Draft Final

California Renewable Diesel Multimedia Evaluation

Tier I
Report

Prepared

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For the

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Multimedia Working Group

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Background

Currently, the majority of biological-source diesel fuels are fatty-acid methyl esters (FAME) produced through transesterification, but there are rapidly emerging alternatives to the transesterification production of diesel biofuels. Renewable diesel (also referred to as co-processed diesel or "green" diesel) is considered an alternative fuel that has potential in California. Renewable diesel is similar to biodiesel in that both use similar feedstocks, but they have different processing methods and create chemically different products.

Renewable diesel is derived from non-petroleum renewable resources, including, (but not limited to) plant and algae oils, animal fats and wastes, municipal solid waste, sludge and oils derived from wastewater, and other wastes. We focus here on Hydrogenation-derived renewable diesel (HDRD). HDRD is produced by refining fats or vegetable oils—typically in existing oil refineries. This process is also known as the Fatty Acids to Hydrocarbon (Hydrotreatment) or FAHC Hydrotreatment process. In this process, renewable feedstocks such as vegetable oils and animal fats are converted into diesel fuel as well as propane, and other light hydrocarbons through treatment with hydrogen. Because it is free of ester compounds, renewable diesel has a chemical composition that is almost identical to petroleum-based diesel.

Preliminary evaluations indicate several potential advantages of renewable diesel relative to FAME and petroleum-based diesel. These advantages include:

- Renewable diesel can be used directly in today's diesel-powered vehicles without modification.
- Renewable diesel is compatible with current diesel distribution infrastructure and does not require new or modified pipelines, storage tanks, trucking infrastructure, or retail station pumps.
- Renewable diesel can be produced using existing oil refinery capacity and does not require extensive new production facilities.
- Renewable diesel's fuel properties, specifically its high cetane number, suggest it will provide similar or better vehicle performance than conventional ultra-low sulfur diesel (ULSD).
- Renewable's ultra-low sulfur content enables the use of advance emission control devices.
- The production of renewable diesel through the FAHC process does not produce a glycerin co-product.

Preliminary tests of renewable diesel emissions indicate that, relative to standard diesel, there is a potential for significantly better emissions profile during combustion with reduced particulate, NOx, hydrocarbons, and CO emissions. In addition to producing a fuel that uses recycled carbon, renewable diesel benefits include: a high level of quality control; compliance with ASTM standards; easy blending with biodiesel.

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". Because renewable diesel is a new fuel, the California Air Resources Board

(CARB) must provide a "multimedia risk assessment" before adopting new fuel specifications that allow renewable diesel blends.

This Tier I Renewable Diesel report is the first step in a three-tier process to evaluate the cumulative health and ecological impacts from releases to air, surface water, groundwater and soil at all stages of the renewable diesel life cycle: feedstock production, fuel production, storage and distribution, and fuel use. The risk posed by renewable diesel is assessed as a relative risk compared to the California Air Resources Board (CARB) ultra-low sulfur diesel (ULSD) currently in use. Throughout this report the term ULSD refers to CARB-ULSD.

Study Approach

The goal of this Tier I report is to identify what is currently known about the life-cycle health, ecological, and resource impacts of renewable diesel and identify key uncertainties and data gaps. It provides important input to the Multimedia Working Group with regard to the need for and scope of Tier II and Tier III studies for renewable diesel formulations.

Meeting this goal requires the following elements:

- Identifying the physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel, and additive components,
- Summarizing all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios,
- Summarizing the expected environmental behavior (transport and fate) associated with a portfolio of release scenarios for 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 and consensus control fuel or fuel components.

The purpose of a life-cycle assessment (LCA) applied to renewable diesel is to quantify and compare environmental flows of resources and pollutants (to and from the environment) associated with both renewable diesel and petroleum-based diesel, over the entire life cycle of the respective products. The flows of resources and pollutants provide framework for assessing human-health, environmental-systems and resource impacts. LCA addresses 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.

This report does not address 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.

Release Scenarios

Releases associated with the production, storage and distribution, and use of renewable diesel can be regarded as normal (routine) or off-normal (unplanned but not necessarily unlikely). Different feedstock supplies 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 releases during the use of renewable diesel include combustion tailpipe emissions, both to the air and to surface waters in the case of marine use. The specific magnitude of these normal production- and use-releases within California are not yet well characterized and will remain difficult to quantify until more process specific data become available and more engine/vehicle combustion tests are conducted.

There are a several companies planning to market renewable diesel in California and elsewhere, but they have different production and marketing plans. A key issue for release scenarios upstream from the combustion stage is whether blending renewable diesel stock will occur at the refinery or at a distribution facility.

Normal or routine releases during the production of renewable diesel include:

- Hexane or CO_2 released to the air during seed extraction,
- Odors associated with waste biomass, and
- Used process water discharges of various pH and trace-chemical composition.

Normal releases during the use of renewable diesel include combustion tailpipe emissions, both to the air and to surface waters in the case of marine use. The specific magnitude of these normal production- and use-releases within California are not yet well characterized and will remain difficult to quantify until more process specific data become available and more engine/vehicle combustion tests are conducted.

Off-normal releases or unanticipated releases can occur primarily during the production, distribution and storage of renewable diesel. Off-normal releases may include spills or leaks of bulk feedstock, production chemicals, such as hexane or blending stocks such as ULSD, or finished renewable diesel 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, or
- a bulk-fuel transport pipeline.

For a company that plans to produce 100% renewable diesel and then blend it with conventional diesel post-production, and possibly at some location remote from the production facility, the release scenarios are different from a company that plans to co-process “green” plant or animal oil with conventional crude oil. In the former case, storage and transport of 100% renewable diesel must be considered in terms of how it differs from experience with conventional and ULSD diesel. Some questions that arise:

- Can it be transported via pipelines?
- What are the spill consequences for 100% renewable diesel compared to CARB-ULSD?

Renewable Diesel Production, Storage, Distribution and Use

In contrast to a biodiesel that contains mono-alkyl esters, the California Low Carbon Fuel Standard defines a “renewable diesel” fuel as:

> *“... a motor vehicle fuel or fuel additive which is all the following:*
> *(A) Registered as a motor vehicle fuel or fuel additive under 40 CFR part 79; A-9*
> *(B) Not a mono-alkyl ester;*
> *(C) Intended for use in engines that are designed to run on conventional diesel fuel; and*
> *(D) Derived from nonpetroleum renewable resources.”*

Renewable diesel, produced from a variety of renewable feedstocks, is not composed of esters and is composed chemically of saturated hydrocarbon chains similar to conventional petroleum. The renewable production process is designed to take advantage of the infrastructure of an existing refinery. Several of the renewable diesel products currently available meet the ASTM standard for conventional diesel. As part of the US Renewable Fuel Standard, US EPA reported that renewable diesel has a slightly higher energy content compared to biodiesel.

There are two chemical approaches to producing renewable diesel and an emerging approach based on synthesis of hydrocarbons through enzymatic reactions. One chemical approach is based on hydrotreating vegetable oils or animal fats. Hydrotreating can take place in the same facilities used to process petroleum-based diesel. The second method involves partially combusting a biomass source to produce carbon monoxide and hydrogen—syngas—and then utilizing the Fischer-Tropsch reaction to produce complex hydrocarbons. Although some operations are in the planning stages, there are currently no formal efforts to engage the Fischer-Tropsch process in California. California Air Resources Board staff have requested that this report focus on the impacts of hydrotreated renewable diesel (HDRD/FAHC) produced in existing refineries. Hydrotreating is a hydrodeoxygenation process used to remove oxygen and nitrogen containing compounds as well as metals from the fuel feedstock.

There are two general production strategies for HDRD production and distribution:

- Co-processing vegetable/animal triglycerides in a conventional petroleum production stream using a hydrotreating process. Currently this results in diesel fuel that has a specified percentage of “green-derived” carbon, e.g., 20% renewable diesel (R20).
- Production of a pure HDRD (R100) in a dedicated hydrotreating facility that does not use conventional petroleum. The resulting fuel can be used as a 100% green fuel or blended with conventional ULSD to any concentration.

Soybeans are expected to be the main feedstock for renewable diesel in California. Oil is extracted from soy by crushing the beans and applying n-hexane as a solvent. Soy-based renewable diesel is sufficiently similar in physical-chemical properties to ULSD that it can be readily used in a range of blending applications.

Palm used to produce palm oil are grown primarily in tropical or subtropical areas such as Malaysia and Indonesia. Palm oil 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.

Canola and Rapeseed oils show promise as renewable diesel feedstock. These oils have properties similar to soy oil. The oil yield of canola, however, is much higher than soy; the seed contains 45% oil.

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. Vegetable oil waste grease and brown trap grease can also be used to make renewable diesel.

Petroleum-based diesel fuels 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 fuels primarily by their boiling point ranges, and chemical additives.

Renewable diesel is required to meet the same ASTM standards as conventional diesel and is composed of saturated hydrocarbons similar to conventional diesel along with performance and stability additives. The ASTM Standard Specification for Diesel Fuel Oils, when met, allows renewable diesel to be suitable for a variety of diesel engines.

The USEPA specifications for conventional diesel fuel include the requirement for additives. The required additives are:

- Corrosion Inhibitor,
- Demulsifier,
- Anti-oxidant, and
- Metal deactivator.

Chemical additives are commercially available to address the oxidative stability, cold-flow properties, and microbial contamination of renewable diesel. It is expected that these additives would be the same as or very similar to additives currently in use for conventional diesel fuel.

In general, the handling and storage of renewable diesel that meets ASTM 975 standards is the same as for petroleum diesel including the needed protection from ignition sources. Tanks used for transport and storage must be suitable for combustible liquids and precautions must be taken to prevent product spills on to the ground, into drains, and into surface and ground waters. In the evaluation of the multimedia impacts of new diesel formulations, material compatibility and storage stability are important considerations, but little information is available on pure renewable diesel materials compatibility.

Blended HDRD can be transported via the same methods used for conventional diesel, including pipelines, rail cars, tank trucks and drums. The choice of transport vessel depends on the quantity of renewable diesel being transferred and the cold flow properties of the fuel. It is straight forward technically to blend pure HDRD fuels (R100) with conventional diesel. R100 can be blended to as much as 65 – 70 volume % in conventional diesel to fulfill the minimum density requirement.

A key consideration in this Tier I review is how the levels of criteria and hazardous air pollutants emitted during combustion differ from those emitted from and energy-equivalent quantity of renewable diesel verses ULSD.

While emissions testing is ongoing, initial studies concluded that in diesel engines:

- HDRD fuel showed significant emission benefits compared to ultra-low sulfur conventional diesel fuel. Higher blend percentages resulted in greater benefits.
- Blends below 10% renewable diesel can result in reductions in CO and HC, but not PM or NOx.
- While specific (density adjusted) fuel consumption is better with the HDRD relative to ULSD, volumetric fuel consumption is 5% higher because of the lower HDRD density.
- HDRD fuels avoid some of the unwanted effects associated with FAME-based biodiesel fuels (instability, hygroscopicity, fouling, catalyst deactivation, etc).

- Due to the absence of sulfur and aromatic compounds, NExBTL exhaust emissions show significant reductions in many regulated and non-regulated compounds compared to "traditional" petroleum diesel.

Renewable Diesel Toxicity

The greatest difficulty we anticipate with determining the human and ecological toxicity of renewable diesel fuels is that renewable diesel fuel is not a defined chemical formulation or a defined mixture of components, but can be formulated from a number of different feedstocks with different chemical components.

Limited tests on the inherent acute oral and dermal toxicity of pure renewable diesel indicate that renewable diesel has a very low inherent toxicity, but these tests are difficult to interpret since there were no controls using conventional diesel or tests using diesel blend.

There have been some initial mutagenic testing of pure renewable diesel using reverse mutation assay (Ames Test) and the chromosome aberration test using human lymphocytes in vitro were conducted using pure renewable diesel. In the Ames test, no significant increases in the frequency of revertant colonies were recorded for any dose, either with or without metabolic activation. In the human lymphocyte test, the pure renewable diesel was considered to be non-clastogenic to human lymphocytes in vitro.

Insight on aquatic toxicity comes from acute short-term exposure of fish, water flea, and green alga to a pure renewable diesel water accommodated fraction. This study concluded that the No Observed Effect Loading rate was greater than 100 mg/L for all three species.

There has as yet been no comprehensive testing of the relative toxicity of the emissions from combusting renewable diesel (blends and/or pure fuel) compared to existing diesel and/or biodiesel. Based on the level of variation in emissions toxicity assessment for petroleum diesel, the chemical similarity of renewable diesel and petroleum diesel, and the likelihood for blends that still contain a significant fraction of petroleum diesel, we expect that it will be difficult of not impossible to organize and interpret a study to compare the toxicity of petroleum diesel relative to renewable diesel blends. Therefore, unless the market evolves to the point where renewable blends contain more than 50% non-petroleum diesel feedstock, there appears to be little value in calling for emissions toxicity studies for renewable diesel.

Major differences in health and ecological impact between existing diesel and renewable diesel blends are more likely to be associated with additives than with the hydrocarbon mix. So the key issue with regard to different life-cycle health/ecological impacts from existing diesel blends and renewable diesel blends will likely be linked to differences in additives.

Additionally, the chemical comparison to conventional diesel is important for determining whether or how much additional toxicity tests are required. If a co-processed "green" renewable diesel is the intended product and is chemically indistinguishable from conventional diesel, then no additional toxicity testing should be conducted. Further, if a post-production 100% pure renewable diesel is blended to a proportion such that it is chemically indistinguishable from conventional diesel, then no additional toxicity testing should be required in this case as well.

Transport and Fate

The multimedia working group will determine whether there is a need for a Tier III study with a detailed transport and fate assessment for renewable diesel. The fate and transport of a fuel and its component chemicals in the environment depend on the multimedia transport properties of its constituent chemicals. The purpose of the multimedia evaluation of renewable diesel is to identify impacts that may be different from the existing baseline fuel, conventional petroleum-based CARB-ULSD in the case of renewable diesel. Based on the fuel chemical composition analysis provided by both KOR and Neste Oil Corp., renewable diesel can be regarded as substantially similar to other conventional diesel fuels. The main difference between conventional ULSD and pure HDRD is that the pure renewable diesel has no sulfur or oxygen and has a very low aromatic compound content. Co-processed 20% renewable diesel can be expected to be even closer in chemical composition to conventional ULSD.

Based on the reported similarities in chemical composition, and thus the physicochemical properties governing fate and transport in the environment, between renewable diesel and conventional ULSD, the multimedia environmental behavior of renewable diesel should also be expected to be similar. The transport and partitioning behavior, as well as biodegradation in soils can be expected to be similar. The release scenarios and materials compatibility issues should be essentially the same as conventional diesel that is already in wide use.

Even when releases of renewable diesel would not cause significantly greater impacts to the environment, human health, or water resources when compared to ULSD, the impact from releases of associated additives and production chemicals can be of concern. The specific chemical composition of the additives used by various renewable diesel manufactures is not specified and the environmental impact of these additives is not well described.

In the case of co-processed 20% renewable diesel, it may be expected that any additive used in renewable diesel is currently in use in CARB-ULSD and would continue to be used with no substantive difference in environmental impact due to additives. If this is the case, then new studies on multimedia transport and impact from additives would not be necessary under the assumption that the impacts of additives in ULSD are either acceptable or at lease well-characterized. However, when the additives used in renewable diesel are different from those in ULSD with regard to composition and/or quantity, then a multimedia transport and impact assessment will be needed to determine the magnitude and significance of these additives.

Tier I Conclusions

Through a review of the current knowledge on renewable diesel production, use, and environmental impacts, this report provides a foundation to aid the CalEPA Multimedia Working Group formulate recommendations to the California Environmental Policy Council regarding the consequences of increased use of renewable diesel in California. A key goal of this report is to identify any important knowledge gaps for a Multimedia Assessment and recommend approaches to address these gaps. This does not always involve additional experiments, but could include additional requests for information from the proponents of any new fuel to be used in California.

