

Development of Rapeseed Biodiesel for Use in High-Speed Diesel Engines

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***University of Idaho
Department of Biological and
Agricultural Engineering***

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Disclaimer Statement

This report contains a summary of research results. These are not to be construed as recommendations for the use of any agricultural chemical that may be mentioned. Pesticide users are responsible for reading the label and following all directions.

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PREFACE

Vegetable oil as an alternative fuel (Biodiesel) has been under study at Idaho since 1979. Researchers at Idaho have pioneered the use of vegetable oil, particularly rapeseed oil (*Brassica napus*), as a diesel fuel substitute. Although short term test using neat vegetable oil have shown promising results, longer term tests using vegetable oil produced injector coking, more engine deposits, ring sticking, and thickening of the engine lubricating oil. This experience led to the use of modified vegetable oil as a renewable fuel. Although there are many procedures or ways to modify vegetable oil for fuel use, the transesterification process has been found to be the most viable modification process for Idaho researchers.

The national need for this research has been firmly established. Vegetable oil based fuels and lubricants could reduce U.S. dependence on imported petroleum products not only for fuel but also for lubricants, hydraulic fluids, dilutants and other fluids. The United States is now depending on foreign sources for more than 50% of the crude petroleum used. Even if this were an inexhaustible supply, world politics are such that the foreign flow of oil could be terminated at any time.

The specific activities of this project in the last three years relate to demonstrating the potential of commercializing Biodiesel fuel (rapeseed ethyl esters, rapeseed methyl esters and ethyl ester of hydrogenated waste cooking oil) as viable substitutes for petroleum-based diesel fuel. The U.S. Department of Energy's Pacific Northwest & Alaska Regional Bioenergy Program has been the primary sponsor for this activity. This research was conducted by a team of scientists at the University of Idaho, Department of Biological and Agricultural Engineering. The report summarizes data taken during the period of August 3, 1993 to May 31, 1996 as part of DOE BPA Contract #93BI09233.

Activities and projects reported include:

- Commercialization of Biodiesel Conferences;
- Demonstration of the On-the-Road Use of Biodiesel;
- Development of Rapeseed Biodiesel for Use in High-Speed Diesel Engines;
- Expanded Rapeseed Ethyl Ester Demonstration and Testing, and cooperative Development of Hydrogenated Soy Ethyl Ester Biodiesel;
- Comprehensive Emissions and Performance of Biodiesel at the Southwest Research Institute;
- Long-term Demonstration and Performance Testing Activities;
- Biodegradability and Toxicity Studies with Biodiesel;
- Economics of Biodiesel; and
- Other industrial applications of vegetable oil esters.

This research was to emphasize oil produced from rapeseed. Reasons for this emphasis relate to the fact that rapeseed is higher in oil than most seeds, it can be grown in many places, oil can be extracted and used much easier than alcohol can be produced, especially on farms. The

U.S. Agricultural sector has the capacity to produce sufficient rapeseed oil for on-farm Biodiesel (about 10% of the diesel fuel used in the U.S.), although this may not be the best use of the fuel. This research was conducted to develop the technology necessary to produce, process, and utilize vegetable oil as a diesel fuel substitute for in the Pacific Northwest. The project was expanded to include waste vegetable oils which would reduce the cost of Biodiesel.

Copies of this report can be obtained from the Department of Biological and Agricultural Engineering, University of Idaho, Moscow, Idaho 83844-2060. The price charged will be that in effect at time of order but not less than \$100.00 US plus shipping.

Charles L. Peterson
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EXECUTIVE SUMMARY

Biodiesel, produced from winter rapeseed as methyl or ethyl esters has been shown, as a result of this research, to be an excellent fuel for diesel engines. The major advantages are that it is renewable, it is biodegradable performing as well or better than the controls, it passed all of the toxicity tests at a rate equivalent or higher than diesel, it has a high flash point in the neat form, it is almost odorless, it reduces total CO₂ released to the atmosphere because of that used by the plant in growing the oil, and it reduces some tailpipe emissions notably HC and CO. Areas needing further study are the NO_x and PM tradeoff in the emissions, cold weather properties, feedstock supply, and cost to the end user.

