Improved Oxidative Stability of Biodiesel Fuels: Antioxidant Research and Development

AF 4 Project 1
Measurable Targets for the period January 1, 2007 to April 30, 2007

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Abstract: Biodiesel is a domestic, renewable fuel that is gaining wide acceptance, especially in Europe. When blended with conventional petroleum diesel, biodiesel reduces hydrocarbon, particulate and carbon monoxide emissions, while having minimal to no effect on NOx. It also improves lubricity, lowers sulfur, and has a high cetane number. The promise of biodiesel is tremendous, but some significant obstacles remain to its complete acceptance by diesel engine manufacturers, most significantly with respect to oxidative stability. This project will investigate the factors associated with biodiesel oxidative stability, including natural and synthetic antioxidants, storage and processing conditions. Results of this project will provide much needed guidelines to industry with regards to storage conditions and antioxidant additive levels. Additionally, biodiesel production changes will be recommended which will optimize the preservation of natural antioxidant levels in the fuel. Finally, factors required for the development of a user-level sensor for biodiesel oxidative stability will be quantified.

Introduction: Biodiesel is a renewable fuel for diesel engines that is derived from natural oils and fats (e.g., vegetable oils, recycled cooking greases or oils and animal fats) and that specifically meets the specifications of ASTM[#] D 6751. It is composed of monoalkyl esters of long-chain fatty acids, produced by the transesterification with alcohol of the above natural oils. Biodiesel is a US Department of Energy (DOE) designated alternative fuel and is registered as a fuel and fuel additive with the US Environmental Protection Agency (EPA). Research on the use of alternative fuels such as biodiesel is mentioned as one of many elements of the DOT Strategic Plan.[i]

Biodiesel offers many benefits over conventional petroleum diesel. It burns cleaner, with net emissions reductions in particulates, hydrocarbons, and carbon monoxide (and with zero to slight increases in NOx). Biodiesel also possesses a high cetane number (averaging over 50) and improves petroleum diesel cetane performance when blended. Since it is naturally low in sulfur content, it also lowers sulfur emissions when blended with petroleum diesel. Biodiesel blending also imparts improved lubricity to petroleum diesel.

Since it is domestically produced, biodiesel shows great potential for reducing U.S. dependence on foreign energy supplies. It provides a “closed economic loop” in that the

[#] ASTM International, originally known as the American Society for Testing and Materials (ASTM) feedstock can be grown locally, the biodiesel can be produced locally, and the fuel can be used locally. Furthermore, it is evident that very minimal to no infrastructure change is necessary to implement widespread biodiesel use. Biodiesel blends can be used in any diesel engine and can be transported and stored using existing infrastructure.

Pure biodiesel is environmentally non-toxic and biodegradable. With its high energy balance of 3.2 to 1, biodiesel provides a beneficial 78% life cycle CO_2 reduction. [ii]
While biodiesel shows such tremendous potential, there are still unresolved challenges to its complete acceptance. In the list of Research Priorities from the Biodiesel Technical Workshop in Denver CO in November 2005, the top two items identified by this group of experts were: 1) Fuel Quality and Quality Standards, and 2) Fuel Stability. A distant third priority was cold flow properties. The fuel quality and standards issues are being addressed in the ASTM Fuel Standards subcommittee. Thus, the single most critical acceptance issue requiring research and development is that of biodiesel stability; in particular, oxidative stability.

Oxidative Stability. All fuels (whether petroleum or biofuels) are subject to degradation over time during storage. Currently, best practice involves limiting the storing of biodiesel or biodiesel blends to six months or fewer.

