COMPREHENSIVE HEALTH AND ENVIRONMENTAL EFFECTS OF BIODIESEL AS AN ALTERNATIVE FUEL

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Abstract

Biodiesel fuel which is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, i.e., rapeseed or soybean oils or animal fats, is used in diesel (compression ignition) engines as an alternative fuel. Registration of biodiesel in the U.S. requires full compliance with regulations of Section 211(b) of the Clean Air Act, requiring comprehensive reporting on the health and welfare (environmental) effects pertaining to the types of emission from biodiesel fuel. Under this regulation, manufacturers of fuels and fuel additives are required to conduct certain tests and submit information regarding the composition of emissions produced by such fuels and fuel additives and the effects of these emissions on the public health and welfare. As a result, search and review of relevant scientific literature in the public domain and private studies were conducted on biodiesel's chemical, toxicological, and environmental information. These results were compiled into abstracts, summary tables by routes of exposure, and summary texts in accordance with registration requirements.
Biodiesel offers significant advantages as an alternative fuel in meeting U.S. Federal clean air standards for reducing targeted emissions. The commonly used blend of 20% biodiesel and 80% diesel fuel yielded percent reductions ranging from: 16-33% in total particulates, 11-25% in carbon monoxide, and 19-32% in total hydrocarbons. Emissions of polyaromatic hydrocarbons were lower for biodiesel blended fuels compared with diesel. Mutagenicity studies on Salmonella typhimurium, for a variety of test fuels (e.g., rapeseed methyl ester, rapeseed ethyl ester, soy methyl ester), all showed substantial reductions in mutagenicity for biodiesel compared with diesel fuel. Biodiesel blends were less mutagenic than diesel fuel and were more mutagenic than 100% biodiesel. Persistence and environmental fate information was found for a single soil/water system and several water studies. In the soil/fresh water system, degradation was monitored by increased bacterial growth and disappearance of methyl esters. Biodiesel (soy diesel) underwent faster biodegradation than diesel, with a faster rate under aerobic conditions than anaerobic conditions. In aquatic environments, the predominant method for evaluation of degradation was evolution of CO2. In general, 100% biodiesel and high biodiesel blends degraded rapidly and fairly extensively, having CO2 evolution percentages ranging from 64-91%. This degradation was more extensive than diesel fuel, which had CO2 evolution percentages from 15-18% in the same time periods of 14-28 days. Biochemical Oxygen Demand (BOD) values were also higher for biodiesel than for diesel.

Introduction

The U.S. Clean Air Act, Section 211(b) grants the Environmental Protection Agency (EPA) broad authority to require testing of fuels and fuel additives for purposes of gaining or maintaining registrations. Under this regulation, manufacturers of fuels and fuel additives are required to conduct certain tests and submit information regarding the composition of air emissions produced by such fuels and fuel additives and the effects of these emissions on the public health and welfare. It is in this latter context, also called Tier I testing, that the current research project was conducted for the National Biodiesel Board to evaluate and summarize a comprehensive search of the open literature as well as private studies pertaining to emissions of biodiesel fuel.

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, i.e., vegetable oils or animal fats, for use in compression ignition (diesel) engines. The transesterified biodiesel displays properties similar to diesel fuel; however, it offers significant advantages as an alternative fuel in meeting U.S. federal clean air standards for reducing targeted emissions. Biodiesel's characteristics of biodegradability, high flash point, virtual lack in toxicity, and improved emissions performance on diesel engines with significant reductions in smoke, sulfur, particulate matter, carbon monoxide, and
hydrocarbons mark its importance as a sustainable fuel for meeting long-term environmental goals. A draft specification is currently under review by the American Society for Testing and Materials and is listed in Table 1.

To maintain biodiesel’s viability in the marketplace, it is important that its products be fully compliant with U.S. regulatory requirements, including their certification under Section 211(b) of the Clean Air Act, 40 CFR Section 79.52 (d). The current literature search, or Tier 1 requirements, for biodiesel was conducted and compiled in accordance with EPA specifications in which information was reviewed for health and welfare effects. Health effects was defined to include both animal and human toxicity studies of any duration, via any exposure route, as well as in vitro, metabolic, and structure-activity analyses. Welfare effects encompassed toxicity studies for multiple categories of organisms (plants, animals, fish, and others) as well as fate and persistence, bioaccumulation, and emission concentrations.