Hydrogenated soy ethyl esters (HySEE) were also found to perform adequately in engine tests. While all of the tests to date show the use of the waste oils is possible, additional data needs to be developed before HySEE will be recommended for general use. Processing these materials requires that heat be supplied to keep them above their melting temperatures and recipe adjustments must be made to account for the variable free fatty acid content of the oil. HySEE has cold weather properties that would require heated lines and fuel tanks in even the moderate seasons of the Pacific Northwest.

Specific findings of this research are summarized below.

- **Commercialization of Biodiesel Conferences**

Two Commercialization of Biodiesel Conferences were held, one in Moscow, Idaho and the other at Mammoth Hot Springs, Yellowstone National Park. Conference proceedings are available for the first conference and will soon be available for the second. Two position statements were developed: the first, Establishment of Engine Warranties - Biodiesel (methyl or ethyl ester of plant oil or animal fats is a new fuel which is being tested under a wide range of conditions including both neat and blended with petrodiesel. Users of this fuel should be aware, however, that currently there is no fuel specification for Biodiesel and therefore, engine manufactures cannot fully recognize it as equivalent to diesel. Users of this or any fuel not meeting manufacturers' published fuel specification requirements assume warranty liability for failure of components or emission certification traceable to the fuel. Non-fuel related warranty issues are not affected by the use of Biodiesel; second, Environmental and Health Benefits - Biodiesel; with respect to petroleum diesel, demonstrates the potential for improved performance in the areas of safety, health, and environmental protection. It offers the following benefits: improved biodegradability; reduced CO and HC emissions; reduced particulate emissions in most cases, especially soot; safer for handling in the neat form due to the high flash point; increased oxidizing catalytic converter effectiveness with organic compounds; CO₂ recycling, thus reducing greenhouse gas emissions; and a positive energy balance.

Biodiesel may also offer the following benefits, however, additional research data are needed for verifications: reduced oral and dermal toxicity; reduction of ozone precursors; reduced PAH emissions; and reduced mutagenic and carcinogenic compounds associated with Biodiesel exhaust.

The following issues need resolution: increased NO_x levels associated with Biodiesel exhaust; aldehyde levels show reductions in some tests; the insoluble nature of biodiesel clouds information on water toxicity; some PAH's, such as benzo(a)pyrene may be increased; and the benefits of biodiesel blends (with petroleum diesel) are less than for the neat fuel. Some of these effects are nonlinear.

- **Demonstration of the On-the-Road Use of Biodiesel**

A 1994 Dodge 2500 turbocharged and intercooled diesel pickup fueled with 100 percent ethyl ester of rapeseed oil was driven a total of 33,700 miles. The truck averaged 18 mpg using 1875 gallons of REE. No problems or unusual events were encountered with the truck operation except for the failure of fuel lines which was corrected by changing the line material. The truck was completely unmodified as to the engine or fuel system. The truck passed through 21 different states and Mexico. At one point, it completed a trip coast-to-coast and back. The drivers were enthusiastic about its performance, range and driveability.

Two additional on-road pickups were operated on a mixture of 20 percent Biodiesel and 80 percent diesel. In 1992, a Ford F250 with a Navistar 7.2 L, precombustion chamber diesel and a Dodge 2500 with Cummins 5.9 L diesel were purchased. The Ford has been operated on 20% raw rapeseed oil-80% 2-D and the Dodge on 20% methyl ester of rapeseed oil-80% 2-D.

1992 Dodge. This pickup was operated on 20 percent RME and has surpassed 145,000 km (90,000 miles) and is expected to reach the 161,000 km (100,000 miles) in Sept. 1996 and will undergo a complete engine analysis. The mild steel tank for RME carried in the bed of the truck and the small mixing chamber also of mild steel experienced considerable rust. The vehicle also has had frequent fuel filter replacements thought to be in large part due to the rust problem. The tanks were changed to stainless steel and the fuel supplier changed which has almost eliminated the excessive filter plugging. The Dodge injectors were cleaned at 79,340 km (49,300 miles) due to rust, otherwise the vehicle has been driven normally; oil analyses did not indicate any abnormal engine problems.