This degradation of the diesel fuels is generally due to oxidation, which is indicated by increased acid number and viscosity, as well as the formation of gums and sediments. The oxidation process starts with the formation of hydroperoxides by the addition of an oxygen molecule to a carbon atom adjacent to a C=C double bond. As oxidation proceeds, the peroxides break away to form aldehydes and short-chain acids. Alternatively, peroxides may generate free radicals, which promote polymerization and crosslinking among the olefinic (C=C containing) molecules. Therefore, oxidation reactivity is related to the degree of C=C bonds in the fuel. Increased content of the C=C bonds correlates to decreased oxidative stability of the fuel. The increase in instability of a given diesel fuel molecule is generally directly proportional to the number of C=C bonds in the molecule (i.e., a molecule containing two C=C bonds has half the stability of a molecule containing one C=C bond). The oxidative stability of a diesel fuel is estimated using the iodine number (ASTM D 1510), and the longer-term stability of a diesel fuel can be evaluated using an accelerated stability test (ASTM D 2274). The iodine value is defined as the amount of iodine (in grams) absorbed by 100 mL fuel, and it is a very crude but commonly used indicator of the level of saturation of an oil. Biodiesel usually has a significantly higher content of unsaturated fatty acid derived esters, therefore their iodine values are noticeable higher than that of petroleum diesel. [iii]

Some metals act as catalysts for the oxidation process, notably brass, bronze, copper, lead, tin, and zinc. Steel and aluminum equipment are recommended for the manufacture, processing and storing of biodiesel. However, some feedstock for biodiesel production possibly contains some metals at very low concentration. For instance, 0.03-0.05 ppm and 0.02-0.06 ppm copper are present in the crude and refined soybean oil, respectively and could possibly be retained in biodiesel[iv].

Oxidation of oils can be reduced or slowed by means of antioxidants (AO). Soybean oil and other vegetable oils possess natural AOs, which provide some degree of protection against oxidation. These are generally lost or reduced as a result of the biodiesel production process, however.[v]

Objective: *The overall objective of this proposed research is to improve the acceptability of biodiesel as a commercial fuel 1) by developing new AOs in order to enhance stability and 2) by exploring alternative processing strategies that will retain natural AOs in biodiesel.* This project supports the *Alternative Fuels* focal area in fulfilling the Mission of the MIOH.

Measurable targets for Project 1 are as follows:

1. Measure baseline oxidative stability properties of soybean biodiesel , including Oxidation Stability Index (OSI), ester content, acid number, viscosity, and polymer content will be documented for fresh biodiesel. These results will include blends of 2%, 5%, 20%, 50% and 100% biodiesel with standard ultra low sulfur diesel (ULSD). These will also be determined for biodiesel blends with various levels of trace metals, likely to be encountered under storage:

2. Oxidative stability properties of soybean biodiesel , including Oxidation Stability Index (OSI), ester content, acid number, viscosity, and polymer content will be documented for biodiesel with various levels of natural and synthetic antioxidants, as described in the proposal..

Reporting Period for Project 1: January 1, 2007 to April 30, 2007

1. A graduate student has been hired and is actively engaged in the project. He has mastered the use of the Rancimat device for the determination of oxidative stability of biodiesel blends, as well as other techniques, such GC-FID and GC-MS.
2. Soy, cottonseed and poultry fat Biodiesel (BD) has been obtained from Biodiesel Industries, and baseline oxidative stability measurements of pure BD and BD blends with ultra-low sulfur diesel (ULSD) have been determined.
3. Sample storage containers have been acquired and blends are being prepared for storage and later tests.
4. Preliminary studies on changes in oxidative stability with different concentrations of six different natural and synthetic antioxidants are underway.

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[i] Department of Transportation Strategic Plan 2003-2008; http://www.dot.gov/stratplan2008/strategic_plan.htm#_Toc52257065

[ii] Biodiesel Handling and Use Guidelines. DOE/GO 102004-1999, Revised Nov. 2004

[iii] J. Van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe; Biodiesel Production Technology, August 2002–January 2004; NREL/SR-510-36244, June 2004.

[iv] Ibid. Biodiesel Handling and Use Guidelines. DOE/GO 102004-1999, Revised Nov. 2004

[v] Characterization of Biodiesel Oxidation and Oxidation Products; CRC Project No. AVFL-2b, Task 1 Results: Technical Literature Review. SwRI® Project No. 08-10721, August 2005.