Table 1. BIODIESEL SPECIFICATION FOR PURE (100%)

| PROPERTY LIMITS UNITS | Flash Point 100 min. degrees | Water & Sediment 0.050 max. vol. % | Carbon Residue, 100% sample 0.050 max. wt. % | Sulfated Ash 0.020 max. wt. % | Kinematic Viscosity, 40 C 1.9-6.0 mm2/sec | Sulfur 0.05 max. wt. % | Cetane 40 min. | Cloud Point by customer degree C | Copper Strip Corrosion No. 3 max. | Acid Number 0.80 max. mg KOH/gm | Free glycerin 0.020 max. wt. % | Total glycerin 0.240 max. wt. % |

Methods

The project involved a series of activities organized into literature search, document identification, acquisition, and control, and literature review, evaluation, and reporting.

Relevant private company reports and commercially available databases were selected for searching on the basis of content, scope, and relevancy for information on health and welfare effects. Databases were searched back either for the past 30 years or to their origin (if less than 30 years), for health or welfare effects information, even though the use of biodiesel first occurred in the early 1970s. The literature searches were targeted to biodiesel and its blends and
methyl esters associated with biofuels. Databases that were searched for health and/or welfare effects are presented in Table 2.

Information on both human and welfare effects was compiled from broad searches querying for all information on biodiesel. Databases were searched using the common name, biodiesel, CAS number (67762-38-3), and numerous synonyms and subject keywords (e.g., rapeseed oil methyl ethers, C16-C18 methyl esters, and soy methyl esters) to ensure that retrievals were comprehensive. Once citations relevant to biodiesel material were being retrieved, searches which required further delimiting (i.e., results were too large in number, or not related to health or welfare effects) were performed using additional health and/or welfare related keywords. Examples of health and/or welfare keywords included: health or toxic, acute, chronic, subacute, subchronic, mutagen, carcinogen, effect and environment, effect and ecosystem, fate and environment, transport and environment, persistence and environment, biodegradation and environment, aquatic, fish, wildlife, bird, avian, invertebrate, etc.

Table 2: DATABASE SEARCHED HEALTH EFFECTS WELFARE EFFECTS


Searches covered all years of every database listed, within the 30-year limitation period as prescribed in 40 CFR 79.52(f), unless otherwise indicated. Each search conducted was saved in an electronic file, which included all queries and their results. These files contained all citations prior to screening for relevancy to health or welfare effects. For thoroughness, as well as to avoid exclusion of critical information, some search strategies (e.g., C16-C18 methyl esters) were purposely very broad, rather than limited with specific effect-related keywords (e.g., “biodiesel and health effects” or “biodiesel and toxicity”). Due to this comprehensive aspect, these searches contained many more articles than were selected for summary tables, text, and bibliographies.

Literature searches were screened to identify relevant health and welfare effects information. Citations identified as relevant for health effects lie within the following main categories: non-cancer toxicity, carcinogenicity, mutagenicity/genotoxicity (in vivo and in vitro), other in vitro studies, metabolism,
pharmacokinetics, irritation, and structure-activity relationships (SAR) for all routes of exposure and for all durations of exposure. Information identified as relevant for welfare effects lies within the following major categories: aquatic organisms, terrestrial wildlife, domestic animals, plants and fungi, agricultural vegetation, soil microorganisms, persistence and environmental fate, bioaccumulation, nuisance odor and visibility, and emissions. These exact or similarly described categories for health and welfare effects are referred to in EPA's 211(b) test rule.

Search downloads were screened for relevant citations for health or welfare effects using a series of criteria. Once citations were deemed relevant, they were included in the respective reference bibliography for either effect, and were evaluated for compilation into summary tables and text. For both health and welfare effects, summary text and tables are ordered by either biodiesel exhaust or biodiesel fuel itself. The summary text provides interpretive general findings and conclusions for biodiesel exhaust and biodiesel fuel.