1992 Ford. The second pickup was selected for operation on a blend of 20% raw rapeseed oil and 80% 2-D because of the precombustion chambered engine and has surpassed 113,000 km (70,000 miles). The injectors had accumulated excessive deposits and were cleaned at 73,200 km with a noticeable improvement in performance. It has no problems starting as long as the fuel mixture is kept below about 30% vegetable oil. It is expected to reach 161,000 km (100,000 miles) in 1997; oil analysis have not indicated any unusual engine wear.

- **Development of Rapeseed Biodiesel for Use in High-Speed Diesel Engines**

Commercial Process - A commercial process design was developed for producing 100,000 gallons of rapeseed ethyl ester per year or approximately 500 gallons per day. This process uses a scaled up version of the process which is currently being used at the Biological and Agricultural Engineering Department at the University of Idaho. This process, a batch process currently of approximately 250 gallons per batch, uses ethanol, KOH and a water wash. The water wash has been reduced to about 0.5 gallons of water per gallon of REE. Reuse of the end water in the initial wash could cut this use by one third.

Storage - Methyl and ethyl esters, prepared from various vegetable oils by the process of transesterification, have shown much promise as fuels for all types of diesel engines. This project was designed to determine the extent of deterioration of Rape Methyl Ester (RME) and Rape Ethyl Ester (REE) in storage. The study involved triplicate samples of RME and REE stored in glass and steel containers at room temperature (inside) and at the local ambient outdoor temperatures (outside). The study was conducted for 24 months. At the beginning of the study and at 3 month intervals, samples were taken for measurement of peroxide value, acid value, density, viscosity, and heat of combustion. At the conclusion of the study, engine performance tests were conducted with the two year stored REE and RME, new REE and RME, and low sulfur diesel reference fuel. On the average, the esters tended to increase over time in all of the previously mentioned properties with the exception of heat of combustion, which decreased. Regression models are presented to predict the deterioration with time. Engine power varied less than 1% for both Biodiesel fuels compared to the stored counterparts while smoke density decreased 3.2% for the stored RME and increased 17.5% for stored REE.

Pour Point Depressant Screening - The cloud and pour points of rapeseed ethyl ester (REE) and hydrogenated soy ethyl ester were evaluated using a winterization method and a number of pour point depressants and compared to the baseline values for each fuel. ASTM standard D2250 and D97 were followed to measure cloud and pour points respectively. The lowest pour point from these tests (-30°C) was from winterization followed by 0.5% Rohm-Tech (viscoplex, type 10-30). None of the additives performed sufficiently better than number one diesel fuel, which was selected as the pour point depressant for engine testing and environmental quality.

- **Expanded Rapeseed Ethyl Ester Demonstration and Testing, and Cooperative Development of Hydrogenated Soy Ethyl Ester Biodiesel**

Performance tests demonstrated that HySEE can be used to successfully fuel a diesel engine. In general, the tests performed have shown that torque and power were reduced about 5 percent compared to 2-D and fuel consumption increased 7 percent. Specific conclusions of

this study were: fuel characterization data show some similarities and differences between HySEE and 2-D. a) Specific weight is higher for HySEE, viscosity is 1.9 times that of 2-D at 40°C (104°F), and heat of combustion is 12% lower than 2-D. b) Sulfur content for HySEE is 36% less than 2-D; the average HySEE injector coking index was 3.07 and 2-D was 1.00. Visually, all injector coking was low especially compared with older tests that included raw vegetable oils; opacity was decreased by as much as 71 percent compared to 2-D; at rated load, engine power produced by HySEE decreased by 4.8 percent compared to 2-D; peak torque for HySEE at 1700 RPM was reduced by 6 percent compared to 2-D while at 1300 RPM it was reduced only 3.2 percent, demonstrating a flatter torque curve characteristic of Biodiesel; the average fuel consumption (g/s) on a mass basis was 7 percent higher than that of 2-D. The differences in fuel consumption and power reflect the differences in heat of combustion and density between the two fuels. Thermal efficiencies for HySEE and 2-D were not significantly different; and emissions tests showed a 54 percent decrease in HC, 46 percent decrease in CO, 14.7 percent decrease in NO_x, 0.57 percent increase in CO₂ and a 14 percent increase in PM when HySEE was compared to 2-D. The HC, CO and NO_x differences were statistically significant.

