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A paler shade of green? The toxicology of biodiesel emissions: Recent findings from studies with this alternative fuel☆,☆☆

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ABSTRACT

Background: Biodiesel produced primarily from plants and algal feedstocks is believed to have advantages for production and use compared to petroleum and to some other fuel sources. There is some speculation that exposure to biodiesel combustion emissions may not induce biological responses or health effects or at a minimum reduce the effects relative to other fuels. In evaluating the overall environmental and health effects of biodiesel production to end use scenario, empirical data or modeling data based on such data are needed.
Scope of review: This manuscript examines the available toxicology reports examining combustion derived biodiesel emissions since approximately 2007, when our last review of the topic occurred. Toxicity derived from other end uses of biodiesel - e.g., spills, dermal absorption, etc. - are not examined. Findings from biodiesel emissions are roughly divided into three areas: whole non-human animal model exposures; in vitro exposures of mammalian and bacterial cells (used for mutation studies primarily); and human exposures in controlled or other exposure fashions.
Major conclusions: Overall, these more current studies clearly demonstrate that biodiesel combustion emission exposure- to either 100% biodiesel or a blend in petroleum diesel- can induce biological effects. There are reports that show biodiesel exposure generally induces more effects or a greater magnitude of effect than petroleum diesel, however there are also a similar number of reports showing the opposite trend. It is unclear whether effects induced by exposure to a blend are greater than exposure to 100% biodiesel. Taken together, the evidence suggest biodiesel emissions can have some similar effects as diesel emissions on inflammatory, vascular, mutagenic, and other responses.
General significance: While acute biodiesel exposures can show toxicity with a variety of endpoints, the potential effects on human health need further validation. Additionally there are few or no findings to date on whether biodiesel emissions can induce effects or even a weaker response that petroleum diesel with repeated exposure scenarios such as in an occupational setting.
This article is part of a Special Issue entitled Air Pollution, edited by Wenjun Ding, Andy Ghio and Weidong Wu.

1. Introduction

Biodiesel is a liquid fuel produced by reactions of fatty acids with methanol resulting in fatty acid methyl esters (FAMEs). Typically plant based oils rich in triglycerides are utilized though animal derived lipids, and waste oils including phospholipids, can supply the fatty acids but to a much lesser extent. In the US, soy is the primary feedstock utilized while in Europe and Canada, rapeseed and canola are the main sources; canola oil is rapeseed oil that is low (<2%) in erucic acid (docosenoic acid) [19], though a variety of feedstocks have been utilized in both regions. Blends of biodiesel with petroleum diesel are typically used for many onroad and offroad applications [44]. In the US, a 20% and 5% biodiesel in petroleum diesel blend (B20 and B5 respectively) are the typical ratios for vehicles, though neat biodiesel (B100) can be utilized in engines designed for pure petroleum diesel (B0). (Throughout the rest of this paper, diesel refers to petroleum diesel.)

Though the B100 is intended to be primarily methylated or ethylated fatty acids, some nonderivatized fatty acids are contained in the fuel. For soy-based biodiesel, the main fatty acids that were methylated to produce the fuel were C18 fatty acid derived (oleate (C18:1), linoleate (C18:2), linolenate (C18:3)) [28,50]. Additionally other classes of compounds, e.g., aromatics, carbonyls, branched alkanes and alkenes, can

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be detected in the precombustion phase within the engine [23], making the combustion components mixture more complex, and likely the emission compounds more complex as well. Processes that better optimize the availability of cellulose-derived fatty acids for methylation have come under more intense research investigations, due in part to a projected increase use of cellulosic "waste" to meet U.S. Congressional targets for renewable fuels; cellulosic material will increase from approximately 0.8 million gallons in 2013 to a projected 206 million gallons in 2016 [14,47]. The methylation step is usually catalyzed with potassium hydroxide [35] though enzymatic conversion is an alternative catalyst [8]. Byproducts of the reactions include glycerin and methanol; what to do with the large volume of these byproducts is a current issue. Biodiesel production in the US as well as globally has been rapidly expanding in terms of both production and use (Fig. 1; U.S. Department of Energy). The expansion in production is dependent on multiple and complex factors including financial incentives and government policies and regulations.

Biodiesel fuel use offers potential advantages over petroleum based fuels. Production of the fuel could be done locally, which could possibly minimize concerns of availability and transportation issues. Emissions of carbon dioxide (CO_2), a greenhouse gas, are lower with combustion of biodiesel compared to petroleum diesel (US EPA, [26]). Particulate matter (PM), of concern related to premature mortality and increased morbidity [49], also is emitted at lower concentrations [46]. Lower PM2.5 concentrations were observed in an occupational setting with B20 emissions compared to B0 [41]. The total (methylene chloride) soluble organic fraction of biodiesel PM is a greater percentage than diesel; but what must be factored into the amount of organics emitted per distance or per engine work load is that there is an overall reduction in total mass of PM [12]. McCormick [26], citing data primarily generated with heavy duty engines, more comprehensively reviewed the impact of burning biodiesel on the production of regulated ambient air criteria pollutants, greenhouse gases, as well as PM size (which affects the lung deposition distribution and percent deposited within lung sites), and hydrocarbons which may be active in the induction of human health effects and biological responses. His conclusions were than B20 use made little difference in NOx emitted and overall airshed NOx levels, that the greenhouse gas CO_2 decreased with B20 and B100 combustion, and that more data were needed to make firmer conclusions concerning changes in PM size changes and air toxics concentrations emitted.

