd8c48c4e
- The Effects of Fatty Acid Composition on Biodiesel Oxidative Stability. http://www3.interscience.wiley.com/cgi-bin/fulltext/109857530/PDFSTART

Compatibility

- Impact of Biodiesel on Fuel System Component Durability. http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/39130.pdf
- Elastomer Compatibility Testing of Renewable Diesel Fuels, 2005. http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/38834.pdf

Life Cycle

- An Overview of Biodiesel and Petroleum Diesel Life Cycles. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19980501-gen-203.pdf
- Biodiesel Energy Balance. http://www.uidaho.edu/bioenergy/NewsReleases/Biodiesel%20Energy%20Balance_v2a.pdf
- Energetic and Economic Feasibility Associated with the Production, Processing, and Conversion of Beef Tallow to a Sustainable Diesel Fuel. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20060601_gen373.pdf
- Exergy Analysis Applied to Biodiesel Production. http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6VDX-4MD469X-1&_user=4421&_coverDate=08%2F31%2F2007&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000059598&_version=1&_urlVersion=0&_userid=4421&md5=2ab63b26d47e3a484d69ee9302485ad6
- Environmental Impacts of Biodiesel Use. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19981001_gen-110.pdf

General

- Biodiesel Handbook. (An electronic copy of book that covers many of these topics above). http://www.chemlibnetbase.com/books/2240/1893997790_fm.pdf
- Biodiesel Analytical Methods (Aug. 2002- Jan. 2004). http://www.nrel.gov/docs/fy04osti/36240.pdf
- Business Management for Biodiesel Producers (Aug. 2002- Jan. 2004). http://www.nrel.gov/docs/fy04osti/36242.pdf
- Biodiesel Cold Weather Blending Study. http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/cftr_72805.pdf
- Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and biodiesel/Diesel Blends. Final Report: Report 1 in a series of 6, 2003. http://www.nrel.gov/docs/fy03osti/31460.pdf
- US Biodiesel Overview, 1995. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19950101_gen-263.pdf
- Environmental Effect of Rapeseed Oil Ethyl Ester. http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V4S-48YVSF4-5&_user=4421&_coverDate=12%2F31%2F2003&_fmt=full&_orig=search&_cdi=5766&view=c&_acct=C000059598&_version=1&_urlVersion=0&_userid=4421&md5=5bddf0f619d91e694ec64cbe8d42a29c&ref=full
- Assessing the Viability of Using Rape Methyl Ester (RME) As An Alternative to Mineral Diesel Fuel for Powering Road Vehicles in the UK (covers biodegradability and toxicity). http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V1T-3VCVKSK-7&_user=4421&_coverDate=02%2F28%2F1998&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000059598&_version=1&_urlVersion=0&_userid=4421&md5=d4fe0729bea53b522f1b97702683779e#toc16