• Long-term Demonstration and Performance Testing Activities

Test quantities of ethyl and methyl esters of four renewable fuels were processed, characterized, and performance tested. Canola, rapeseed, soybean oils, and beef tallow were the feedstocks for the methyl and ethyl esters. Previous results have shown methyl esters to be a suitable replacement for diesel fuel; however, much less has been known about the ethyl esters. A complete set of fuel properties and a comparison of each fuel in engine performance tests are reported. The study examined short term engine tests with both methyl and ethyl ester fuels compared to number 2 diesel fuel (2-D). Three engine performance tests were conducted including an engine mapping procedure, an injector coking screening test, and an engine power study.

The gross heat contents of the Biodiesel fuels, on a mass basis, were 9 to 13 percent lower than 2-D. The viscosities of Biodiesel were twice that of diesel. The cloud and pour points of 2-D were significantly lower than the Biodiesel fuels. The Biodiesel fuels produced slightly lower power and torque and higher fuel consumption than 2-D.

In general, the physical and chemical properties and the performance of ethyl esters were comparable to those of the methyl esters. Ethyl and methyl esters have almost the same heat content. The viscosities of the ethyl esters were slightly higher and the cloud and pour points were slightly lower than those of the methyl esters. Engine tests demonstrated that methyl esters produced slightly higher power and torque than ethyl esters. Fuel consumption when using the methyl and ethyl esters are nearly identical. Some desirable attributes of the ethyl esters over methyl esters were: significantly lower smoke opacity, lower exhaust temperatures, and lower pour point. The ethyl esters tended to have more injector coking than the methyl esters and the ethyl esters had a higher glycerol content than the methyl esters.

- **Comprehensive Emissions and Performance Testing of Biodiesel at Los Angeles Metropolitan Transit Authority**

Two pickup trucks, both with 5.9 L, turbocharged and intercooled, direct injection diesel engines, were tested for regulated emissions at the Los Angeles County Metropolitan Transit Authority Emissions Testing Facility, one in 1994 and the other in 1995. Emissions testing was conducted using the Dynamometer Driving Schedule for Heavy Duty Vehicles (Code of Federal Regulations 40, Part 86, Appendix 1, Cycle D). Emissions data generated included total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), oxides of nitrogen (NO_x) and particulate matter (PM). All tests were with a chassis dynamometer capable of transient testing.

The 1994 tests included both a double arterial cycle of 768 seconds duration and the EPA heavy duty vehicle cycle of 1,060 seconds duration; however only the tests with the EPA cycle are discussed in this paper. Rapeseed methyl (RME) and ethyl esters (REE) and blends were compared with a low sulfur diesel reference fuel (2-D or diesel). In these tests, 100% REE reduced HC (8.7%), CO (4.3%) and NO_x (3.4%) compared to 100% RME.

The 1995 tests included only the EPA heavy duty cycle. Fuels used in 1995 were low sulfur diesel reference fuel, 100 percent REE, and blends of 20% REE-80% diesel and 50%REE-50% diesel. In 1995, the vehicle was tested with and without the OEM catalytic converter.

The 1994 tests resulted in a reductions in HC (52.4%), CO (47.6%), NO_x (10.0%) and increases in CO₂ (0.9%) and PM (9.9%) compared to diesel. The 1995 tests resulted in reductions in HC (63%), CO (33%), NO_x (10%), CO₂ unchanged and increases in PM (30%) for 100% REE compared to 2-D. The catalytic converter had an affect on only the HC and PM. It reduced HC for diesel 10.5% and for REE 13.6%. It also reduced PM for diesel 45% and for REE 56%.

