

Toxicology, Biodegradability and
Environmental Benefits of Biodiesel

by

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The University of Idaho has been involved with the production and testing of Biodiesel since 1979. This paper will describe results of current research dealing with the environment, toxicology biodegradability, and recent emissions tests. This data will provide prospective on where the industry is going and the effect of Biodiesel on the environment. (A complete set of data slides used in the discussion is available by contacting the NBB office).

First, a look at the University of Idaho program. The tractor on the US Department of Energy Display is a University of Idaho tractor. It has had 100% rape oil in it for about five years, and a 50% blend of rape methyl ester in it for the last seven years. It has been in operation for over 12 years. A second tractor is under test that has had Biodiesel fuel in it for seven years. Three pickups are available for on-road tests: one is a Ford which runs on 20% raw rapeseed oil. The Ford Navistar engine with precombustion chamber allows it to bum raw rapeseed oil. This vehicle has accumulated nearly 3 1,000 miles, and, as long as the blend doesn't get too high it performs well. The Dodge, operated by the Idaho Department of Water Resources, Energy Division has over 40,000 miles on a blend of 20% rape methyl ester. A third on-road vehicle is a 1994 Dod2e that is running 100% ethyl ester of rapeseed oil. Recent emissions tests were performed at Los Angeles Metropolitan Transit Authority (LA-MTA). Two vehicles were driven to California for the tests. The 94 Dodge accumulated 2400 miles, and carried all of the fuel needed for the emissions tests as well as for travel back and forth.

For producing fuel from rapeseed two small presses are available, both were donated by a local seedsman, Brocke, Inc. An open vat batch process is used for transesterification. Most recently recipes have been developed for using ethanol in the transesterification process. Ethanol is preferable to methanol because of the hazardous handling problems with methanol and because ethanol is a renewable, agriculturally produced product. An Idaho ethanol producing company, Simplot)lot Corporation, has cooperated in these tests. They not only produce ethanol, but they also have a lot of waste vegetable oil from their french fry operation. This looks like it may be a very good marriage for a potential small Biodiesel plant.

At the University of Idaho, several different kinds of engine testing have been conducted. An electric dynamometer and three long term engine test cells are available. Basic engine tests, injector coking and durability tests have been performed. The conclusion is that biodiesel is essentially similar to diesel in terms of effect on the engine.

One of the values of biodiesel is that it's a renewable fuel. When ethanol is combined with rapeseed oil or soybean oil, two renewable products are being used. Biodiesel is safer than petroleum diesel. The higher flashpoint is a very significant benefit of vegetable oil. Biodegradability is important, particularly if the fuel is used in environmentally sensitive areas. Examples of places with potential to use Biodiesel are Glacier National Park, Yellowstone National Park and the Grand Canyon. In some wilderness areas or along pristine streams: anywhere diesel fuel spills are very damaging to the environment, biodegradability and toxicity can be very important.

Safety

Diesel fuel has a flashpoint of about 175' F. Rape methyl ester and ethyl esters are over 300' F. In handling, storage and transport, in collisions or other situations where this fuel might tend to burn the benefits of methyl and ethyl esters are obvious from a safety standpoint.

Biodegradability

The biodegradability project requires data on COD and BOD, biodegradation in aqueous solutions, and biodegradation in soils. The COD and BOD data are not yet available. It is generally better if COD and BOD data have very low values, because it indicates how much of this material is in water, sewage or in an effluent. However, when biodegradation is of interest, and it is desirable to have the material to break down very quickly, high BOD and COD would be desired. Methyl and ethyl esters have high COD and BOD values. Biodegradation was determined in an aqueous solution using a shake flask test. One of the slides shows biodegradation for 28 days. It compares rapeseed methyl ester, rapeseed ethyl ester, diesel and dextrose. Note in this test that both esters degraded more rapidly than the dextrose control. The esters degraded at almost identical rates to about 95% at the end of 28 days. The diesel fuel in this test was about 40% biodegraded after 28 days. The biodegradation in soils has not yet been completed.

Acute Aquatic Toxicity with Daphnia Magna

The acute aquatic toxicity test with Daphnia Magna was carried out by CH2M Hill in Eugene, OR under contract. First, the methyl and ethyl esters of the vegetable oils are not soluble in water, and because of that they form a sheen on the surface of the water. This sheen could be easily skimmed off, but if not, the Daphnia Magna get captured in this film. In some cases it is

difficult to tell if it is the sheen that kills them or the toxic nature of the product. The LC50 for Daphnia Magna are plotted on a log scale to show the relative relationships. The data compares table salt (NaCl), diesel and methyl and ethyl ester of rapeseed. The data is given as LC50: this cycle was doubled in length to 758 seconds. The Arterial cycle used a replication of going from 0 to 40 and back down to 0. The EPA cycle for heavy duty vehicles is 1060 seconds. Twenty-six arterial cycles and 13 EPA Heavy Duty cycles were conducted during our series of tests. The vehicle is actually driven on the dynamometer. The driver has a crosshair that he follows on a computer screen and can deviate for not longer than two seconds or it invalidates the test. The vehicle tested was a 1994 Dodge with a Cummins diesel 5.9 liter, turbocharged and intercooled, direct injection engine.