Renewable diesel offers several beneficial characteristics that will help California meet State renewable fuel goals:

- Renewable diesel is chemically similar to the ultra-low sulfur diesel (ULSD) fuel already in wide use in California and environmental releases from the life-cycle of these fuels can be expected to behave in the environment in a manner similar to ULSD releases.
- Renewable diesel is compatible with existing refining and distribution infrastructure and can be used in current diesel engines without modification.
- Pure renewable diesel has reduced aromatic hydrocarbon content and, since many of the chemicals of environmental concern are aromatic hydrocarbons, this reduction will likely reduce the overall environmental toxicity of the fuel.
- Limited toxicity testing on rats (oral and dermal exposures), water fleas and green algae, and including mutagenic assays, reveals that pure 100% renewable diesel has limited inherent toxicity and that pure renewable diesel formations are unlikely to exceed the inherent toxicity or mutagenicity of standard diesel. Major differences in health and ecological impact between existing diesel and renewable diesel blends are more likely to be associated with additives than with the hydrocarbon mix.
- Renewable diesel fuels that are made from waste products such as tallow will likely have reduced life cycle environmental impacts compared to fuels made from plant crops. These reduced impacts stem from possible reductions in pesticide, herbicide, and fertilizer use. Further, the use of food supply crops as a fuel is not likely sustainable as global population grows. Further studies are needed to substantiate this logic.
- The results indicate that life-cycle health impacts of renewable diesel blends are not likely to differ significantly from those of petroleum diesel.

On the other hand, the knowledge gaps associated with renewable diesel use in California include:

- **Additives impacts.** The most important information gaps are associated with possible differences in additive use. To provide a stable, useful, and reliable fuel, additive chemicals will need to be introduced into almost all renewable diesel blends. These additives will be required to address issues such as oxidation, corrosion, foaming, cold temperature flow properties, biodegradation, water separation, and NO_x formation. While many of these additives are already used in conventional diesel fuels currently in use, the specific chemicals and amounts to be used in renewable by various producers has not been well defined for the emerging industry in California.

  It is important to note that although the use of additives in diesel fuels (conventional or renewable) is common, the impact of various additives is not well known. A careful evaluation of the possible chemicals used in additives would be beneficial to California and may lead to a "recommended list" or "acceptable list" that would minimize the uncertainty of future impacts as new fuels and industry standards are developed. Additional research on the impacts of a "recommended list" of acceptable additives needs to be considered with respect to releases to water and soils and fugitive emissions to air.
- **Production and storage releases.** Increased renewable diesel 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 process chemicals. There is also the issue of occupational exposures.

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. 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.

As the volume of tallow that is rendered out of state and shipped by rail or truck into California increases, there is a potential impact from releases of large volumes of raw triglycerides to soils or water. The impact of such a release is not well known and additional research would be beneficial as large-scale tallow usage increases.

- **Air Emissions Toxicity Testing.** While there has been air emission toxicity using pure renewable diesel, these studies did not directly compare results to a baseline diesel fuel. Based on the level of variation in emissions toxicity assessment for petroleum diesel, the chemical similarity of renewable diesel and petroleum diesel, and the likelihood for blends that still contain a significant fraction (80%) of petroleum diesel, we expect that it will be difficult, if not impossible, to organize and interpret a study to compare the toxicity of petroleum diesel relative to 20% renewable diesel blends. Therefore, unless there market evolves to the point where renewable blends contain more than 50% non-petroleum diesel feedstock, there appears to be little value in calling for emissions toxicity studies for renewable diesel.
- **Priority list of renewable diesel fuel 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 that may require evaluation, it is critical to identify the priority feedstocks, fuel blends, and additives requiring study for any additional 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 renewable and biofuels industry expands. More sustainable sources of renewable diesel such as yellow or brown grease or tallow may be preferable and should be encouraged.

During this review, we discovered that there are strong similarities between the chemical composition of petroleum diesel and renewable diesel. These similarities and the likelihood that renewable diesel will be used as a blend with petroleum diesel limits the need for additional Tier II Multimedia experiments or an extensive life-cycle impact assessment.

A key goal of this report is to identify important knowledge gaps for a Multimedia Assessment and recommend approaches to address these gaps. This does not always involve additional experiments, but could include additional requests for information from the proponents of any new fuel to be used in California.

As part of the overall multimedia assessment, each company proposing to market renewable diesel within California should provide the California ARB with a production, blending, additives, and distribution strategy that includes potential volumes to be stored and transported along with potential release scenarios that the company may foresee. Each company should also provide a comparative chemical analysis of the product they intend to market (blend or other wise). This analysis should be compared to conventional diesel currently in the market place.

1. Renewable Diesel Background Information

1.1. Introduction

This multimedia assessment provides the State of California information that will support decisions about the relative impacts posed by renewable diesel to the State's resources, human health, and environment. "Renewable diesel" and "biodiesel" 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.

Currently, the majority of biological-source diesel fuels are fatty-acid methyl esters (FAME) produced through transesterification, but there are rapidly emerging alternatives to the transesterification production of diesel biofuels. Renewable diesel (also referred to as co-processed diesel or "green" diesel) is considered an alternative fuel that has potential in California. Renewable diesel is similar to biodiesel in that both use similar feedstocks, but they have different processing methods and create chemically different products (**Figure 1.1**).

Renewable diesel is derived from non-petroleum renewable resources, including, (but not limited to) plant and algae oils, animal fats and wastes, municipal solid waste, sludge and oils derived from wastewater, and other wastes. Hydrogenation-derived renewable diesel (HDRD) is produced by refining fats or vegetable oils—typically in existing oil refineries. This process is also known as the Fatty Acids to Hydrocarbon (Hydrotreatment) or FAHC Hydrotreatment process. In this process, renewable feedstocks such as vegetable oils and animal fats are converted into diesel fuel as well as propane, and other light hydrocarbons through catalytic treatment with hydrogen (Hilber et al., 2007; Knothe, 2010). Because it is free of ester compounds, renewable diesel has a chemical composition that is almost identical to petroleum-based diesel (CEC, 2007).

Preliminary evaluations (CEC, 2007; U.S. DOE, 2010) indicate several potential advantages of renewable diesel relative to FAME and petroleum-based diesel. These advantages include:

- Renewable diesel can be used directly in today's diesel-powered vehicles without modification.
- Renewable diesel is compatible with current diesel distribution infrastructure and does not require new or modified pipelines, storage tanks, trucking infrastructure, or retail station pumps.
- Renewable diesel can be produced using existing oil refinery capacity and does not require extensive new production facilities.
- Renewable diesel's fuel properties, specifically its high cetane number, suggest it will provide similar or better vehicle performance than conventional ultra-low sulfur diesel (ULSD).
- Renewable diesel's ultra-low sulfur content enables the use of advance emission control devices.
- The production of renewable diesel through the FAHC process does not produce a glycerin co-product.

In addition to producing a fuel that uses recycled carbon, renewable diesel benefits include: a high level of quality control; compliance with ASTM D975, Standard Property Descriptions for Diesel Fuel Oils (Appendix A); easy blending with FAME biodiesel.

Preliminary tests of renewable diesel emissions indicate that, relative to standard diesel, there is a potential for significantly better emissions profile during combustion with reduced particulate, NOx, hydrocarbons, and CO emissions (Rothe et al, 2005; Kaufman, 2007). Emissions testing for US EPA Tier 1 requirements released by Kern Oil and Refining Co. (Fanick, 2009) report total hydrocarbon, total particulate, carbon monoxide, and NOx emissions that satisfy the requirements for ASTM D975. Analogous testing by Neste Oil Co. (Fanick, 2008) reported reduced emissions of these compounds in comparison of the NExBTL renewable diesel product with European sulfur-free EN590 grade diesel (Fanick, 2008). Disadvantages include less desirable cold flow properties and the need for a lubricity additive.

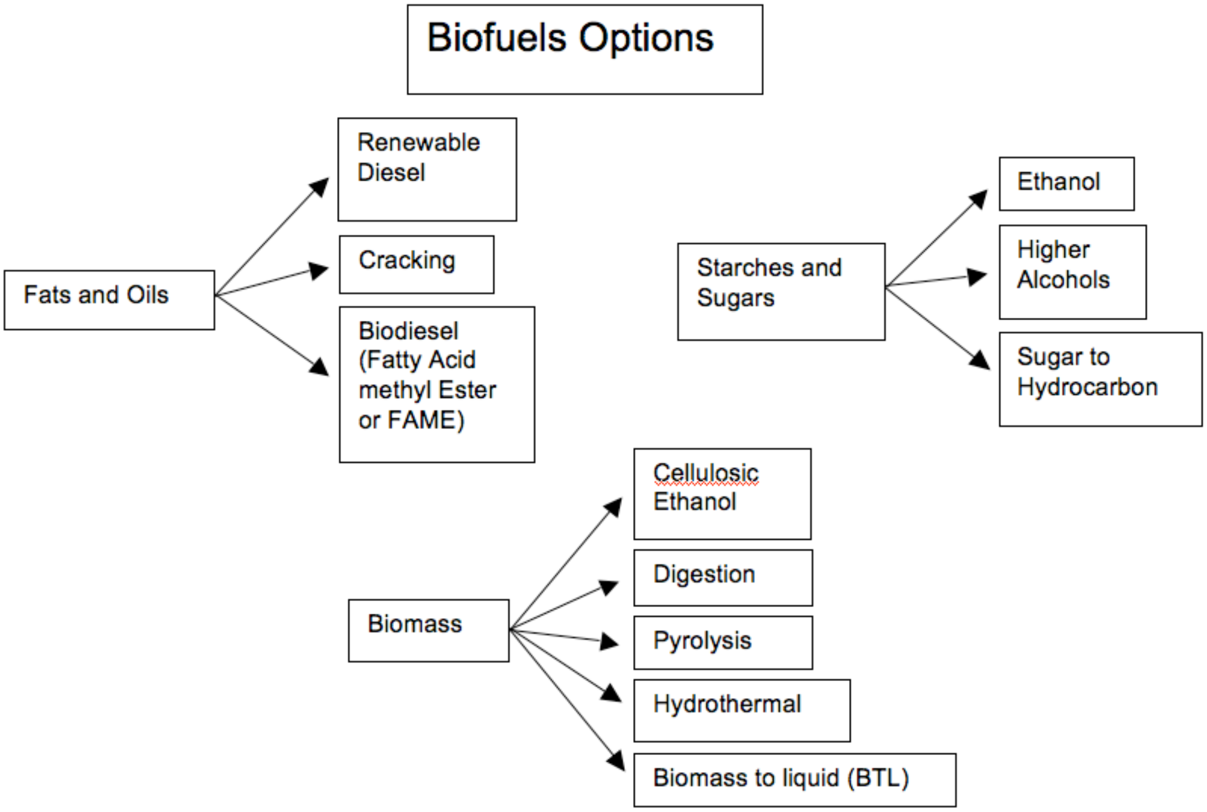


Figure 1.1. Summary of biofuel options.

Because renewable diesel is an existing fuel produced by a new process, the California Air Resources Board (CARB) must provide a "multimedia risk assessment" before adopting new fuel specifications that allow renewable diesel blends (as required by California Health and Safety Code, Section 43830.8). In addition, 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).

This Tier I Renewable Diesel report is the first step in a potential three-tier process to evaluate the cumulative health and ecological impacts from releases to air, surface water, groundwater and soil at all stages of the renewable diesel life cycle: feedstock production, fuel production, storage and distribution, and fuel use. The risk posed by renewable diesel is assessed as a relative risk compared to the ultra-low sulfur diesel (ULSD) currently in use.

The goal of this Tier I report is to identify what is currently known about the life-cycle health, ecological, and resource impacts of renewable diesel and identify key uncertainties and data gaps. Meeting this goal requires the following elements:

- Identifying the physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel, and additive components,
- Summarizing all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios,
- Summarizing the expected environmental behavior (transport and fate) associated with a portfolio of release scenarios for 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 and consensus control fuel or fuel components.

This report does not address 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. These issues arise from a scientific debate concerning the sustainability of wide-scale energy conversion from fossil fuels to biofuels (Wang and Haq, 2008, NRC, 2009). Some researchers have suggested that the demand for biomass feedstocks will result in the clearing of virgin rainforests and grasslands and that this clearing with result in high initial "carbon debts" 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). Such issues have led 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 and other land-use conversions (Clark 2008). It is clear that the issue of sustainability and a more complete life cycle impact assessment of biofuels are important aspects of the decision to expand biofuels use. However such evaluations are beyond the scope of the multimedia working group, which is mandated to focus on the human health, ecological, and resource risks associated with the production, transportation, storage, and use of biofuels and not the broader impacts of increased/decreased use of various raw feedstocks. Because the life-cycle carbon impact of alternative fuels are addressed in the working reports of the California Low-Carbon Fuels Standard (LCFS) Program, only the issues not explicitly addressed in the LCFS--health, ecological, and resource impacts--are the primary objectives of this report.

This Tier I report sets the stage for determining the need for and level of detail needed in any subsequent Tier II and Tier III multimedia assessments. The process follows the guidance set forth in the report "Guidance Document and Recommendations on the Types of Scientific Information to be Submitted by Applicants for California Fuels Environmental Multimedia Evaluations" (CalEPA, 2008).

During any Tier II activities, Cal-EPA together with its collaborators at the University of California will evaluate critical uncertainties and data gaps identified during Tier I evaluations and propose any action needed to address potential life-cycle impacts renewable diesel may have to the State's resources, human health and environment. During Tier III activities, potential life cycle impacts are compared to the selected baseline fuel and the results and conclusions are reported to California Environmental Policy Council. **Figure 1.2** provides an overview of the life-cycle stages that we address in this report. We consider four major life stages—feedstock production/collection, renewable diesel production, transport and storage, and fuel use (combustion).

The Multimedia Working Group has already issues a Tier I multimedia assessment for FAME biodiesel, produced through a transesterification process. In addition the Tier II and Tier III reports for FAME biodiesel are in process (CARB, 2009).

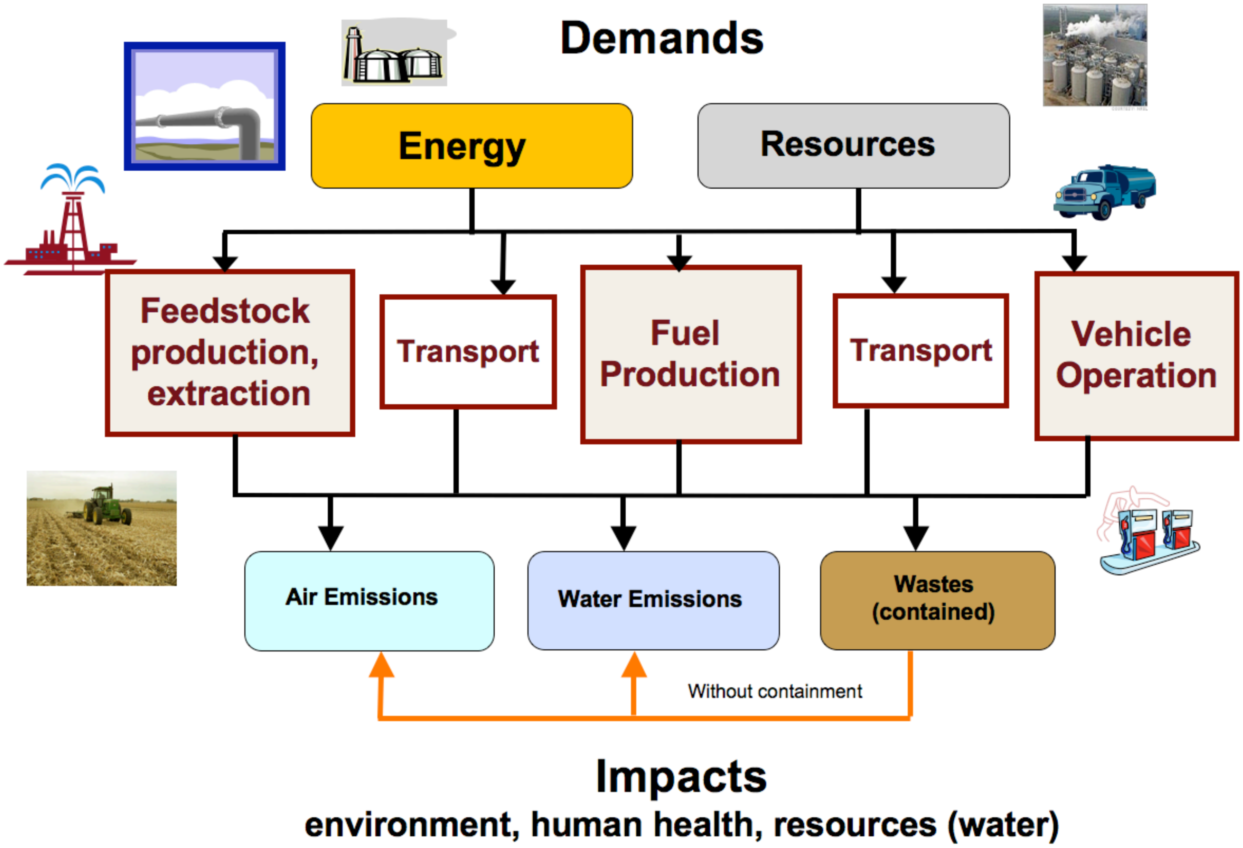


Figure 1.2. Generalized summary of renewable diesel life cycle impacts.