Results

Biodiesel Exhaust

For biodiesel exhaust no health effect studies were found. Mutagenicity studies were located for Salmonella typhimurium, for a variety of test fuels (e.g., rapeseed methyl ester, rapeseed ethyl ester, soy methyl ester) as 100% or blended with diesel, and test materials (e.g., total exhaust, vapor phase of exhaust, exhaust particulate extracts). Of the 10 studies identified, all showed substantial reductions in mutagenicity for biodiesel compared with diesel fuel. Biodiesel blends were less mutagenic than diesel fuel and were more mutagenic than 100% biodiesel (neat biodiesel). A single in vitro study was located for a non-mutagenic endpoint, and provided a toxic dose of biodiesel exhaust volume (from 3-9 L) to kill 50% of cultured mammalian lung cells.

Welfare effects search found a single lethality study reported for fish (bluegill). Acute bioassays of bluegill dosed with engine exhaust from combusted 100% soy methyl ester at fuel/water ratios ranging from 0.12-23.25 mL/L produced a mean mortality (from five tests) of 25.9%, with a mortality range of 18% to 38%.

Information on emissions for biodiesel were from controlled engine emissions studies using neat biodiesel or blends of biodiesel/diesel. The biodiesel fuels tested in summarized studies primarily included: soy methyl esters; rapeseed methyl and ethyl esters; safflower seed, sunflower seed, and cottonseed methyl esters; palm oil methyl esters, canola methyl esters, isopropyl soyate, and methyl tallowate. Observed trends in basic emissions from biodiesel and biodiesel/diesel blended fuels when compared to diesel were decreased emissions of total hydrocarbon, carbon monoxide, carbon dioxide, and total
particulates, and, typically, small increases in nitrogen oxide emissions. When various percent biodiesel blends were tested in the same study, these trends tended to become more apparent as the percent biodiesel increased.

Estimates for these “percent of change” data are presented below to illustrate trend information, and represent only that subset of studies for which data are already reported as percents by the authors. For example, the commonly used blend of 20% biodiesel/80% diesel fuel yielded percent reductions ranging from: 16-33% in total particulates, 11-25% in carbon monoxide, and 19-32% in total hydrocarbons. In general, the soluble organic fraction of the particulate increased slightly, but this increase was offset by a corresponding decrease in solid carbon fraction of the particulate. For nitrogen oxide emissions, a reduction of 2.6% to an increase of 6% were noted for blends of biodiesel compared with baseline diesel. In one engine exhaust test program conducted on two test fuels, 100% biodiesel and 100% diesel, hydrocarbon emissions and sulfates were essentially eliminated by neat biodiesel. Carbon monoxide emissions were reduced by 50% with neat biodiesel. Nitrogen oxide emissions, however, were about 13 percent higher with neat biodiesel compared with diesel. Particulate emissions with neat biodiesel were 30% below levels observed for diesel fuel.

The thirteen studies presenting aldehyde and formaldehyde emissions showed mixed results with some studies reporting decreases in aldehydes and others reporting increases. One study indicated an approximately 20% increase in total aldehydes with biodiesel use, although another study reported a decrease of 4% for 30% rapeseed methyl ester/70% diesel blend compared with baseline diesel. Three studies showed no change in aldehyde emissions from biodiesel compared with diesel fuel. One study comparing 100% biodiesel and 100% diesel fuel noticed significant reductions of formaldehyde and acetaldehyde levels for biodiesel, 30% lower than the levels observed for diesel fuel.

Emissions of polyaromatic hydrocarbons (PAHs) were lower for biodiesel blended fuels compared with diesel. Compared to diesel fuel, neat biodiesel reduced PAH compounds by 75 to 85%, with the exception of benzo(a)anthracone, which was reduced by roughly 50%. In the particulate phase, PAH emissions also tend to decrease for biodiesel and blends, ranging from 13.2-16.5 μg/km for rapeseed methyl esters versus 39.1-55.6 μg/km for diesel. Installation of a catalytic converter was observed to lower levels of PAHs.