- **Biodegradability, Toxicity and Other Environmental Studies with Biodiesel**

Biodegradability - The biodegradability of various biodiesel fuels including neat rapeseed oil (NR) and neat soybean oil (NS) as well as their modified products rape ethyl ester (REE), rape methyl ester (RME), soyate ethyl ester (SEE), and soyate methyl ester (SME), and the blends of REE/diesel at different volumetric ratios in the aquatic environment was determined by the standard CO₂ evolution method (EPA 560/6-82-003) and calibrated by gas chromatography (GC) analysis. The results were compared to those of Phillips 2-D reference diesel. The biodegradation rates of REE at varying concentrations were also tested by both methods. The results demonstrate that all the biodiesel fuels are "readily" biodegradable compounds (defined as being 60% or more biodegraded after 28 days). The biodegradation pattern in the mixture is discussed; the reasons why biodiesel is more degradable that diesel are also discussed; and the results from both CO₂ evolution and GC methods are compared.

The biodegradability of HySEE was determined by the same methods. The results were compared to those of REE and 2-D diesel and demonstrated that HySEE is "readily" biodegradable, the same as found in earlier REE tests.

Toxicity - Biodiesel fuels are reported to be non-toxic resulting in less potential hazard to fish and other aquatic life in case of accidental spills. Data are reported on static tests with rapeseed methyl ester (RME) and rapeseed ethyl ester (REE) performed according to EPA/600/4-90/027. The acute aquatic toxicity tests were conducted with both rainbow trout and daphnia magna by CH2M Hill in Corvallis, Oregon under contract to the University of Idaho. The LC_{50} (the point at which 50% have died and 50% are still alive determined by interpolation) values for each of the substances tested with daphnia magna in parts per million were as follows: control (table salt [NaCl] = 3.7, 2-D = 1.43, RME = 23, REE = 99, and methyl soyate = 332. Duplicate tests with rainbow trout were run with 10 organisms per replicate. LC_{50} numbers were not reported because of the failure to kill a sufficient number of fish at the concentrations tested, even with the diesel control fuel. The 20% and 50% blends had scattered losses of fish but none of the tests had less than 85% survival at any concentration after 96 hours.

Carbon Cycle - An outline of the carbon cycle for rapeseed oil derived fuels is presented. Plant processes, fuel chemistry and combustion are examined with respect to the carbon. A diagram is presented to graphically interpret the information presented. A comparison of carbon dioxide emissions from combustion of rapeseed oil biodiesel and petroleum diesel is made. Complete combustion converts hydrocarbon fuels to carbon dioxide and water. The carbon cycle is fixation of carbon and release of oxygen by plants through the process of photosynthesis, then the recombining of oxygen and carbon to form CO_2 through processes of combustion or respiration. The carbon dioxide released by petroleum diesel was fixed from the atmosphere during the formative years of the earth. Carbon dioxide released by Biodiesel is fixed by the plant in a recent year and is recycled. Many scientists believe that global warming is occurring because of the rapid release of CO_2 in processes such as combustion of petroleum diesel. Using Biodiesel could reduce the CO_2 accumulation in the atmosphere.

• **Economics of Biodiesel**

This study estimated the cost of producing biodiesel in the eastern Washington and northern Idaho areas using locally grown canola. Studies of canola production costs and returns have shown that returns can cover all economic costs only if excellent yields are obtained. In this study, estimated economic costs of producing spring canola seed amounted to about 20 cents per pound based on a yield of 1,300 pounds per acre. The biodiesel cost estimates used a price of 13 cents per pound to more nearly reflect the market price for canola seed. Costs were estimated for extracting oil from the seed and for processing the oil into biodiesel. Seed procurement cost, including seed at 13 cents per pound, transport and storage, was 70 percent of the final cost of biodiesel. Oil extraction was another 5.5 percent of the cost. The other 24.5% of the costs were for transesterification of the oil, transportation of the oil,

transportation, equity capital and overhead. The estimated cost of a gallon of biodiesel was \$2.56 when canola seed cost 13 cents per pound. When the price of canola increased to 15 cents, the estimated cost of each gallon of biodiesel was \$2.91. When the price of canola dropped to 9 cents per pound, the estimated cost of one gallon of biodiesel was \$1.69.