1.2. History

Raw vegetable and animal oils contain an abundance of triglycerides that have value as feed stocks to produce motor vehicle fuels. Although these oils can be used directly in diesel engines and provide reliable short-term performance, engine manufacturers discourage this practice because it can cause severe engine problems in the long term (US EPAa, 2010). This is primarily due to the raw oils forming engine deposits as well as coking and plugging in engine injector nozzles, piston rings, and lubricating oil. This happens due to polymerization of the triglycerides in the raw oils as the fuel is combusted. To prevent these problems, it is necessary to convert the raw oils into a more appropriate form of biomass-based diesel fuel—either esters or hydrocarbons. It has been known for a number of years that triglycerides can be hydrogenated into linear alkanes in a refinery hydrotreating unit with the presence of conventional sulfated hydrodesulphurization catalysts (Donnis et al., 2009). This process is referred to here as the Fatty Acids to Hydrocarbon Hydrotreatment (FAHC-Hydrotreatment) process.

Hydrogenation-derived renewable diesel (HDRD) processes have been used at fossil fuel refineries since the 1950s (Donnis et al., 2009) to remove impurities and to produce higher quality oil. The first work on hydroprocessing of bio-oils was by Nunes (1984), who described a reaction of soy oil with hydrogen over silica- and alumina-supported catalysts. During the 1980s Elliot and others successfully hydrotreated pyrolysis-derived oils at Pacific Northwest National Laboratories (PNNL) (Elliot and Baker, 1988). Research at PNNL and NREL has lead to contemporary commercial development of the process by Neste, UOP, and Conoco-Phillips (Elliot, 2007).

A number of manufacturers around the world are developing HDRD refining processes and testing them in commercial trials. The following paragraphs provide brief descriptions of some of the projects (US DOE, 2010):

ConocoPhillips (United States, Ireland)

Conoco Phillips has been producing HDRD at its Whitegate refinery in Cork, Ireland since 2006. The primary renewable feedstock is soybean oil, but other vegetable oils and animal fats could be used as well. The HDRD is being produced using existing refinery equipment and is blended and transported with petroleum-based diesel. Initial production has been 1,000 barrels per day. ConocoPhillips has also partnered with Tyson Foods to produce HDRD using animal fat, beginning in 2007 projections for ramping up to as much as 11,000 barrels per day for 2009. But these plans have been delayed. Currently the tallow used to make renewable diesel is commonly used to make cosmetics, soaps, candles, and some pet food.

Neste Oil (Finland)

Neste Oil has been producing pure HDRD using its NExBTL process at its Porvoo refinery in Kilpilahti, Finland since 2007. A second plant was added to the Porvoo refinery in 2009, for a total production capacity of 340,000 metric tons per year at this facility. US EPA registration and toxicity and biodegradability testing has been submitted. Neste Oil is 50% owned by the Finnish government.

Petrobras (Brazil, Portugal)

Brazilian oil company Petrobras developed the H-Bio process, which produces HDRD using hydrotreating units in existing oil refineries. Petrobras had employed the H-BIO process in three of its refineries by 2007 with plans for more facilities to reach a total vegetable oil consumption of more than 7,000 barrels per day. More recently, Petrobras has announced plans in partnership with Galp Energia to develop production facilities in Portugal for up to 250,000 tons (~1.8 million barrels) of biodiesel per year, from Brazilian palm feedstocks, by 2018.

Dynamic Fuels (Syntroleum/Tyson) (United States)

Syntroleum formed a joint venture with Tyson Foods to produce HDRD and jet fuel using its Biofining process. Production from its first plant was scheduled to come online in 2010 at a rate of about 5,000 barrels of synthetic fuel per day.

UOP-Eni (United States, Italy)

UOP-Eni is an American (UOP LLC, a Honeywell company) and Italian oil and gas company (Eni) project supported by the U.S. Department of Energy (DOE) to build a commercial scale facility at Eni's Livorno, Italy refinery. The U.S. Department of Energy has supported UOP's Renewable Energy and Chemicals unit in developing HDRD production technologies. The first "Ecofining" facility developed by UOP and Eni was scheduled to come online in 2009, processing 6,500 barrels per day of vegetable oils.

Other companies that have plans to produce renewable diesel through hydrogenation include Nippon Oil in Japan, BP in Australia (co-processed R5), Syntroleum and Tyson Foods in the U.S. The Nippon Oil plant expects to be operating commercially in three years. The BP plant is planned to have a demonstrated capacity of 1,900 barrels per day.

UOP, NesteOil, LiveFuels, and Sapphire Energy each independently introduced "green crude" or biocrude from algae as a petroleum substitute.

1.3. Legislative Incentives for Biofuels

Over the last decade, there have been a number of state and federal mandates to encourage the development and use of a broad range of biofuels. To reduce our nation's dependence on imported oil, Congress passed the Energy Policy Act of 1992 (EPAct). The Energy Conservation and Reauthorization Act of 1998 amended and updated many elements of the 1992 EPAct. The 1998 amendment allowed "qualified fleets to use B20 in existing vehicles to generate alternative fuel vehicle purchase credits, with some limitations". This amendment significantly increased the use of B20 by government and alternative-fuel-provider fleets.

The Energy Policy Act of 2005 and the Energy Independence and Security Act of 2007 (EISA) provide tax incentives and research funds for biofuels. The Energy Policy Act of 2005 was signed into law in August 2005. This legislation supports the growth of the biodiesel and renewable diesel industry. Consumer and business federal tax credits for biofuels were extended to 2008 and the credits were provided to small agri-biofuel 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).

The Renewable Fuels Standards (RFS) program was created under the EPAct of 2005, and established the first renewable fuel volume mandate in the United States. As required under EPAct, the original RFS program (RFS1) required 7.5 billion gallons of renewable fuel to be blended into gasoline by 2012 (US EPA, 2010c,d). This Act requires 75% of new vehicle purchases made by federal governments, state governments, and alternative fuel providers must be alternative fuel-vehicles. Compliance was mandatory for the agencies that operated, leased, or controlled 50 or more lightweight vehicles. The alternative fuels on which these vehicles could run included: pure biodiesel (B100), renewable diesel blends or biodiesel blends, blends of 85% or more of ethanol with gasoline (E85), natural gas and liquid fuels domestically produced from natural gas, hydrogen, electricity, coal-derived liquid fuels, and liquefied petroleum gas (CEC, 2007).

Under the Energy Independence and Security Act (EISA) of 2007, the RFS program was expanded in several key ways:

- EISA expanded the RFS program to include diesel, in addition to gasoline;
- EISA increased the volume of renewable fuel required to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022;
- EISA established new categories of renewable fuel, and set separate volume requirements for each one.
- EISA required EPA to apply lifecycle greenhouse gas performance threshold standards to ensure that each category of renewable fuel emits fewer greenhouse gases than the petroleum fuel it replaces.

RFS2 lays the foundation for achieving significant reductions of greenhouse gas emissions from the use of renewable fuels, for reducing imported petroleum, and encouraging the development and expansion of our nation's renewable fuels sector (US EPA 2010c,d). While most of the focus to date has been on FAME biodiesel (B100, B20) and ethanol, there is increased interest on HDRD renewable diesel (R100, R20) because of its infrastructure and performance advantages.

In 2006, Governor Arnold Schwarzenegger signed the California Global Warming Solutions Act, requiring reductions in greenhouse gas (GHG) emissions by 2020 down to 1990 levels (California Office of the Governor, 2006; Young, 2008). It is the responsibility of the California Air Resources Board (CARB) to determine the technologically and economically feasible methods of achieving these goals. The first goal of the agency was to quantify 1990 emissions levels, and create a framework for reporting emissions from industrial sources. The emissions goal was set at "427 million metric tons of carbon dioxide equivalents" in December 2008 and to be achieved by 2020. In June 2008, CARB released a scoping plan to "reduce overall carbon emissions in California, improve our environment, reduce our dependence on oil, diversify our energy sources, save energy, and enhance public health while creating new jobs and enhancing the growth in California's economy" (CARB, 2008). Goals include strengthening energy efficiency programs, increasing electricity production from renewable sources and approving new fuels meeting the California Low Carbon Fuel Standard (LCFS). The LCFS resulted from Executive Order S-1-07, with the goal of reducing transportation-based emissions. On April 23, 2009, the Air Resources Board approved the specific rules and carbon intensity reference values for the LCFS that will go into effect on January 1, 2011. The Board approved the technical proposal without modifications by a 9-1 vote. This technical proposal sets the 2020 maximum carbon intensity reference value for gasoline to 86 g of carbon dioxide equivalent released per MJ of energy produced. The regulation is based on an average declining standard of carbon intensity that is expected to achieve 16 million metric tons of greenhouse gas emission reductions by 2020. One standard was established for gasoline and its alternatives, and a second similar standard was set for diesel fuel and its alternatives.

The Internal Revenue Service (IRS) gives renewable diesel the same tax credit given to plant-derived biodiesel ($1/gal tax credit). To attain this credit the renewable diesel fuel must meet US EPA registration requirements for fuel and fuel additives under the Clean Air Act, and the ASTM standard for conventional diesel (D975).

2. Renewable Diesel Life Cycle Impacts

2.1. Life Cycle Assessment

The purpose of a life-cycle assessment (LCA) applied to renewable diesel is to quantify and compare environmental flows of resources and pollutants (to and from the environment) associated with both renewable diesel and petroleum-based diesel, over the entire life cycle of the respective products. The flows of resources and pollutants provide framework for assessing human-health, environmental-systems and resource impacts. LCA addresses 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 renewable diesel 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 2.1** illustrates our approach for renewable diesel LCA.

The focus of the Multimedia Working Group efforts is on the direct health and environmental impacts associated with pollutant emissions from renewable diesel 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 detail by other California programs—particularly the LCFS program (CalOAL, 2010).

There are other ongoing efforts to evaluate lifecycle impacts of non-petroleum diesels (e.g., Huo et al., 2008; 2009, focusing on biodiesel and renewable diesel derived from soy feedstocks; Kalnes et al., 2009, comparing biodiesel and renewable diesel) and this literature is expected to continue to grow.

The life-cycle of renewable diesel fuels include the following stages:

- Biomass production and preparation (for renewable diesel derived from plant biomass),
- Oil extraction processes (for renewable diesel derived from plant biomass),
- Collection of recycled oils, greases, and tallow,
- Renewable diesel production--refining the final product blend,
- Transportation, storage and distribution of renewable diesel product, and
- End-use of the fuel product--combustion.

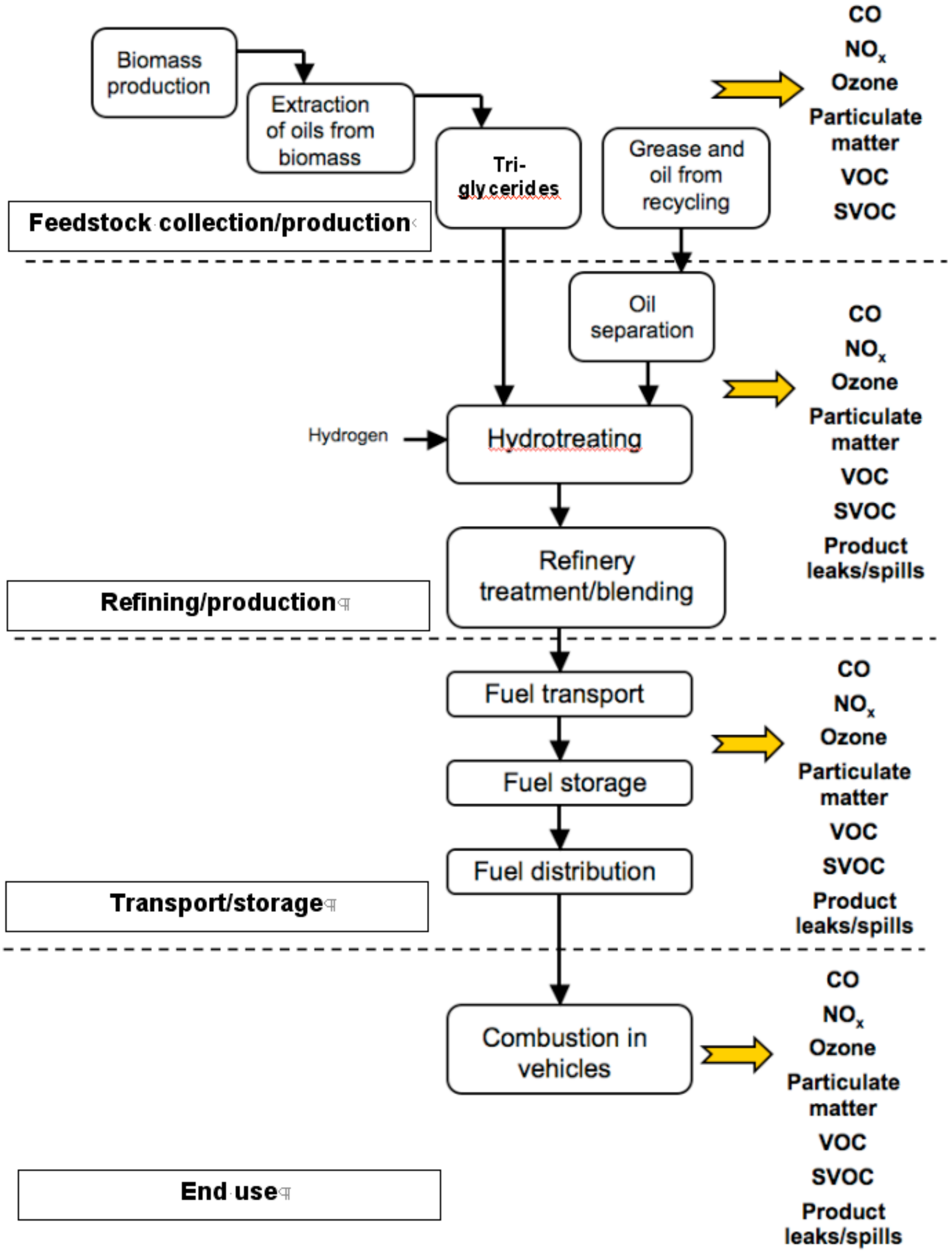


Figure 2.1. An illustration of life cycle stages and some potential life-cycle pollutant emissions for renewable diesel fuels.

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, and
- Hazardous wastes.

Modeling damages from the life-cycle emissions attributable to petroleum requires characterization of emissions factors for both the life cycle of the fuel and the production and operation of the vehicle.

2.2. US EPA Life Cycle Assessment of Renewable Fuels

As part of the U.S. EPA RFS2 rulemaking, a life cycle assessment of alternative and petroleum transportation fuels was conducted. EPA used a variety of agricultural and process engineering models and spreadsheet analysis tools, including the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET), Forest and Agricultural Sector Optimization Model (FASOM) and Food and Agricultural Policy Research Institute (FAPRI), to analyze life cycle impacts of petroleum and renewable fuels (US EPA 2010a,b).