Biodiesel Fuel

Health effects search for the biodiesel fuel reported controlled oral and dermal studies in animals. Acute toxicity information was summarized for lethality. Albino rats (males and females) were treated one time via gastric intubation with 100% biodiesel (rapeseed methyl ester or rapeseed ethyl ester), or blends of 50% or 20% biodiesel with diesel, and observed over two weeks. Treatment with
neat rapeseed methyl and ethyl esters and 50% or 20% blends of biodiesel/diesel resulted in no lethalities, and LD50 values were reported to be greater than the highest dose used, 5000 mg/kg. No changes were reported for gross necropsy or body weight.

Acute information was available for animals exposed to biodiesel via dermal exposures. Albino rats (males and females) were treated one time (for 24 hours) with 100% biodiesel (rapeseed methyl ester or rapeseed ethyl ester) and observed over two weeks. Fuels were applied to clipped and unabraded skin and were partially occluded. Treatment with neat rapeseed methyl and ethyl esters resulted in no lethalities, and LC50 values were reported to be greater than the single dose used, 2000 mg/kg. No changes were reported for gross necropsy or body weight. Very slight to slight erythema (skin reddening/irritation) was noted for all animals for both the methyl and ethyl ester, but this had subsided within 12 to 14 days of application. Some desquamation was observed on all treated animals.

For welfare effects, information was available for lethality and behavioral effects in both fish and invertebrate. Lethality information was summarized for a fish (rainbow trout) and an invertebrate (Daphnia magna, the water flea). The 48 hour LC50 value for rapeseed methyl ester in rainbow trout was in the range of 2.8-4.6 µg/L. For Daphnia magna, 48 hour LC50’s for 100% rapeseed ethyl ester, 100% rapeseed methyl ester, 100% methyl soyate, and 100% diesel were reported to be 99, 23, 332, and <1.43 ppm, respectively.

Behavioral information was summarized for a fish (rainbow trout) and an invertebrate (Daphnia magna, the water flea). For rainbow trout, after 96 hours of exposure, the lowest dose at which a behavioral effect was seen for 50% rapeseed methyl ester was 500 ppm, and for 20% rapeseed ethyl ester was 100 ppm. Effects included twitching and erratic swimming, and were seen at 24 hours and 48 hours as well. In the case of Daphnia magna, an observation of immobility was made following treatment with rapeseed methyl ester, but no dose information was provided.

Persistence and environmental fate information was found for a single soil/water system and several (6) water studies. In the soil/fresh water system, degradation was monitored by increased bacterial growth and disappearance of methyl esters. Biodiesel (soy diesel) underwent faster biodegradation than diesel, with a faster rate under aerobic conditions (100% degradation in 7 days) than anaerobic conditions (100% degradation in 14 days).

In aquatic environments, biodiesel fuels which were evaluated included rapeseed ethyl ester, soy methyl ester, and soy ethyl ester (specifically stated). Not all studies provided information on biodiesel blends. The predominant method for evaluation of degradation was evolution of CO2 (the soy diesel studies used
bacterial cell growth, methanol production and disappearance of methyl esters biodiesel, and a single study used gas chromatography in addition to CO2 evolution). In general, 100% biodiesel and high biodiesel blends degraded rapidly and fairly extensively, having CO2 evolution percentages ranging from 64% to 91% (typically after 14 to 28 days). This degradation was more extensive than diesel fuel, which had CO2 evolution percentages from 15% to 18% in the same time periods. When biodiesel blend information was given, they too underwent greater/faster degradation than diesel fuel. Typically, the higher the biodiesel blend the faster the biodegradation. When a parameter such as biochemical oxygen demand (BOD5) was measured for rapeseed methyl ester, rapeseed ethyl ester, and methyl soyate, these values were higher than those for diesel fuel.

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List of References Contained in Literature Search

Health Effects Bibliography


Department of Environmental Toxicology, University of California, Davis, California, for The Montana State Department of Environmental Quality and U.S. Department of Energy.


Welfare Effects Bibliography