- **Other Industrial Applications of Vegetable Oil Esters**

Rapeseed oil has been found to be a potentially useful substitute for mineral oil based hydraulic fluid. A comparison of hydraulic fluid properties of raw rapeseed oil with commercially available hydraulic fluids is presented. Raw rapeseed oil was compared with commercially available Mobil EAL 224H, PlantoHyd 40, and Hy-TransPlus, hydraulic fluids. The results showed that rapeseed oil has good hydraulic fluid properties comparable to Hy-TransPlus, Mobil EAL, and PlantoHyd 40N hydraulic fluids. Some of the hydraulic fluid properties such as flash point, viscosity index and mist spray flammability of rapeseed oil were better than the petroleum based hydraulic fluids.

Rapeseed ethyl esters have other potential industrial uses including a bed release for trucks or equipment handling asphalt; a surfactant for agricultural chemicals; a lubricant for wood working tools; a solvent for cleaning engine parts; a tar remover for vehicles including private passenger cars; a lubricant for hard rock drills in the deep drilling and mining industries; a lubricant for machine tooling operations and other similar uses.

INTRODUCTION

In the latter half of 1993, the Department of Energy, Pacific Northwest and Alaska Regional Bioenergy Program funded a project with the University of Idaho, Biological and Agricultural Engineering Department. This project was to examine many aspects of production of methyl and ethyl esters for use as an alternative diesel fuel and for other industrial purposes.

Renewable alternative fuels will improve the environment, reduce the use of petroleum reserves, reduce foreign imports and increase use of renewable fuels, all of which are high U.S. priorities. They can also be or benefit to the local economy.

Northern Idaho and eastern Washington dryland farmers are somewhat limited in the number of crops that can be grown economically. Many believe that adding a crop to the traditional grain-legume rotation would be desirable. Ideally, the new crop would utilize existing equipment, interrupt plant disease cycles, and be seeded and harvested at slightly different times than the traditional crops. Additionally, the crop should promote higher yields for other crops in the rotation. Rapeseed and canola production have the potential to meet this need.

University of Idaho personnel have, since 1979, researched use of locally produced rapeseed oil as a diesel fuel substitute. Past research has shown that transesterified vegetable oils are very acceptable diesel fuel substitutes (Peterson, 1995). Transesterification is the process of reacting a triglyceride, such as rapeseed oil, with an alcohol such as ethanol in the presence of a catalyst, potassium hydroxide or sodium hydroxide, to produce an ester and glycerol. The process produces two phases; a heavier glycerol phase and the lighter ethyl ester phase. The glycerol has many industrial uses. The ethyl ester, following washing, can be used directly as a diesel fuel, either in blends with diesel or, as in this test, as the only fuel component. University of Idaho personnel have produced more than 7,500 L (2,000 gal) of ethyl esters from rapeseed oil for use in a 1994 Dodge pickup.

To assess the potential for both fuel and industrial uses of vegetable oils and their ethyl and methyl esters several different studies were initiated.

1. A diesel powered on-road vehicle was obtained and operated on 100 percent ethyl ester of rapeseed oil for 35,300 miles. Engine oil analysis was monitored at each 4,000 mile interval during the course of this study. Chassis dynamometer testing was performed at 10,000 mile intervals to track the engine performance .
2. Emissions tests of the vehicle were conducted at the Los Angeles Metropolitan Transit Authority Emissions Test Facility (LA-MTA). In meeting the need to accumulate mileage on the vehicle, the requirement for traveling to Los Angeles with the truck, and the necessity of attending meetings in Kansas City and Milwaukee the truck was driven Coast-to-Coast-to-Coast.

3. The Engine Manufacturer's Association (EMA) in 1982 adopted a 200 hour preliminary durability screening test to assess the potential impact of alternative fuels on diesel engine durability. The test is intended for research and development purposes and is designed to try to initiate durability problems in a reasonable amount of time. Successful completion of the test is no assurance that the fuel will be acceptable. However, the test will eliminate some candidate fuels, and patterns of performance and engine durability will be uniformly evaluated for all test fuels.