During the EPA LCA analysis, production emission factors for the biofuels, ethanol, biodiesel, and renewable diesel, were evaluated. Emissions from the production of biofuels include the emissions from the production facility itself as well as the emissions from production and transport of the biomass and any other fuels used by the biofuel plant, such as natural gas, coal, and electricity. Table 2.1. from the EPA LCA study shows that compared to ethanol (including wet and dry milled biomass, and cellulosic production) or biodiesel, renewable diesel had the lowest production plant emissions.

Table 2.2. from the US EPA LCA study compares the projected renewable diesel use volumes to other biofuel volumes (in billion gallons per year). The US EPA LCA assumes that ethanol and biodiesel will be the major fuels used to meet Renewable Fuel Standards in the future. As a result, the US EPA LCA did not address distribution or use impacts because it was assumed that renewable diesel production would constitute less than 0.5 billion gallons per year.

A review of this analysis was commissioned by the American Petroleum Institute (Unnasch et al. 2010) and found several questionable assumptions and concerns with the use of the GREET model. With regard to biofuels, the review concluded that optimistic assumptions make biofuels look very feasible. With regard to petroleum usage, the review concluded that the analysis could be refined to reflect appropriate data. The review also noted that a key challenge in applying the GREET LCA model is in identifying input assumptions that are appropriate for these complex models and EPA should review and better justify the input assumptions adopted. Further that there was no uncertainty analysis, only sensitivity case studies.

Table 2.1. Biofuel Production Plant Emission Factors in 2022 (grams per gallon produced)(US EPA, 2010a)**.**

Biofuel Production Plant Type	VOC	CO	NOx	PM10	PM2.5	SOx	NH3
Corn Ethanol, Dry Mill NG	4.000	1.900	5.500	2.200	0.265	7.000	0.000
Corn Ethanol, Dry Mill NG (wet DGS)	4.000	1.900	5.500	2.200	0.222	7.000	0.000
Corn Ethanol, Dry Mill Coal	4.000	1.900	5.500	2.200	1.884	7.000	0.000
Corn Ethanol, Dry Mill Biomass	4.000	1.900	5.500	2.200	0.421	7.000	0.000
Corn Ethanol, Dry Mill Biomass (wet DGS)	4.000	1.900	5.500	2.200	0.313	7.000	0.000
Corn Ethanol, Wet Mill NG	2.330	1.039	1.677	0.998	0.288	0.012	0.000
Corn Ethanol, Wet Mill Coal	2.334	3.501	4.857	4.532	1.984	4.595	0.000
Cellulosic Ethanol (switchgrass or corn stover, enzymatic)	1.937	11.722	16.806	2.792	1.116	0.625	0.000
Cellulosic Ethanol (forest waste, thermochemical)	0.363	5.154	7.427	0.854	0.435	0.271	0.000
Biodiesel, Soybean oil	0.040	0.454	0.733	0.062	0.062	0.005	0.000
Renewable Diesel, Soybean Oil	**0.029**	**0.329**	**0.530**	**0.045**	**0.045**	**0.004**	**0.000**

Table 2.2. Projected Renewable Fuel Volumes (billion gallons)(US EPA, 2010a).

	Advanced Biofuel					**Non-Advanced Biofuel**	
	Cellulosic Biofuel	**Biomass-Based Diesel[a]**		**Other Advanced Biofuel**			
Year	**Cellulosic Ethanol**	**FAME[b] Biodiesel**	**Non-Co-processed Renewable Diesel**	**Co-processed Renewable Diesel**	**Imported Ethanol**	**Corn Ethanol**	**Total Renewable Fuel**
2009	0.00	0.50	**0.00**	**0.00**	0.50	9.85	10.85
2010	0.10	0.64	**0.01**	**0.01**	0.29	11.55	12.60
2011	0.25	0.77	**0.03**	**0.03**	0.16	12.29	13.53
2012	0.50	0.96	**0.04**	**0.04**	0.18	12.94	14.66
2013	1.00	0.94	**0.06**	**0.06**	0.19	13.75	16.00
2014	1.75	0.93	**0.07**	**0.07**	0.36	14.40	17.58
2015	3.00	0.91	**0.09**	**0.09**	0.83	15.00	19.92
2016	4.25	0.90	**0.10**	**0.10**	1.31	15.00	21.66
2017	5.50	0.88	**0.12**	**0.12**	1.78	15.00	23.40
2018	7.00	0.87	**0.13**	**0.13**	2.25	15.00	25.38
2019	8.50	0.85	**0.15**	**0.15**	2.72	15.00	27.37
2020	10.50	0.84	**0.16**	**0.16**	2.70	15.00	29.36
2021	13.50	0.83	**0.17**	**0.17**	2.67	15.00	32.34
2022	16.00	0.81	**0.19**	**0.19**	3.14	15.00	35.33

[a] Biomass-Based Diesel includes FAME biodiesel, cellulosic diesel, and non-co-processed renewable diesel.

[b] Fatty acid methyl ester (FAME) biodiesel.

2.3. Life Cycle Impacts and Information Gaps

A recent study by the National Research Council on the "Hidden Costs of Energy" (NRC, 2009) used life-cycle assessment to consider the health impacts for a range of both light-duty and heavy-duty fuel/vehicle combinations. This study evaluated motor-vehicle damages over four life-cycle stages: 1) vehicle operation, which results in tailpipe emissions and evaporative emissions; (2) production of feedstock, including the extraction of the resource (oil for gasoline, biomass for biofuels, or fossil fuels for electricity) and its transportation to the refinery; (3) refining or conversion of the feedstock into usable fuel and its transportation to the dispenser; and (4) manufacturing and production of the vehicle. Importantly, the study found that vehicle operation accounted in most cases for less than one-third of total damages, with other components of the life cycle contributing the rest. And while life-cycle stages 1, 2, and 3 were somewhat proportional to actual fuel use, stage 4 (which is a significant source of life-cycle emissions that form criteria pollutants) was not.

The NRC estimates of damage per vehicle-mile traveled (VMT) among different combinations of fuels and vehicle technologies were remarkably similar. Because these assessments were so close, the NRC (2009) noted that it is essential to be cautious when interpreting small differences between fuel/vehicle combinations.

The NRC considered annual health damage for 2005 as base year and 2030 as a future scenario. Although diesel-fueled light-duty vehicles had some of the highest damages per VMT in 2005, diesel-fuel use in light-duty vehicles are expected to have some of the lowest impacts per VMT in 2030. This change assumes full implementation of the Tier 2 vehicle emission standards of the U.S. Environmental Protection Agency (EPA). This regulation, which requires the use of low-sulfur diesel, is expected to significantly reduce PM and NOx emissions, resulting in significant reductions to of population exposures to direct and indirect fine-particle pollutants.

Heavy-duty vehicles have much higher damages per VMT than light-duty vehicles because they carry more cargo or people, and therefore have lower fuel economies. However, between 2005 and 2030, these damages are expected to drop significantly, assuming the full implementation of the EPA Heavy-Duty Highway Vehicle Rule.

The finding that life-cycle impacts are insensitive to a range of vehicle/fuel combinations (differences between vehicle/fuel combinations were often less than the confidence interval for each single fuel/vehicle combination) indicates that any life-cycle impact study for renewable diesel will be unlikely to resolve any key differences in health/ecological impacts between petroleum-based diesel and renewable diesel blends.

3. Release Scenarios

3.1. Defining Release Scenarios

For the Tier I evaluation of release scenarios, we focus on identifying releases that could have the greatest impact on the environment, human health, and important resources such as surface and ground waters. In order to define release scenarios it is important to understand differences in fuel production, blending, and distribution plans among the different fuel products.

There are a several companies planning to market renewable diesel in California and elsewhere, however they have different production and marketing plans. A key issue for release scenarios upstream from the combustion stage is whether blending renewable diesel stock will occur at the refinery or at a distribution facility.

An additional challenge in setting up scenarios is that feedstock sources 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. Tallow from the southern United States may be shipped by rail to an out-of-state oil refinery to produce renewable diesel that is transported to California via existing fuel pipelines.

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

3.2. Normal Releases

There are various regulations in place for renewable diesel transport. At the federal level, the 1972 Clean Water Act (CWA) (33 U.S.C. §1251 et seq.) and the 1990 Oil Pollution Act (OPA) (33 U.S.C. §2702 et seq.) "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.

Normal or routine releases during the production of renewable diesel include:

- Hexane or CO_2 released to the air during seed extraction,
- Odors associated with waste biomass, and
- Used process water discharges of various pH and trace-chemical composition.

Normal releases during the use of renewable diesel include combustion tailpipe emissions, both to the air and to surface waters in the case of marine use. The specific magnitude of these normal production- and use-releases within California are not yet well characterized and will remain difficult to quantify until more process specific data become available as well as more engine/vehicle combustion tests are conducted.

3.3. Off-Normal Releases

Off-normal releases or unanticipated releases can occur primarily during the production, distribution and storage of renewable diesel. Off-normal releases may include spills or leaks of bulk feedstock, production chemicals, such as hexane or blending stocks such as ULSD, or finished renewable diesel 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, or
- a bulk-fuel transport pipeline.

The amendment of the Oil Pollution Act in 2002 introduced the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). 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 within Part 112 of Title 40 of the Code of Federal Regulations, (40 CFR 112) to ensure that fuel production/distribution 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).

For a company that plans to produce 100% renewable diesel and then blend it with conventional diesel post-production, and possibly at some location remote from the production facility, the release scenarios are different from a company that plans to co-process “green” plant or animal oil with conventional crude oil. In the former case, storage and transport of 100% renewable diesel must be considered in terms of how it differs from experience with conventional and ULSD diesel. Some questions that arise:

- Can it be transported via pipelines?
- What are the spill consequences for 100% renewable diesel compared to ULSD?

4. Production of Renewable Diesel

4.1. Renewable Diesel Production Chemistry

There are two chemical approaches to producing renewable diesel and an emerging approach based on synthesis of hydrocarbons through enzymatic reactions. One chemical approach is based on hydrotreating vegetable oils or animal fats. Hydrotreating can take place in the same facilities used to process petroleum-based diesel. The second method involves partially combusting a biomass source to produce carbon monoxide and hydrogen—syngas—and then utilizing the Fischer-Tropsch reaction to produce complex hydrocarbons. Because there are currently no plans to engage the Fischer-Tropsch process in California, California Air Resources Board (ARB) staff have requested that this report focus on the impacts of hydrotreated renewable diesel (HDRD/FAHC) produced in existing refineries.

Hydrotreating is a hydrodeoxygenation process used to remove oxygen and nitrogen containing compounds as well as metals from the fuel feedstock. Both crude oil and bio-oils contain minerals as well as aromatic and oxygenated compounds that contribute little to the combustion performance and emission profile of the fuel. With hydrotreating, the feedstock oil flows through a fixed bed reactor under high pressure, where it is mixed and reacted with hydrogen gas. Marker et al. (2005) describe this process as having hydrogen gas injected at approximately 1.5% the mass of vegetable oil feedstock with lower amounts required for a predominately saturated fatty acid feedstock such as coconut oil.

Olefins and aromatic compounds react with hydrogen atoms, converting them into paraffins. Cobalt-Molybdenum and other catalysts are used to increase the rates of reaction (Gary et al., 2007). Aromatic rings are broken in catalyzed reactions with hydrogen, forming saturated hydrocarbons and methyl functional groups attached to carbon chains creating iso-parrafins (Liu et al., 2008). Hydrotreatment of vegetable oils produces alkanes with one carbon atom less than the fatty acid chains, although the exact nature of the product mix depends on reaction conditions and catalysts used; thus, a vegetable oil consisting of the typical C16 and C18 fatty acids would yield C15 and C17 alkanes (Knothe, 2010).

According to Gary et al. (2007) hydrogen gas for this process can be produced by reacting steam and methane, where the gas and vapors pass through catalysts in a heated reactor. This reaction is illustrated in **Figure 4.1**. The reaction also produces carbon monoxide, which is converted to CO_2 in a second stage, where the reactants are again mixed with steam, and pass over solid chromium and iron oxide catalyst. CO_2 is then removed from the gas phase through absorption processes.

$$CH_4 + 2H_2O \xrightarrow{Catalyst} CO_2 + 4H_2$$

Figure 4.1. Hydrogen production from methane, adapted from Gary et al. (2007).

Hydrotreating can alter the sulfur and aromatic content of crude oil for the production of ULSD (Gary et al., 2007). Metals bonded to aromatics and hydrocarbon chains are released and replaced by hydrogen, however some bonding sites have a higher affinity for nitrogen compounds, potentially inhibiting the desulphurization reactions (Liu et al., 2008). Minerals shed from the organic compounds are deposited on catalyst surfaces, extinguishing capacity over time (Gary et al,, 2007). For this reason, it has been argued that the use of conventional refining facilities for production of renewable diesel may be less cost-effective in the long-term than establishment of dedicated facilities (Kalnes et al., 2009). Hydrogen sulfide, ammonia and CO_2 are produced as gasses and must be captured by emission control devices.

4.2. Renewable Diesel Reactor Configuration and Design

Many of the companies that are now making renewable diesel, including UOP (Green Diesel), Neste (NexBTL) and Conoco-Philips, have developed proprietary processes for the hydrogenation of non-petroleum feedstocks with hydrogen gas. These processes remove impurities from the feedstock as well as saturate free fatty acids (Kalnes et al., 2007).

There are two general production strategies for HDRD production and distribution:

- Co-processing vegetable/animal triglycerides in a conventional petroleum production stream using a hydrotreating process. Currently this results in diesel fuel that has a specified percentage of “green-derived” carbon, e.g., 20% renewable diesel (R20).
- Production of a pure HDRD (R100) in a dedicated hydrotreating facility that does not use conventional petroleum. The resulting fuel can be used as a 100% green fuel or blended with conventional ULSD to any concentration.

As an illustration of the chemical processes that take place in renewable diesel reactors, we consider the case of vegetable oils that are composed primarily of triglycerides. These are organic molecules that include chains of carbon atoms bonded to hydrogen atoms and various functional groups. Soy and canola oils are largely unsaturated fatty acids—most carbon atoms are double bonded. Saturated fatty acids are composed mostly of single bonds between carbon atoms, and achieve a stable valence state through bonding to hydrogen atoms (Petrucci et al., 2002). Saturated fatty acids are less susceptible to oxidation and decomposition from heat and therefore provide a more stable fuel. **Figure 4.2** illustrates the hydrogenation of triglycerides.

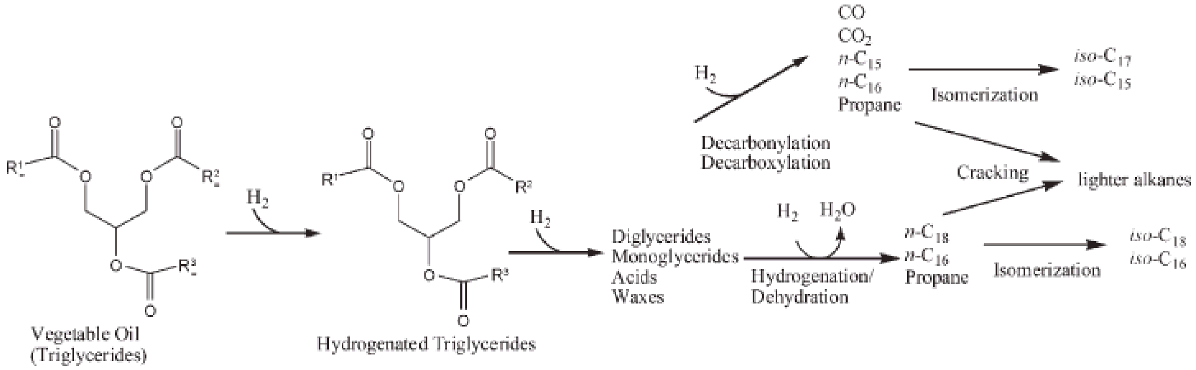


Figure 4.2. Hydrogenation of Triglycerides

Hydrogen is generated onsite through reactions with methane (Huo et al., 2008). Neste's NexBTL process requires the input of sodium hydroxide and phosphoric acid as a step in the pretreatment of the oil. Additional chemical inputs have not been specified for the UOP Green Diesel process.