In order to better understand the balance of advantages and disadvantages of the use of biodiesel in the nation's energy structure, a comprehensive, up to date, life cycle analyses is needed to be in order to determine the overall utility of using a liquid fatty acid based fuel. Life cycle analyses include cradle to grave scenarios, from the production of the feedstock with effects on the environment (soil quality, water usage, wildlife composition changes), production issues (energy input, transportation issues, occupational health protection, byproduct management, etc), storage and transport of the fuel (with potential issues such as spills and leaks), plus issues related to consumer exposure to the fuel (dermal, inhalation) and combustion emissions released occupationally and into the ambient environment, such as discussed in an Oak Ridge National Laboratory Report from a 2009 Cradle to Grave Workshop [9]. One component of the life cycle analyses lacking in adequate data and findings is the endstage use where potential human toxicity could occur. With regards to human biological and health responses, potentiating the toxicity would be predisposing sensitivity factors such as disease states, increased exposures levels, and decreased detoxification mechanisms, among some factors.

The purpose of this review is to examine more recent findings of the toxicity of specifically biodiesel combustion emissions related to human health. Throughout this report when biodiesel or petroleum diesel is mentioned, it refers to combusted fuel products and not the liquid fuel itself. Potential biological responses to biodiesel not combusted, e.g., dermal absorption of the fuel, are not examined in this review. The reader is referred to a 2007 review [38] of then reported effects of biodiesel toxicology with additional literature reported in a book chapter related to biodiesel emission toxicology [25]. A search with the term "biodiesel" in PubMed revealed 66 and 129 hits for the years 2006 and 2007, respectively, but an increase to 1812 and 1620 hits in 2014 and 2015, respectively. Included in this update are reports utilizing a variety of approaches that assist in determining potential health related outcomes from exposures to biodiesel or components of biodiesel. Typically surrogates of health effects are measured and reported as an early biomarker in a pathway believed to be involved in the development of an adverse response or disease. The reader is referred to the most recent US Environmental Protection Agency (U.S. EPA) Integrated Science Assessment (ISA) final reports for PM [49], carbon monoxide [45], and oxides of nitrogen [48] for toxicological information related to those specific emissions found in biodiesel components.

2. In vivo exposures using animal models

Exposure of mice to B100 and B0 (i.e., petroleum diesel) PM via pharyngeal aspiration induced increases in total cells recovered in the bronchoalveolar lavage fluid relative to unexposed control mice at 1 and 7 days post exposure, with the outcome resolving at day 28 after exposure. [51]. The increase at day 1 was attributed to mainly neutrophilia, and at day 7 to an increased macrophage number. B100 induced a greater increase in neutrophils (Day 1) and macrophages (Day 7) than B0 implying a greater inflammatory potency. Similarly total protein in lavage fluid as a marker of permeability was increased more in B100 treated mice compared to B0. In lung tissue homogenate, only B100 induced an increase in lactate dehydrogenase activity (as a marker of cell viability) on Day 1 post exposure, while both PM types induced increases on Day 7 and 28. B100 PM induced significantly more on Day 28 than B0. There was a persistence of increased tissue oxidation markers (carbonyls and 4-hyroxynonenal) out to 28 days with B100 exposure, but

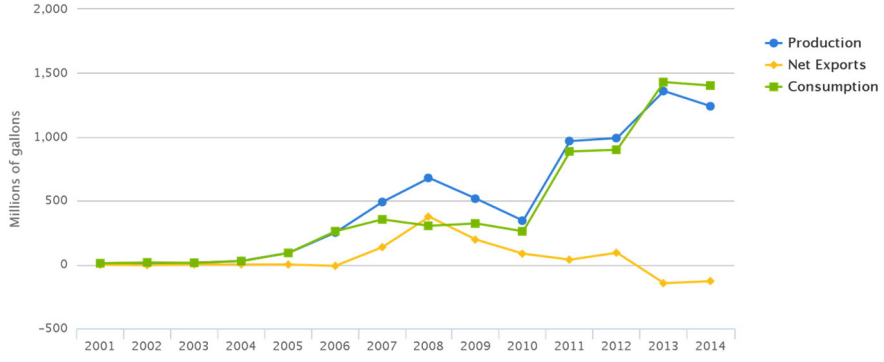

Fig. 1. U.S. biodiesel figures (production, consumption, exports) up to 2015. Numbers are given in millions of gallons. Source: U.S. Department of Energy. http://www.afdc.energy.gov/data/10325 Accessed 11 January 2016.

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