The fuel changing system consists of five gallon fuel containers with quick-couplers both on them and in the vehicle. To reduce the time for changing fuels the vehicle fuel filter was removed and filters were placed on the fuel containers. Timing tests determined that it takes about 20 seconds of idling before the return line starts flowing the new fuel. For the actual tests, the time used was 50 seconds of separation time. The fuel changing procedure was to connect the delivery line to the vehicle and the return line to a waste tank, idle the vehicle for 50 seconds, then connect the return into the fuel delivery tank and continue idling the engine until ready for the next test. The fuels tested were: Phillips low sulfur diesel control fuel, rapeseed methyl ester and rapeseed ethyl ester (REE) for main effects. Following, the neat fuels, 20/80% and 50/50% blends of rapeseed esters and diesel control fuel were tested.

The test design was three replications of main fuels on each cycle, two replications of the blends on the arterial cycle, two replications of the 20% blends on the EPA cycle. The 50% blends were not run on the EPA cycle. The order of testing was randomized. Because emissions testing is not very predictable (it doesn't take much of an instrumentation problem to really slow the tests down), the test was designed with the less important tests at the end. The arterial cycle was tested first because it was the shortest and easiest to repeat, then the EPA cycle was tested.

Some back-to-back runs were included to test for effect of the previous fuel on the next test. The data show that the fuel change procedure was successful. The EPA test cycle, a slightly longer test gave different absolute values, but relative differences were the same. Statistically significant differences ($p < .05$) were measured for HC, CO, CO₂ and NO_x. PM differences were not statistically different.

Emissions Data: Arterial and EPA cycles

Hydrocarbons were reduced significantly. They start out at .85 gm/mile for diesel and drop to about .3 gm/mile for the RME and REE.

Carbon Monoxide (CO) shows an initial large drop with 20% ester and then a lesser drop with 50% ester. The drop from 50% to 100% ester was almost the same reduction as from 20% to 50%. The ethyl ester has slightly lower CO than the methyl ester. Eight different replications are presented at the 100% level. CO dropped from about 3.5 gm/mile for diesel down to about 1.7 gm/mile for REE.

Carbon Dioxide (CO₂) level is increased as it should if carbon monoxide is reduced. The CO₂ goes from 658 gm/mile for diesel to 658 gm/mile for REE and RME.

Nitrous Oxides (NO_x) are reported by several researchers to be increased with Biodiesel. This data shows a reduction in nitrous oxides, very consistently, throughout all these tests. NO_x started at 6.2 gm/mile for diesel and goes down to around 5.6 gm/mile with 100% ester (with slightly more reduction with REE than RME).

Particulate Matter (PM) increased. A drop was measured at 20% ester, but then it increased as the percent ester in the blend increased. PM starts at .3 gm/mile with 100% diesel, drops down to .27 at 20% ester, and goes up to .33 gm/mile at 100% ester. The PM data is not statistically different.

Summary of Emissions Tests

The last set of slides are summaries of the emissions data with the RME and REE averaged together. CO and CO₂ are plotted on the same chart. The CO drops and the CO₂ increases. HC and NOX are shown together and both drop nearly linearly. The last slide shows PM for ester blends and diesel, PM drops slightly at the 20 percent blend and increases at 100 percent ester. In the test, hydrocarbons were reduced 53%, carbon monoxide was reduced 49.7%, nitrous oxides were reduced about 10%, carbon monoxide increased about 1% and particulate matter increased by 13.6% when 100% esters are compared with the low sulfur diesel control fuel.

Conclusions

The data reported in this paper shows levels of safety, biodegradability, toxicity and emissions.

1. Biodiesel is safer because the flashpoint is over 100 degrees F higher than that of diesel.
2. Biodegradability of rape esters was higher than the biodegradability of reference dextrose and much higher than diesel fuel.
3. Toxicity of Biodiesel was at least 15 times less than diesel and probably even much less than that.
4. Emissions results for 100 percent ester compared with diesel control fuel show a 53% reduction in HC, a 50% reduction in CO, 10% reduction in NOX and 13.6% increase in PM. A slight drop in PM was observed with a 20 percent ester/80 percent diesel blend.