To carry out hydrotreating, existing refineries can be retrofitted with additional equipment (see **Figure 4.3** for an example) rather than needing completely new infrastructure as with fast pyrolysis oil production. (Huber et al., 2007). However it has been pointed out that it may be more cost-effective to construct a dedicated unit for processing of vegetable oils, due to the apparent competition between hydrodeoxygenation and hydrodesulfurization applied to obtain ultra-low sulfur petrodiesel (Kalnes et al., 2009; Knothe, 2010).

Most published results on the performance of renewable diesel refineries are based on the use of soybean oil, however palm oil, yellow grease and tallow have been proposed (Marker, et al., 2005).

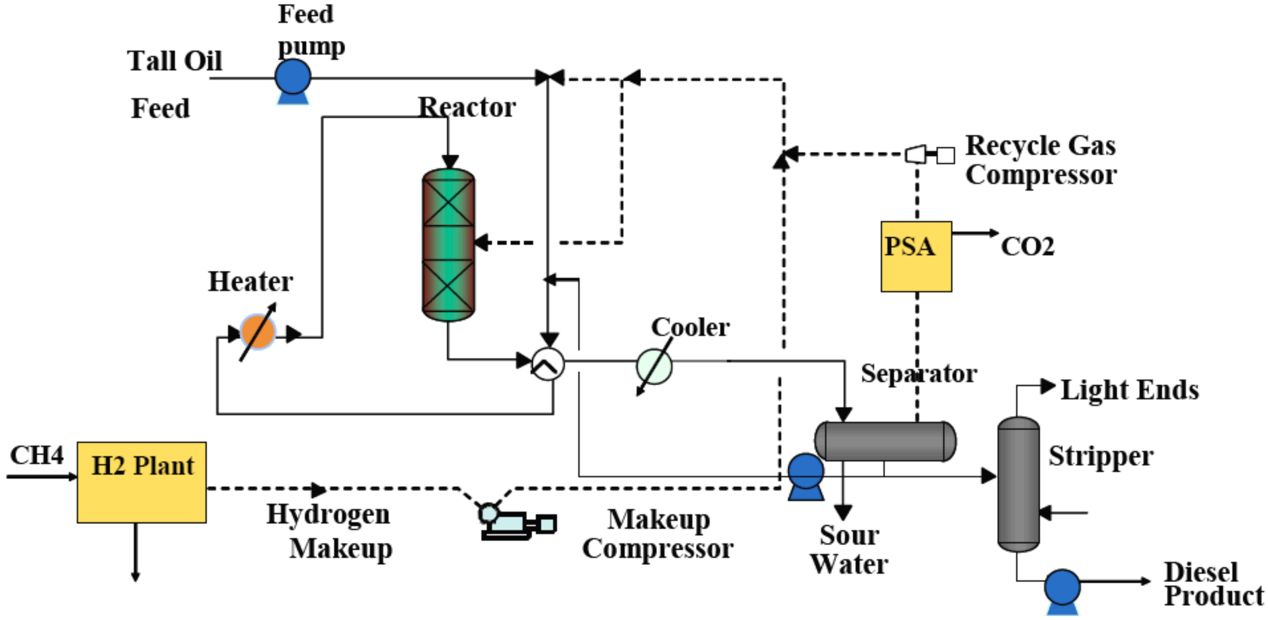


Figure 4.3. Stand-alone Renewable Diesel Production Unit used to produce a pure HDRD product (R100). Adapted from Kalnes et al. (2007).

Oxygenated compounds provide less energy per unit mass of fuel, and are thus considered to act as a "dead" volume, lowering the heating value (Fitzgerald, 2008). UOP has considered both a hydrodeoxygenation (HDO) and decarboxylation (DeCO2) as reaction pathways for removing oxygen from compounds in the diesel feedstock oils. These reaction pathways are illustrated in **Figure 4.4**.

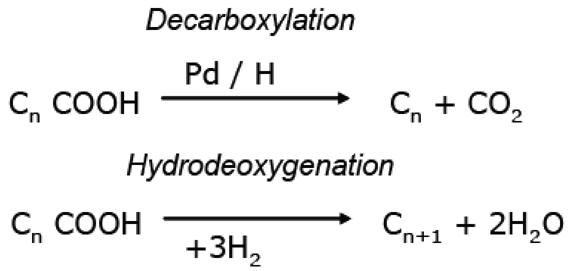


Figure 4.4. Chemical reaction pathways that remove carbon dioxide and oxygen from renewable diesel (adapted from Marker et al., 2005)

Decarboxylation requires less hydrogen influent and allows for longer catalyst life. However if feedstock sulfur concentrations are too high, it is not effective (Marker, et al., 2005). Hydrocarbons bonded to carboxyl groups are converted into paraffins, CO_2 or water.

4.3. Overview of Renewable Diesel Feedstocks

In this section we review the characteristics, technical issues, and potential life-cycle implications fo the four most-commonly proposed feedstocks for renewable diesel. This includes soybean oil, palm oil, waste grease, canola and rapeseed oils, and animal tallow.

Soybean Feedstock

Soybeans are expected to be the main feedstock for renewable diesel in California. In 2006, soy was grown on 74.6 million acres of US farmland, producing on average 42.7 bushels per acre (Huo, et al., 2008). Oil is extracted from soy by crushing the beans and applying n-hexane as a solvent. Growing, harvesting, and extracting the oil require fossil fuel energy sources, and generate some greenhouse gas emissions (Huo et al., 2008; 2009). When n-hexane is used as a solvent in soy oil extraction; there is the potential for leaks and spills at processing facilities (Huo, et al., 2008).

Soybean Physical Characteristics

A mass yield of between 70% and 80% of the feedstock can be expected (Huo, et al., 2008). Soy based renewable diesel (Green Diesel) has a “higer heating value” (HHV also known as the gross calorific value or gross energy) that exceeds than both FAME biodiesel and nearly doubles that of pyrolysis-based fuels (Marker, et al., 2005). Kalnes et al. (2007) observe that soy-based renewable diesel is sufficiently similar in physical-chemical properties to ULSD that it can be readily used in a range of blending applications.

Soybean Chemical Composition

The carbon content of the UOP renewable diesel called “Green Diesel” is approximately 87.2%, and no oxygen is present (Huo, et al., 2008). The sulfur content of Green Diesel is reported to be below 10 ppm, (Marker, et al., 2005), which is comparable with ULSD and FAME biodiesel. Co-products of the process include propane and naphtha, which can be used as inputs to gasoline production. The current literature provides no discussion of preservatives and anti-corrosive additives for renewable diesel from soy. Due to its cloud point, it is expected that additives would be required for normal engine operation in cold climates.

Palm Oil

Palms used to produce palm oil are grown primarily in tropical or subtropical areas such as Malaysia and Indonesia. Palm oil is characterized by high concentrations of medium-chain saturated (palmitic acid) and monounsaturated (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 sustainability is an issue of concern that is outside the scope of this study but relevant to its prospects as a fuel. With 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. Significant amounts of CO2 seep into the atmosphere from these bogs (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.

Waste Grease

There are two primary types of waste grease based on the source of the grease—yellow grease and trap grease (brown 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 1.25 billion kg of yellow grease annually (Kemp, 2006). Since yellow grease is a waste product, it is relatively inexpensive and available in all regions. Trap grease or 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. Since the grease currently has no other market value, its cost is extremely low.

Physical and flow properties of brown and yellow grease have not yet been published. Further research is needed to determine whether these feedstocks produce fuel products significantly different from soybean oils. Due to the acidity of yellow and brown grease, Marker et al. (2005) note that refinery piping must be constructed with 317L stainless steel. It can be assumed that less resilient materials can be corroded in normal use.

Canola and Rapeseed Oils

Canola and Rapeseed oils show promise as renewable diesel feedstock. These oils have properties similar to soy oil. But the oil yield of canola is much higher than soy because the canola seed contains 45% oil compared to 19% in soy beans.

Hydrotreating canola and rapeseed oil feedstocks saturates the carbon-to-hydrogen bonds, providing oxidative stability and improved flow properties. Oil extraction is accomplished with the addition of steam and phosphate compounds for de-gumming, followed by alkali refining and bleaching. Sodium hydroxide is used to precipitate impurities in the oil, although it does not remove chlorophyll compounds. Process wastewater must be treated, since phosphorus contributes to nutrient loading in natural waters and chlorine compounds are toxic to many species (Mag, 1983).

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, along with some production in the United States. North Dakota is the leading US state in the production of canola and typically grows approximately 90% of the total US domestic production of Canola.

Rapeseed oil is composed of oleic, linoleic, linolenic, eicoscenoic, erucic, stearic, and palmitic acids, which are prone to oxidation. There are currently tests plots in California that produce canola fuel feedstock. There is little experience with canola in California, but 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.

Rapeseed is used as a source for renewable diesel plant oils primarily in Europe. Harvest is accomplished by direct thrashing and rapeseed straw is incorporated into the soil. The rapeseed is dried, cleaned and stored. Once transported to the oil mill, the seed is pressed and the crude rapeseed oil extracted. Rapeseed meal is a by-product of this process and is used as animal feed which can be used in place of soy meal imported from North America.

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 after it rises to the surface. Since it is a waste by-product, it is relatively inexpensive, sustainable, and is locally available (Hilber, et al. 2007).

4.4. Overview of Renewable Diesel Chemical Composition

Here we consider the composition of renewable diesel with particular emphasis on how renewable diesel differs from FAME biodiesel and ULSD with respect to overall chemistry, environmental performance, and combustion performance. We begin with a review of EPA registrations that provide some information needed for this analysis. We also consider information provided by the fuel producers regarding the composition of their product.

4.4.1. U.S. EPA Registration

US EPA requirements for registration and analysis of designated fuels and fuel additives is stipulated in sections 211(b) and 211(e) of the Clean Air Act (CAA). The US EPA Tier I emission testing requirements are identified in 40 CFR Part 79, subpart F, Section 7.57. These regulations require that manufactures or importers of gasoline, diesel fuel, or a fuel additive provide a chemical description of the product, and certain technical, marketing and health-effects information. The registration requirements are organized in a three-tiered structure. Standard mandatory requirements are contained in the first two tiers. The third tier provides for additional testing as needed.

Two renewable diesel producers have provided the California ARB with US EPA Tier I documents. These producers are Kern Oil Company, which produces a co-processed HDRD (R20), and Neste Oil Corporation, which uses a "bio-only" hydrotreating process to produce a pure HDRD (R100). We use these documents reporting our efforts to characterize the chemical composition of potential renewable diesel fuels that may be used in California.

4.4.2. Renewable Diesel versus FAME Biodiesel

Both renewable diesel and FAME biodiesel are "biomass-based fuels", which according to the California Low-Carbon Fuels Standard (LCFS) (CalOAL, 2010) are defined as "a biodiesel (mono-alkyl ester) or a renewable diesel that complies with ASTM D975-08ae1…".

Biodiesel is chemically distinct from petroleum diesel and has a separate ASTM standard (D6751), which specifies the standard for biodiesel when it is used as a blend component with petroleum diesel.

In contrast to a biodiesel that contains mono-alkyl esters, the California LCFS defines a "renewable diesel" fuel as:

> *"... a motor vehicle fuel or fuel additive which is all the following:*
>
> *(A) Registered as a motor vehicle fuel or fuel additive under 40 CFR part 79; A-9*
> *(B) Not a mono-alkyl ester;*
> *(C) Intended for use in engines that are designed to run on conventional diesel fuel; and*
> *(D) Derived from nonpetroleum renewable resources."*

Renewable diesel, produced from a variety of renewable feedstocks, is not composed of esters and is composed chemically of saturated hydrocarbon chains similar to conventional petroleum (e.g., Knothe, 2010). The renewable production process is designed to take advantage of the infrastructure of an existing refinery. Several of the renewable diesel products currently available meet the ASTM standard for conventional diesel (D975). As part of the RFS, US EPA reported that renewable diesel has a slightly higher energy content compared to biodiesel (US EPA 2010a,d,).

4.4.3. Chemical Composition of Renewable Diesel Compared to Conventional Diesel

Petroleum-based diesel fuels 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 fuels primarily by their boiling point ranges, and chemical additives. Renewable diesel fuel consists of a mixture of hydrocarbons that meets the ASTM standard for petroleum diesel along with performance and stability additives along with some aromatic hydrocarbons.

Co-processed HDRD (R20)

In response to the requirements of the 211(b) fuel analysis, Kern Oil and Refining (KOR) Company submitted a co-processed renewable diesel (R20) for detailed chemical analysis and speciation by Southwest Research Institute (Fanick, 2009a). The fuel contained less than 15% sulfur. The results were compared to Title 40 CFR, Subpart 86, and ASTM D975 property specifications, and the results of a USEPA 1990 survey of diesel fuels.

Three techniques were used to evaluate the fuel composition, hydrocarbon speciation, direct filter injection/gas chromatography (DFI/GC), and High Temperature Programmable Temperature Vaporization Gas Chromatography/Mass Spectroscopy (HTPTV-GCMS). Each technique characterizes a different portion of the hydrocarbons in the fuel. The SwRI analysis was performed using replicate samples from two separate fuel totes. The analysis agreed closely between totes. The average result is reported in Table 4.1.

Table 4.1. Comparison of Kern Oil and Refining Company R20 renewable diesel analysis performed by Southwest Research institute to three diesel fuel specifications.

Fuel Property	Test method	EPA Certification Fuel Specification [a]	1990 USEPA Diesel Fuel Survey [b]	ASTM D975	SwRI Analysis
Sulfur, ppm	D5453	7-15	240-1600	<15	6.65
Aromatics, vol %	D1319	27 min.	23.7-54.3	35 max.	29.4
Olefines, vol %	D1319	NA[c]	0.6-3.3	NA	1.6
Saturates, vol %	D1319	NA	45.9-75.0	NA	69.05
Cetane Number	D613	40-50	40.8-51.2	40 min.	53.05
Cetane Index	D976	40-50	43.3-49.9	40 min.	44.5
API Gravity	D287	32-37	NA	NA	36.45
Flash Point, F^{o} (C^{o})	D93	130 (54) min.	NA	126 (52) min.	141 (60.6)
Viscosity@ 40^{o}C	D445	2.0-3.2	NA	1.9-4.1	2.219
Lubricity, HFRR@60^{o}C, micron	D6079	NA	NA	520 max.	442.5
Ash, % mass	D482	NA	NA	0.01	<0.001
Cloud Point, ^{o}C	D2500	NA	NA	D975 spec.[d]	-15.25
Cold Filter Plugging Point, ^{o}C	D6371	NA	NA	D975 spec.[d]	-19
Copper Strip Corrosion	D130	NA	NA	No. 3 max.	1B
Water & Sediment, vol %	D2709	NA	NA	0.05 max.	0.01
Ramsbottom, wt %	D524	NA	NA	0.35 max.	0.115
IBP, ^{o}C	D86	171-204	146-201	NA	163
10%, ^{o}C	D86	204-238	194-258	NA	197
50%, ^{o}C	D86	243-282	240-284	NA	245
90%, ^{o}C	D86	293-321	293-337	282-338	314
EP, ^{o}C	D86	321-366	319-355	NA	343

[a] Data from an April 13, 1992 EPA memorandum from james Greaves, subject "Revised Base diesel Fuel Determination Procedures for the Fuels and Fuel Additives Rulemaking" put into Docket No. A-90-07.

[b] Certification diesel fuel specification in the Title 40 CFR Part 86, Subpart N, 86.1313-2007.

[c] Not Applicable.

[d] "It is unreasonable to specify low-temperature properties that will ensure satisfactory operation at all ambient temperature. The appropriate low-temperature operability properties should be agreed upon between the purchaser for the intended use." (ASTM D975).

The SwRI hydrocarbon speciation analysis showed that the lower molecular weight n-, iso-paraffins, and cycloparaffins accounted for between 13 and 16 percent of the total saturates; the olefins were between 1.3 and 1.5 percent of the hydrocarbons, and the aromatics were between 29 and 30 percent. The unidentified C^{9} – C^{12+} hydrocarbons accounted for the remainder of the hydrocarbons, with a mass percentage between 53 and 55 percent.

The DFI/GC analysis showed that the majority of the hydrocarbons were between C^{12} and C^{18}. Between 15 and 17 percent of the hydrocarbons were between C^{19} and C^{24}, and the concentrations decreased above C^{24}.

The HTPTV-GSMS analysis showed that identified individual hydrocarbons ranged from toluene ($C^{7}H^{9}$) to tricosane (C^{23}). In general, about 60 percent of the compounds were saturates and between 44 and 47 percent of the hydrocarbons were straight-chain hydrocarbons. Between 30 and 34 percent of the hydrocarbons were straight-chain compounds between C^{13} and C^{19}.

Between 13 and 16 percent of the total hydrocarbons were branched-chain compounds between C^{15} and C^{19}.

The KOR R20 diesel fuel met both the USEPA certification and ASTM specifications except for the cetane number (slightly higher for both the USEPA certification specifications and 1990 Survey), and Initial Boiling Point and the 10 percent Boiling Point for the USEPA certification specification. In 2007 the maximum allowable sulfur concentration in diesel fuel was lowered to 15 ppm so the comparison to 1990 sulfur concentrations is inappropriate.

The SwRI study concluded that the KOR R20 fuel was substantially similar to other conventional diesel fuels when compared to two different fuel specifications and the results of an USEPA fuel survey.

Bio-only Pure HDRD (R100)

One of the renewable diesel fuels proposed for use in California is a Bio-only Pure HDRD produced by Neste Oil Corporation using the NExBTL process. In the NExBTL renewable diesel process, animal fats and vegetable oils (triglycerides) are converted into diesel fuel components. The process uses all types of vegetable oils as well as all kinds of animal greases and fats. All of these oils and fats have a similar chemical structure that is comprised of three fatty acid chains joined to a glycerol to form a triglyceride.

The process steps utilize technology adapted from normal refinery processes. The process steps are:

- Feedstock pre-treatment to reduce contaminants to very low levels. During this step, commercial vegetable oil de-gumming technology is used. This step is needed to achieve purity levels required to maintain a long catalyst lifetime.
- Hydrotreating to remove oxygen in which paraffins are formed and branched. In this step, hydrogen is fed into a reactor vessel under pressure together with the feedstock. The resulting product is an iso-paraffin with significantly improved cold flow characteristics, lowering the cloud point to –25°C or even lower. The extent of this process step is controlled depending on the grade of fuel required. Cold flow properties (Cloud point) can be adjusted to between -5 to –30 °C to be applicable to winter operating conditions.
- Product finishing and stabilization. Lubricity can be improved with additives, as is commonly done with conventional sulfur-free fuels.

"Bio-only" hydrotreated plant oils result in a HDRD that is a pure hydrocarbon product that meets sulfur free diesel specifications in all aspects except for density. It is free of sulfur and oxygen, and has a very low content of aromatics (<0.02%). HDRD typically has a very high cetane number. In the case of NExBTL, the blending cetane number varies between 85 and 99 as measured with standard method ASTM D 613-03b. But, HDRD fuels are less dense than conventional diesel fuels. Pure NExBTL fuel meets European EN590 ultra-low sulfur fuel specifications except for density.

The chemical composition of the resulting pure R100 is a combination of straight and branched chain paraffins or alkanes. Neste has determined the chemical speciation of the pure R100 using gas chromatography and mass spectrographic analysis.

The carbon numbers range from $C^{10} – C^{20}$ and the boiling range is from 120°C to 320°C, values that are within the range of conventional diesel. Other analyses indicate Neste's NExBTL consists of n- and iso-parrafins (Rantanen, et al, 2005) and contains very low amounts of polyaromatic hydrocarbons, oxygenated compounds and sulfur. In 2005, VTT Processes in Finland conducted physical properties characterization tests on Neste's fuel (Rothe, et al., unpublished document). The fuel was produced from vegetable oils (Canola/rapeseed or Palm oil). Table 4.2 summarizes the fuel properties of R100 fuel produced by Neste (NExBTL). The NExBTL fuel was found to be similar to the European Union's EN90 and Sweden's EC1 ULSD equivalent fuels.

Table 4.2. Comparative fuel properties for conventional low-sulfur diesel and a HRDF (NExBTL) (Rothe, et al., unpublished document)**.**

Fuel Property	Units	EN590*	NExBTL
Density @ 15°C	kg/m^3	833	783
Viscosity @ 40°C	mm^2s^{-1}	2.35	3.4
Sulfur Content	mg/kg	6	<1
CH_x		1.86	2.1
IBP**	°C	171	216
FBP***	°C	364	321
Total Aromatics	vol %	24.9	<0.02
Cetane Index		49.7	97.9

* European ultra-low sulfur diesel fuel
** Initial boiling point
*** Final boiling point

Neste Oil Corporation has also conducted a life-cycle assessment of the energy and greenhouse gas balance of its R100 NExBRL fuel (Gartner, et al., 2006). This assessment was conducted using an approach consistent with ISO 14040-43 standard. During this analysis, the consumption of non-renewable energy sources, i.e., non-renewable fossil fuels, natural gas, coal, etc., and production of greenhouse gases, i.e., carbon dioxide, methane, nitrous oxide, were considered. The feedstocks considered were Rapeseed (Canola) and Palm oil. For all comparisons, scenarios and sensitivity analyses considered, the assessment found that use of NExBTL R100 saves primary energy and greenhouse gas emissions over the entire life-cycle when compared to conventional fossil diesel fuel. The biggest variation in the results depended on the production, transportation, and extraction of the crude plant oils used to make the R100. The rapeseed energy savings ranged from 30 – 33 Giga-Joule (GJ) primary energy per ton of NExBTL. The rapeseed greenhouse gas savings ranged from 1.2 – 2.5 tons of CO_2-equivalents per ton of NExBTL.

The energy savings for palm oil ranged from 44 GJ to 16 GJ primary energy per ton NExBRL. The greenhouse gas savings ranged from 2.2 tons to 1 ton CO_2-equivalents per ton of NExBTL. The results for palm oil depended mainly on the land use practices on the plantations used to grow the palms. "Good practice" palm oil resulted in about 65% higher savings compared to "typical practice" palm oil. The report cautioned that these results cannot be transferred to other environmental impacts such as acidification, eutrophication, and biodiversity that may arise during palm oil production.

4.5. Solid Waste and Emissions to Water

In evaluating the production of renewable (and other alternative diesel-fuel 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, co-processed HDRD produces propane, carbon dioxide, and water from the oil/fat feedstock, and the fermentation of palm oil mill effluent leads to significant biogas emissions.

Proper identification and management of the waste solvents during oil extraction are required to comply with hazardous waste laws and regulations. Degradation of the fuel could be caused by temperature, oxidation, and/or material incompatibility.

Once the sources, composition, and magnitude of waste streams from renewable diesel 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 specified 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 renewable diesel life cycle.

Hazardous and non-hazardous wastes are generated from many of the refining processes, petroleum handling operations, as well as wastewater treatment. The petroleum refining industry generates relatively large volumes of wastewater, including contaminated surface water runoff and process water. Accidental releases of liquid hydrocarbons have the potential to contaminate large volumes of ground water and surface water possibly posing a substantial risk to human health and the environment. 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 biofuels comes from soybean and oil processing (66%).

The life cycle assessments also include two classifications of solid waste: hazardous and non-hazardous. Almost all of renewable diesel's hazardous solid waste is derived from the refining process. Agriculture accounts for a very small fraction of renewable diesel'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 current diesel is 0.41g/bhp-h of engine work and there is no reliable estimate yet available for renewable diesel.

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

5. Storage and Distribution of Renewable Diesel

In this section we review information that is needed to assess multimedia health and environmental impacts associated with storage and distribution of renewable diesel. A key consideration in this review is materials compatibility, which determines potential for leaks into soil, ground water, and surface water.

5.1. Material Compatibility and Storage Stability

In general, the handling and storage of renewable diesel that meets ASTM 975 standards is the same as for petroleum diesel including the needed protection from ignition sources. Tanks used for transport and storage must be suitable for combustible liquids and precautions must be taken to prevent product spills on to the ground, into drains, and into surface and ground waters.

In the evaluation of the multimedia impacts of new diesel formulations, material compatibility and storage stability are important considerations, but little information is available on pure renewable diesel materials compatibility.

As noted above, the feedstocks for renewable diesel include vegetable oils, fryer grease and tallow. Relative to petroleum, these feedstocks are more acidic, with an expected *Total Acid Number* between 2 and 200. Therefore, existing refineries must be retrofitted with more resistant pipes, seals and pumps (Marker, et al., 2005). Nitrile rubber, neoprene, or PVC gloves are protective equipment required to handle renewable diesel (ASTM F739/Diesel Fuel).

Storage stability refers to the ability of the fuel to resist chemical changes during long-term storage. While storage stability is an important parameter for any diesel fuel little information is available regarding pure renewable diesel. Because renewable diesel typically does not contain unsaturated materials, it can be expected to have good stability, particularly if blended with conventional ULSD.

5.2. Distribution and Blending of Renewable Diesel

Blended HDRD can be transported via the same methods used for conventional diesel, including pipelines, rail cars, tank trucks and drums. The choice of transport vessel depends on the quantity of renewable diesel being transferred and the cold flow properties of the fuel.

It is straight forward technically to blend pure HDRD fuels (R100) with conventional diesel. R100 can be blended to as much as 65 – 70 volume % in conventional diesel to fulfill the minimum density requirement.

5.3. Use of Additives

The USEPA 211(b) specifications for baseline fuel include the requirement for additives. The required additives are:

- Corrosion Inhibitor, 4.5 pounds per thousand barrels of fuel (ptb),
- Demulsifier, 2 ptb,
- Anti-oxidant, 2 ptb, and
- Metal deactivator, 2 ptb.

Chemical additives are commercially available to address the oxidative stability, cold-flow properties, and microbial contamination of renewable diesel. It is expected that these additives would be the same as or very similar to additives currently in use for conventional diesel fuel. In addition, R100 renewable diesel fuels will need to have a lubricity additive.

Cold flow properties including cloud point and pour point for renewable diesel are generally improved with respect to biodiesel and similar or improved with respect to ULSD. For instance, cloud point ranges for renewable diesel range generally between -25 and -5 degrees C (e.g., Table 4.1; Knothe, 2010) although values as high as 7 degrees C have been reported, and cloud point for ULSD ranges around -12 degrees C (Phillips Petroleum, 2002).

Unlike biodiesel that, by virtue of the ester moiety, has intrinsic lubricity (Knothe and Steidly 2005), renewable diesel requires a lubricity additive similar to petroleum-based ULSD. Knothe (2010) points out that blends involving more than 2% biodiesel restores lubricity.

5.3.1. Residual Water

As is the case with conventional diesel, renewable diesel is generally considered to be insoluble in water, it can actually contain as much as 0.05 % by volume of water. Storage stability of renewable diesel is also affected by the presence of water within the tank used for storage or transport (ASTM 2003).

Water in vapor phase (humidity) can enter through vents and seals of fuel tanks 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. Water can cause hydrolytic degradation of the fuel, contribute to microbial growth in the fuel, and cause corrosion of fuel systems and tanks.

The presence of water within renewable diesel 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.

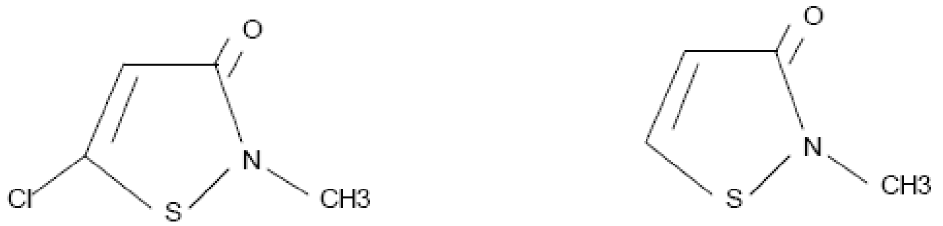
Condensed water in a fuel tank can support the growth of bacteria and mold that use the hydrocarbons in the renewable diesel as a food source. These "hydrocarbon-degrading bacteria and molds will grow as a film or slime in the tank and accumulate as sediment" (Wedel, 1999).

The control of water is primarily a housekeeping issue (i.e. keeping storage tanks clean) and a problem frequently addressed by using fuel filters (ASTM 2003). Additives may also be used to address residual water problems (ASTM 2003).

5.3.2. Additives to Inhibit Biodegradation of Stored Diesel Fuel

Additives used to control microbes in fuel storage tanks are generally water-soluble and migrate into any water phase residing in the fuel storage tank. Given the expected potential for biodegradation of renewable diesel at rates similar to rates of biodegradation of petroleum diesel (Knothe, 2010), the same biocides used in petroleum-based diesel fuel systems can be expected to be used with biofuels. 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 (Irwin, 2007; Cheznow, 2008, personal communication).

The biocide with the largest current market share is manufactured by 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 5.1** and listed in Appendix C, Table C-4.



5-chloro-2-methyl-4-isothiazolin-3-one
CAS Registry N° 26172-55-4
EINECS N° 2475007

2-methyl-4-isothiazolin-3-one
CAS Registry N° 2682-20-4
EINECS N° 2202396

Figure 5.1. Rohm and Haas Kathon FP 1.5 Biocide (Rohm and Haas, 1999).

Other common fuel biocide chemicals are methylene-bis-thiocyanate (MBT) and nitromorphalines (Cheznow, 2008, personal communication). MBT is often used as a biocide in water treatment plants, paper mills, and other industrial processes involving large-scale water use. Carbamates also appear on the material safety data sheets (MSDSs) of some commercial biocides listed in Table 4 of Appendix C.

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

6. Use of Renewable Diesel

In this section we review information that is needed to assess multimedia health and environmental impacts associated with the use, that is combustion, of renewable diesel. We first consider the quality of renewable diesel as a substitute for ULSD in terms of energy performance. A second key consideration in this review is how the levels of criteria and hazardous air pollutants emitted during combustion differ from those emitted from and energy-equivalent quantity of renewable diesel verses ULSD.

6.1. Renewable Diesel Standardization and Fuel Quality

Renewable diesel is required to meet the same standards as conventional diesel. ASTM Standard Specification for Diesel Fuel Oils (D 975-09b) (ASTM, 2009) provides standards that, when met, allows renewable diesel to be suitable for a variety of diesel engines. Appendix A summarizes these standards. Additionally, the American Society for Testing and Materials (ASTM) identifies seven grades of diesel fuel oils that can be used in a variety of diesel engines (Table 6.1).

Table 6.1. ASTM Diesel Fuel Grades (ASTM 2009).

Diesel Fuel Grade*	Description
1-D S15**	Special-purpose, light middle distillate for engines requiring 15 ppm sulfur (maximum) and higher volatility than provided by Grade 2-D S15 fuel.
1-D S500**	Special-purpose, light middle distillate for engines requiring 500 ppm sulfur (maximum) and higher volatility than provided by Grade 2-D S500 fuel.
1-D S5000	Special-purpose, light middle distillate for engines requiring 5000 ppm sulfur (maximum) and higher volatility than provided by Grade 2-D S5000 fuel.
2-D S15**	General-purpose, middle distillate for engines requiring 15 ppm sulfur (maximum). Especially suitable for varying speed and load conditions.
2-D S500**	General-purpose, middle distillate for engines requiring 500 ppm sulfur (maximum). Especially suitable for varying speed and load conditions.
2-D S5000	General-purpose, middle distillate for engines requiring 5000 ppm sulfur (maximum). Especially suitable for varying speed and load conditions.
4-D	Heavy distillate fuel or a blend of distillate and residual oil. Suitable for constant load and speed application.

* S5000 grades of diesel fuel refer to so-called “Regular” sulfur grades. S500 grades refer to so-called “Low Sulfur” grades. S15 grades are commonly referred to as “Ultra-Low Sulfur” grades or ULSD.
** Meets 40 CFR Part 80 fuel quality regulations for highway diesel fuel sold in 1993 and later years.

6.2. Emissions of Pollutants to Air

In terms of human health damage, the key air emissions for any diesel fuel life-cycle take place during refining, fuel loading/transport, and fuel combustion. Pollutants generated during crude oil refining typically include volatile organic compounds (VOCs), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH_3), hydrogen sulfide (H_2S), metals, spent acids, and numerous toxic organic compounds. Emissions occur throughout refineries and arise from the thousands of potential sources such as valves, pumps, tanks, pressure relief valves, flanges. Emissions also originate from the loading and unloading of materials (such as VOCs released during charging of tanks and loading of barges), as well as from wastewater treatment processes (such as aeration and holding ponds). Storage tanks are used throughout the refining process to store crude oil, intermediate products, finished products, and other materials. The tanks are a considerable source of VOC emissions. Combustion of petroleum-based and renewable diesel fuels by motor vehicles results in exhaust emissions that include VOCs, nitrogen oxides, particulate matter, carbon monoxide, toxic air pollutants, and carbon dioxide. These include known carcinogens, such as benzene, and probable human carcinogens, such as formaldehyde or diesel particulate matter.

6.3. Renewable Diesel Impact on Air Quality

Because of the importance of the combustion emissions, the focus below is on air-quality impacts of renewable diesel relative to extant diesel fuels. Emission testing data was available for Conoco-Phillips, Kern Oil Refining Co co-processed HDRD, and Neste Oil Corp.

Conoco-Phillips conducted tests using a 2006 International 6.0L V8 engine. Blends of R5 to R30 produced from soy oil showed reduction in most criteria pollutants relative to conventional ULSD. For a R20 blend, non-methane hydrocarbon emissions were reduced by about 50%, NOx emissions were about 8% lower, and CO emissions dropped by about 60%. Particulate matter (PM) emissions showed only a slight decrease compared to base fuel, and did not improve with higher blend concentrations. (Kaufman, 2007).

Conoco-Phillips renewable diesel emissions testing was also conducted using beef tallow, canola, poultry fat, and yellow grease feedstocks. While there were some emissions variation both up and down compared to soy renewable diesel, all feedstock sources showed lower emissions compared to baseline conventional diesel fuel.

As part of the required 211(b) fuel analysis, Kern Oil Refining Co. submitted its renewable diesel fuel for emissions analysis by Southwest Research Institute (Fanick, 2009a). The KOR renewable diesel fuel was 20% co-processed tallow and conventional petroleum (R20). The emissions testing was conducted using a 2007 6.4L Navistar A350 heavy-duty diesel engine. In general, the engine met 2009 emission standards except for NOx. The 2009 emission standard for NOx is 0.01 g/bhp-hr, and the KOA renewable diesel resulted in NOx 0.1 g/bhp-hr higher than the standard. All other emissions tested--CO, PM, and non-methane hydrocarbons--were significantly lower than the 2009 standard.

As part of required 211(b) fuel analysis, Neste Oil Corporation also submitted its NExBTL fuel for emissions analysis by Southwest Research Institute (Fanick, 2008). The NExBTL fuel tested is a bio-only pure HDRD (R100). Comparative duty diesel engine combustion emissions testing by Neste and the Nutzfahrzeuge Gruppe (Rothe et al, 2005) are summarized in Table 6.2.

Table 6.2. Effect of blending on an HRDF emissions (NExBTL) (Rothe et al, 2005).

	100% NExBTL	50% NExBTL*	10% NExBTL*
Emissions			
PM	-28%	-5%	0
NOx	-10%	-6%	0
HC	-48%	-48%	-33%
CO	-28%	-22%	-11%
Fuel consumption			
specific**	+5%	+2%	0
volumetric	-1.75%	-1%	0

* Blended with EN 590 ultra-low sulfur fuel.

** Adjusted for density differences in fuels

Neste also conducted emissions testing using a 2007 6.4L Navistar A350 heavy duty diesel engine with after treatment running NExBTL (R100) fuel. These test found CO emissions were slightly higher compared to a baseline ULSD fuel (0.05 g/bhp-hr). Emissions were 17% lower for NOx, and no relative change for HC and PM (Fanick, 2008).

During combustion there are also concerns about speciation of volatile- and particulate-phase polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs). In general, the particulate-phase PAHs and NPAHs were higher than the volatile-phase compounds. In the emissions test cited above, the total PAHs and NPAHs for the NExBTL fuel was lower than the baseline conventional diesel fuel (Fanick, 2008).

The Neste studies concluded that in diesel engines:

- HDRD fuel (NExBTL) showed significant emission benefits compared to ultra-low sulfur conventional diesel fuel. Higher blend percentages resulted in greater benefits.
- Blends below R10 can result in reductions in CO and HC, but not PM or NOx.
- While specific (density adjusted) fuel consumption is better with the HRDF, volumetric fuel consumption is 5% higher because of the lower HRDF density.
- HDRD fuels avoid some of the unwanted effects associated with FAME-based biodiesel fuels (instability, hygroscopicity, fouling, catalyst deactivation, etc).
- Due to the absence of sulfur and aromatic compounds, NExBTL exhaust emissions show significant reductions in many regulated and non-regulated compounds compared to “traditional” petroleum diesel.

7. Renewable Diesel Toxicity

7.1. Human and Ecological Risk Assessment

As is the case with any new fuel formulation where large quantities of processed and synthetic chemicals enter into California commerce, renewable diesel fuels raise concerns about the potential toxicity to humans and to the environment from chemical emissions associated with fuel production, transport, storage and use. Estimating toxicity requires that we follow a standard paradigm for risk assessment applied to renewable-diesel components and combustion. This assessment process includes:

1. Hazard identification,
2. Toxicity assessment,
3. Evaluation of the potential for human and ecological exposure, and
4. Definition of sensitive populations at risk of exposure.

The greatest difficulty we anticipate with determining the human and ecological toxicity of renewable diesel fuels is that renewable diesel fuel is not a defined chemical formulation or mixture of components, but can be formulated from a number of different feedstocks with different chemical components. It is beyond the scope of the multimedia-working group to attempt to consider all of these possibilities. Instead we make recommendations with the understanding that it is useful to focus on the toxicity impacts from the life cycle of one or two typical feedstocks for renewable diesel formulations and then attempt to draw generalizations from these results. Manufacture of renewable diesel 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 renewable diesel, as well as their appropriate disposal, and their degradation products. Extraction of oils from plants will generally require the use of organic solvents such as hexane. 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 put into renewable diesel 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 inhalation, dermal contact, and ingestion through water and food. We anticipate that significant data gaps exist at every stage of this process.

7.2. Acute Oral and Acute Dermal Toxicity

The acute oral and dermal toxicity of pure NExBTL renewable diesel has been assessed for Neste Oil Corporation with testing conducted by SafePharm Laboratories (Mullaney, 2005). Both oral and the dermal testing were conducted using the Sprague-Dawley CD strain rat and using Organization for Economic Co-operation and Development (OECD) testing Guidelines (RIVM, 1994).

During the acute oral testing, two groups of three female rats were administered an undiluted oral dose at a level of 2000 mg/kg bodyweight (Mullaney 2005). The rats were monitored for clinical signs and subjected to gross necropsy after 14 days.

There were no observed mortalities or observed evidence of systemic toxicity. All animals showed expected gains in body weight. No abnormalities were observed at necropsy. The acute oral median lethal dose (LD_{50}) of NExBTL in female Sprague-Dawley rats is estimated to be greater than 2500 mg/kg bodyweight.

During the acute dermal exposures, a group of ten rats (five males and five females) was given a single 24-hour, semi-occluded dermal application of undiluted NExBTL renewable diesel to intact skin at a dose level of 2000 mg/kg bodyweight (Mullaney, 2005). The rats were monitored for clinical signs and subjected to gross necropsy after 14 days.

The dermal-toxicity group of rats showed no mortalities or systemic toxicity. There were no signs of dermal irritation in the male rats. All animals show expected gains in body weight. No abnormalities were observed at necropsy. Hyperkeratinisation or crust formation with or without small superficial scattered scabs, possibly caused by the animals scratching at the treatment site, was noted in females during the study. This may be due to a drying/defatting effect caused by the application of the test material. The acute dermal median lethal dose (LD_{50}) of NExBTL in Sprague-Dawley rats was found to be greater than 2000 mg/kg bodyweight.

7.3. Human Health

Mutagenic Assays

The reverse mutation assay (Ames Test) and the chromosome aberration test using human lymphocytes *in vitro* were conducted using pure NExBTL. The testing was conducted by SafePharm Laboratories for Neste Oil Corporation using OECD guidelines.

During the Ames Test assay, *Salmonella typhimurium* bacteria cultures were treated with NExBTL at five dose levels (50, 150, 500, 1500, and 5000 µg/plate) in triplicate, both with and without rat liver metabolic activation (Thompson 2005). There was no visible reduction in growth of the bacterial background lawn at any dose level. An oily precipitate was observed at and above 1500 µg/plate, but this did not prevent scoring of revertant colonies. No significant increases in the frequency of revertant colonies were recorded for any dose, either with or without metabolic activation. The study concluded that NExBTL can be considered non-mutagenic under the conditions of this test.

The in vitro human lymphocyte assay supplements the microbial (Ames Test) assays insofar as it identifies potential mutagens that produce chromosomal aberrations rather than gene mutations (Scott et al, 1990). Duplicate cultures of human lymphocytes, treated with pure NExBTL, were evaluated for chromosomal aberrations using four dose levels along with appropriate vehicle controls and positive controls (Wright, 2007). The final concentrations of NExBTL used were 78.13, 156.25, 312.5, 625, 1250, and 2500 µg/ml. An oily precipitate of test material was noted above 78.13 µg/ml. The dose levels did not induce a statistically significant increase in the frequency of cells with chromosome aberrations in either the absence or presence of a liver enzyme metabolic activation system in either of two separate experiments. The NExBTL was considered to be non-clastogenic to human lymphocytes in vitro.

7.4. Toxicity Testing of Renewable Diesel Fuel Exhaust Emissions

Note: need to add ARB Results

Diesel exhaust (DE) is a complex mixture of gaseous and particulate matter (PM) components containing hundreds of compounds with the particles less than 2.5 µm having the most relevance for human health impacts (Madden, 2008). Exposure to PM induces increased mortality and some types of morbidity, such as hospitalizations for cardiopulmonary problems. In spite of a large literature on the health impacts of combustion emissions from petroleum diesel, a key uncertainty relates to a range of dose-response relationships. Lung disease links to DE have been examined with variable findings using controlled exposures, but to date relatively little is known about cardiovascular responses (Madden, 2008). Induction of other health effects from DE exposure has been examined mainly through either controlled nonhuman animal model exposures or epidemiological approaches.

To date there are no studies comparing the toxicity of combustion emissions from petroleum diesel with those from renewable diesel and it is unlikely that such comparisons can provide any results useful for decision makers. There are two issues that mitigate the value of these comparisons. First, due to changing regulations and emerging technologies to achieve compliance with regulatory standards, DE from emissions associated with more recent engine/fuel combinations contains less PM and less of certain gases than older engine technologies and fuels (Madden, 2008). This makes both the comparisons to older emissions and the choice of a petroleum baseline for renewable diesel complicated. In more recent diesel formulations, the gas-phase emissions contain proportionally more mass than the PM phase, presenting technological problems in terms of the collection of the DE for future studies and across-laboratory comparison. A second problem is the uncertainty and variation in blending ratios.

7.5. Aquatic Toxicity

Acute short-term exposure of fish, water flea, and green alga to a pure NExBTL renewable diesel water accommodated fraction (WAF) was conducted by SafePharm Laboratories for Neste Oil Corporation. Testing was conducted on Rainbow Trout (*Onchorynchus mykiss*) (Goodband 2006), *Daphnia magna* (Goodband, 2005), and green alga (*Scenedesmus subspicatus*) (Vryenhoef 2005) according to OECD Guidelines. The WAF was prepared by loading declorinated tap water with pure NExBTL and stirring the mixture for 23 hours. After a one-hour settling period, a clear colorless water column with a clear oily slick at the surface was observed. The WAF was removed from the middle of the column and used for the toxicity test exposure. The total organic carbon analysis of all the WAFs used showed no difference from controls that contained no NExBTL.

The concentration, homogeneity and stability of the WAF test material were not determined. No comparisons to conventional diesel or renewable diesel blends were conducted. The concentration, homogeneity and stability of the WAF test material were not determined at the request of Neste Corp.

Rainbow Trout were examined for mortality and abnormalities at 3, 6, 24, 48, 72, and 96 hours. No mortalities or abnormalities were observed throughout all testing and the study concluded that the No Observed Effect Loading rate for Rainbow Trout was greater than 1000 mg/l.

Daphnia were examined for immobility at 24 and 48 hours. No *Daphnia* immobilization was observed throughout all testing and the study concluded that the No Observed Effect Loading rate was greater than 100 mg/l.

Neither the growth nor the biomass of *Scenedesmus subspicatus* was affected by a 72 hr exposure to a WAF loading rate of 100 mg/l. The No Observed Effect Loading rate was greater than 100 mg/l.

7.6. Toxicity and Biodegradation in Aerated Soil

The constantly increasing number of motor vehicles and the increasing volume of oil products transport/distribution has made soil pollution by petroleum-based hydrocarbons a topic of interest to impact assessors (Lapinskiene, et al., 2005). For the impact of petroleum diesel and other oils on soil, there is a large literature that demonstrates that small quantities of oil encourage the growth of microorganisms, since hydrocarbons can serve as nutrients. But at higher levels of pollution, the numbers of microorganisms decrease and their relative composition changes along with quantitative indicators of microbiological processes, such as enzyme activity. There are also studies of the influence of oil products on the population of earthworms. Lapinskiene, et al. (2005) compared the soil impacts of diesel fuel to FAME biodiesel by quantitatively evaluating the microbial transformation of these materials in non-adapted aerated soil. The toxicity levels were determined by measuring the respiration of soil microorganisms as well as the activity of soil dehydrogenases. Lapinskiene, et al. (2005) found that conventional diesel fuel is more resistant to biodegradation and produces more humus products than biodiesel. To date, there are no published comparisons of this type for petroleum and renewable diesel (Knothe, 2010). In a marine context, DeMello et al. (2007) found that n-alkanes decomposed at approximately the same rate as fatty acid methyl esters, and this may indicate potential for renewable diesel degradation rates between that of petroleum diesel and biodiesel. Overall, however, the similar chemistry of renewable and petrodiesel fuels would suggest that their impacts on soil ecosystems would not be significantly different, particularly when the renewable diesel is in a blend (Knothe, 2010). Major differences in soil impact are more likely to be associated with additives than with the hydrocarbon mix. So the key issue with regard to different impact on soil organisms from existing diesel blends and renewable diesel blends will likely be linked to differences in additives.

7.7. Summary of Toxicity Issues

Limited tests on the inherent acute oral and dermal toxicity of pure renewable diesel indicate that renewable diesel has a very low inherent toxicity. In these tests, two groups of three female rats were administered an undiluted oral dose at a level of 2000 mg/kg bodyweight (Mullaney 2005). The rats were monitored for clinical signs and subjected to gross necropsy after 14 days. No increases in mortality or systemic toxicity were found. But these tests are difficult to interpret since there were no controls using conventional diesel or tests using diesel blend.

There have been some initial mutagenic testing of pure (NExBLT) renewable diesel using reverse mutation assay (Ames Test) and the chromosome aberration test using human lymphocytes in vitro were conducted using pure NExBTL. In the Ames test, no significant increases in the frequency of revertant colonies were recorded for any dose, either with or without metabolic activation. In the human lymphocyte test, the pure (NExBTL) renewable diesel was considered to be non-clastogenic to human lymphocytes in vitro.

Insight on aquatic toxicity comes from acute short-term exposure of fish, water flea, and green alga to a pure NExBTL renewable diesel water accommodated fraction (WAF). This study concluded that the No Observed Effect Loading rate was greater than 100 mg/L for all three species.

To date there has been no comprehensive testing of the relative toxicity of the emissions from combusting renewable diesel (blends and/or pure fuel) compared to existing diesel and/or biodiesel. Based on the level of variation in emissions toxicity assessment for petroleum diesel, the chemical similarity of renewable diesel and petroleum diesel, and the likelihood for blends that still contain a significant fraction of petroleum diesel, we expect that it will be difficult of not impossible to organize and interpret a study to compare the toxicity of petroleum diesel relative to renewable diesel blends. Therefore, unless there market evolves to the point where renewable blends contain more than 50% non-petroleum diesel feedstock, there appears to be little value in calling for emissions toxicity studies for renewable diesel.

Toxicity testing to date reveals that the types of renewable diesel tested have limited inherent toxicity and that pure renewable diesel formations are unlikely to exceed the inherent toxicity or mutagenicity of standard diesel. Major differences in health and ecological impact between existing diesel and renewable diesel blends are more likely to be associated with additives than with the hydrocarbon mix. So the key issue with regard to different life-cycle health/ecological impacts from existing diesel blends and renewable diesel blends will likely be linked to differences in additives.

Additionally, the chemical comparison to conventional diesel is important for determining whether or how much additional toxicity tests are required. If a co-processed "green" renewable diesel is the intended product and is chemically indistinguishable from conventional diesel, then no additional toxicity testing should be conducted. Further, if a post-production 100% pure renewable diesel is blended to a proportion such that it is chemically indistinguishable from conventional diesel, then no additional toxicity testing should be required in this case as well.

8. Environmental Transport and Fate of Renewable Diesel

The fate and transport of a fuel and its component chemicals in the environment depend on the multimedia transport properties of its constituent chemicals. The purpose of the multimedia evaluation of renewable diesel is to identify impacts that may be different from the existing baseline fuel, conventional petroleum-based ULSD in the case of renewable diesel. Based on the fuel chemical composition analysis provided by both KOR and Neste Oil Corp., renewable diesel can be regarded as substantially similar to other conventional diesel fuels (Fanick, 2008; Fanick, 2009). The main difference between conventional ULSD and R100 is that the pure HDRD has no sulfur or oxygen and has a very low aromatic compound content. R20 co-processed renewable diesel can be expected to be even closer in chemical composition to conventional ULSD.

Based on the reported similarities in chemical composition, and thus the physicochemical properties governing fate and transport in the environment, between renewable diesel and conventional ULSD, the multimedia environmental behavior of renewable diesel should be expected to also be similar. The transport and partitioning behavior, as well as biodegradation in soils (cf. previous section) can be expected to be similar. The release scenarios and materials compatibility issues should be essentially the same as conventional diesel that is already in wide use.

Even when releases of renewable diesel would not cause significantly greater impacts to the environment, human health, or water resources when compared to ULSD, the impact from releases of associated additives and production chemicals can be of concern. The specific chemical composition of the additives used by various renewable diesel manufactures is not specified and the environmental impact of these additives is not well described.

In the case of co-processed R20, it may be expected that any additives used in renewable diesel are currently in use in ULSD and would continue to be used with no substantive difference in environmental impact due to additives. If this is the case, then new studies on multimedia transport and impact from additives would not be necessary under the assumption that the impacts of additives in ULSD are either acceptable or at lease well-characterized. However, when the additives used in renewable diesel are different from those in ULSD with regard to composition and/or quantity, then a multimedia transport and impact assessment will be needed to determine the magnitude and significance of these additives.

9. Tier I Conclusions

Through a review of the current knowledge on renewable diesel production, use, and environmental impacts, this report provides a foundation to aid the CalEPA Multimedia Working Group formulate recommendations to the California Environmental Policy Council regarding the consequences of increased use of renewable diesel in California. A key goal of this report is to identify important knowledge gaps for a Multimedia Assessment and recommend approaches to address these gaps. This does not always involve additional experiments, but could include additional requests for information from the proponents of any new fuel to be used in California.

Renewable diesel offers several beneficial characteristics that will help California meet State renewable fuel goals:

- Renewable diesel is chemically similar to the ultra-low sulfur diesel (ULSD) fuel already in wide use and environmental releases from the life-cycle of these fuels can be expected to behave in the environment in a manner similar to ULSD releases.
- Renewable diesel is compatible with existing refining and distribution infrastructure and can be used in current diesel engines without modification.
- Pure renewable diesel (R100) has reduced aromatic hydrocarbon content and, since many of the chemicals of environmental concern are aromatic hydrocarbons, this reduction will likely reduce the overall environmental toxicity of the fuel.
- Limited toxicity testing on rats (oral and dermal exposures), water fleas and green algae, and including mutagenic assays, reveals that R100 has limited inherent toxicity and that pure renewable diesel formations are unlikely to exceed the inherent toxicity or mutagenicity of standard diesel. Major differences in health and ecological impact between existing diesel and renewable diesel blends are more likely to be associated with additives than with the hydrocarbon mix.
- Renewable diesel fuels that are made from waste products such as tallow will likely have reduced life cycle environmental impacts compared to fuels made from plant crops. These reduced impacts stem from possible reductions in pesticide, herbicide, and fertilizer use. Further, the use of food supply crops as a fuel is not likely sustainable as global population grows. Further studies are needed to substantiate this logic.

  One life-cycle study sponsored by Neste Oil Corporation found pure renewable diesel (R100) from rapeseed oil or palm oil has a quantitative advantage in energy and greenhouse gas balance compared to conventional diesel. For renewable diesel blends, recent studies on the life-cycle impact considered a range of fuel/vehicle combinations. The results indicate that life-cycle health impacts of renewable diesel blends are not likely to differ significantly from those of petroleum diesel.

On the other hand, the knowledge gaps associated with renewable diesel use in California include:

- **Additives impacts.** The most important information gaps are associated with possible differences in additive use. To provide a stable, useful, and reliable fuel, additive chemicals will need to be introduced into almost all renewable diesel blends. These additives will be required to address issues such as oxidation, corrosion, foaming, cold temperature flow properties, biodegradation, water separation, and NO_x formation. While many of these additives are already used in conventional diesel fuels currently in use, the specific chemicals and amounts to be used in renewable by various producers has not been well defined for the emerging industry in California.

It is important to note that although the use of additives in diesel fuels (conventional or renewable) is common, the impact of various additives is not well known. A careful evaluation of the possible chemicals used in additives would be beneficial to California and may lead to a "recommended list" or "acceptable list" that would minimize the uncertainty of future impacts as new fuels and industry standards are developed. Additional research on the impacts of a "recommended list" of acceptable additives needs to be considered with respect to releases to water and soils and fugitive emissions to air. We note that Fuel additives must have a US EPA registration which documented at: (http://www.epa.gov/otaq/additive.htm). For biocides there is a registration process available from http://www.epa.gov/pesticides/regulating/registering/index.htm.

- **Production and storage releases.** Increased renewable diesel 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 process chemicals. There is also the issue of occupational exposures.

  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. 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.

  As the volume of tallow that is rendered out of state and shipped by rail or truck into California increases, there is a potential impact from releases of large volumes of raw triglycerides to soils or water. The impact of such a release is not well known and additional research would be beneficial as large-scale tallow usage increases.
- **Air Emissions Toxicity Testing.** While there has been air emission toxicity using pure renewable diesel, these studies did not directly compare results to a baseline diesel fuel. Based on the level of variation in emissions toxicity assessment for petroleum diesel, the chemical similarity of renewable diesel and petroleum diesel, and the likelihood for blends that still contain a significant fraction (80%) of petroleum diesel, we expect that it will be difficult, if not impossible, to organize and interpret a study to compare the toxicity of petroleum diesel relative to R20 renewable diesel blends. Therefore, unless there market evolves to the point where renewable blends contain more than 50% non-petroleum diesel feedstock, there appears to be little value in calling for emissions toxicity studies for renewable diesel.
- **Priority list of renewable diesel fuel 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 that may require evaluation, it is critical to identify the priority feedstocks, fuel blends, and additives requiring study for any additional 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 renewable and biofuels industry expands. More sustainable sources of renewable diesel such as yellow or brown grease or tallow may be preferable and should be encouraged.

During this review, we discovered that there are strong similarities between the chemical composition of petroleum diesel and renewable diesel. These similarities and the likelihood that renewable diesel will be used as a blend with petroleum diesel limits the need for additional Tier II Multimedia experiments or an extensive life-cycle impact assessment.

A key goal of this report is to identify important knowledge gaps for a Multimedia Assessment and recommend approaches to address these gaps. This does not always involve additional experiments, but could include additional requests for information from the proponents of any new fuel to be used in California.

As part of the overall multimedia assessment, each company proposing to market renewable diesel within California should provide the California ARB with a production, blending, additives, and distribution strategy that includes potential volumes to be stored and transported along with potential release scenarios that the company may foresee. Each company should also provide a comparative chemical analysis of the product they intend to market (blend or other wise). This analysis should be compared to conventional diesel currently in the market place.

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11. Appendices

11.1. Appendix A: ASTM D975-09b Standard Property Descriptions for Diesel Fuel Oils

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 (Test Methods D 93, D 3828, or D 56)(ASTM 2009).

Water and Sediment
These are primarily considered as post-production parameters since 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 (Test Method D 2709 for all fuel grades except D-4 which requires Test Method D 1796)(ASTM 2009).

Distillation
Distillation is a measure of the volatility of a fuel. "The fuel volatility requirements depend on engine design, size, nature of speed and load variations." Note that heavier fuels will provide the best fuel economy due to having greater heat content (Test Method D 86 or D 2887)(ASTM 2009).

Kinematic 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 (Test Method D 445)(ASTM, 2009).

Ash
The ash content describes the amount of inorganic contaminants such as abrasive solids and soluble metallic soaps. "These can contribute to injector, fuel pump, piston and ring wear, engine deposits", and filter plugging (Test Method D 482)(ASTM 2009).

Sulfur
Limits have been placed on sulfur content for environmental reasons. The limits for Grade S15, Grade S500, and Grade S5000 indicate a limit of 15 ppm, 500 ppm and 5000 ppm of sulfur content, respectively. Note: "other sulfur limits can apply in selected areas in the United States and in other countries" (Test Methods D 129, D 1266, D 1552, D 2622, D 3120, D 4294, or D 5453)(ASTM 2009). In California, the California Air and Resource Board has set the sulfur content for diesel fuels at 15 ppm or less (ULSD).

Copper Strip Corrosion Rating
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 diesel came in contact with metals such as copper, brass, or bronze. Grade 4-D does not have a copper corrosion requirement. (D 130)(ASTM 2009).

Cetane Number
The cetane number is a measure of the ignition quality of the fuel. To obtain the highest fuel availability, the cetane number should be as low as possible; otherwise fuel will be ignited too

quickly. For diesel fuels, a minimum cetane number of 40 is recommended, except for grade 4-D which is 30 (D 613 or D 6890)(ASTM 2009).

Cetane Index

"Cetane Index is a specified as a limitation on the amount of high aromatic components in Grades No. 1-D S15, No. 1-D S500, No. 2-D S15 and No. 2-D S500." The index for all four mentioned grades is 40. Note that it is required that either the cetane index or the aromaticity be met. Grades 1-D S 5000 and 2-D S 5000 and 4-D do not have aromatic content requirements (Test Method D 976-80) (ASTM 2009).

Aromaticity

Aromatics content is significant since it is important to "prevent an increase in the average aromatics content in Grades No. 1-D S15, No. 1-D S500, No 2-D S15 and No. 2-D S500 fuels" since they have a negative impact on emissions. For diesel fuels, the maximum percent volume of aromatics is 35. Grades 1-D S 5000 and 2-D S 5000 and 4-D do not have aromatic content requirements (Test Method D 1319(ASTM 2009).

Operability Requirements

Operability temperature limits for Grades No. 1-D S500, No. 1-D S5000, No. 2-D S500, and No. 2-DS5000 may be estimated by a Low Temperature Flow Test, and Cold Filter Plugging Point Test. Note that satisfactory operability below the cloud point may be achieved depending on use of flow-improver additives, equipment design, and operating conditions. Note that it is "unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions" (ASTM 2009).

Cloud Point

This is an important property as it "defines the temperature at which a cloud or haze of wax crystals appears in the oil [and] relates to the temperature at which wax crystals begin to precipitate from the oil in use". Petroleum based diesel fuel generally has a low cloud point as it is not as susceptible to cold temperatures. There is currently no cloud point specification for diesel (Test methods D 5771, D5772, D5773, or D 2500)(ASTM 2009).

Carbon Residue

"Carbon residue is a measure of carbon depositing tendencies of a fuel oil when heated under prescribed conditions". This property is an approximation since it is not directly correlated with engine deposits. For diesel fuels Grades No. 1-D S15, S500, S5000, the residue maximum is 0.15% mass, whereas for Grades No. 2-D S15, S500, S5000, it is 0.35% mass (Test Method D 524). Note that there is no standard for Grade No. 4-D (ASTM 2009).

Lubricity

In some cases, diesel fuel may have insufficient lubricating properties that can negatively impact the operability of diesel fuel injection systems. This occurs due to by "low viscosity and lack of sufficient quantities of trace components that have an affinity for surfaces". Experts agree that lubricity values above 600 microns may not prevent operability issues, whereas fuels with less than 450 microns should have satisfactory lubricity. The standard for diesel fuels is a maximum of 520 microns for an HFFR test at 60^{o}C (Test Method D 6079)(ASTM 2009).

11.2. Appendix B: Renewable Diesel Additive Chemicals

Figure B-1: Common Antioxidants.

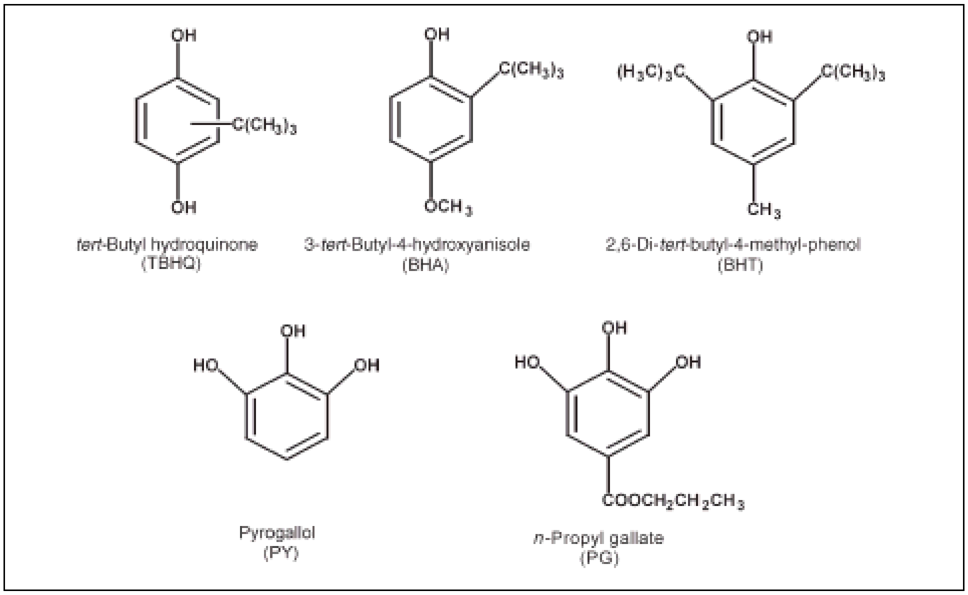
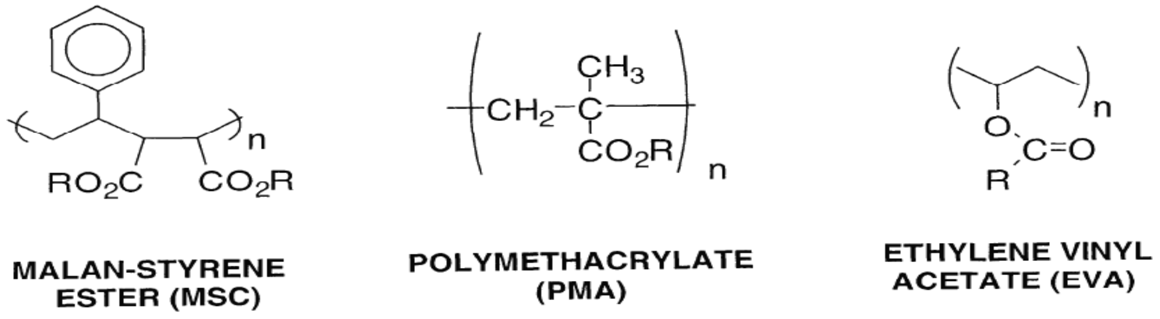


Table B-1. Commercial Biodiesel Antioxidants**.**

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%