Three identical Yanmar 15 kW diesel engines were operated simultaneously for the 200 hour EMA test with six different fuels. The six fuels were 100 percent rapeseed ethyl ester (REE), 100 percent rapeseed methyl ester (RME) and 100 percent Phillips 66 number two low sulfur diesel fuel in test one and 100 percent hydrogenated soybean ethyl ester (HySEE), 80% HySEE - 20% 1-D, and 20% HySEE - 80% 2-D for part two. Even though the three engines are identical there is variability in performance. Due to the variability in power and fuel consumption from engine to engine and only one replication for each fuel, one should reference the paper by Peterson et al. 1994 "Processing, Characterization and Performance of Eight Fuels from Lipids" for a comparison of short term performance variables.

4. As biodiesel fuels become commercialized, their fate in the environment is an area of concern since petroleum oil spills constitute a major source of contamination of the ecosystem. To satisfy a growing interest in renewable, biodegradable, and non-toxic fuel sources, ecotoxicity and biodegradability testing was conducted on methyl and ethyl esters of rapeseed oil and blends of these esters with number two diesel fuel. Tests for acute aquatic toxicity to freshwater organisms were conducted by CH2M HILL in Corvallis, Oregon. Acute oral toxicity to albino rats and acute dermal toxicity to albino rabbits was conducted by WIL Research Laboratories in Ashland, Ohio.
5. Biodegradability of esters is also an area of concern which may impact the ecosystem. Several test methods are available for assessing the biodegradability of a compound. Among them, the CO₂ evolution test (shake flask system) indirectly measures the disappearance of a substrate (ultimate degradation or mineralization) (Lyman et al., 1990). It is relatively simple, economical, and pollution preventing as there are no organic solvents used. Under aerobic conditions and in the presence of certain key nutrients (N, P), microorganisms will metabolize a substance to two final products: CO₂ and water. Therefore, CO₂ is presumed to be the prevalent indicator of organic substance breakdown. If the substrate is the only carbon source, the amount of CO₂ evolved will be proportional to the carbons consumed by microorganisms from the test substrate. In comparison, gas chromatography (GC) analysis directly detects the disappearance of a substrate (primary degradation), and usually involves the use of an extraction solvent such as methylene chloride or hexane. GC instrumentation is relatively expensive compared to the shake flask and titration equipment used in carbon dioxide evolution methods. A comparison of the two methods under the same experimental conditions was

made.

6. The potential for Biodiesel (replacing petroleum diesel with a diesel engine fuel derived from animal fat or vegetable oil such as rapeseed oil) to reduce the carbon dioxide introduced into the atmosphere as a result of engine combustion has been suggested by several authors. Rapeseed oil is a renewable fuel, i.e., the oil is obtained from an annual plant. All of the carbon released by combustion of the plant oil has been fixed by the plant through the process of photosynthesis. Thus carbon dioxide from the air has been absorbed by the plant, converted to the lipids, processed into a diesel fuel and then when the oil is used in the engine the carbon is again released into the atmosphere as carbon dioxide.
7. One step to realizing commercial Biodiesel is how well it stores and what effect storing for long periods has on the performance of the fuel. The problems of fuel deterioration with Biodiesel during storage are more severe than for commercial diesel fuel. Although vegetable oils contain natural antioxidants, their high degree of unsaturation makes them susceptible to gum formation. Since fuel deterioration occurs mainly by oxidative polymerization leading to gum formations one objective of this study was to determine the rate of oxidative polymerization for different fatty acid esters prepared from rapeseed, container types, and environments. Peroxide values measure the levels of the oxidation products in the samples. Another objective of this study was to use short term engine coking and torque tests procedures to determine the effect of storage of the esters on diesel engine performance and to determine whether the presence of the oxidation products adversely affected the engine performance.
8. A steady increase in the number of off-road machines in agricultural and forest industries has increased the demand for petroleum products. During the year 1991, 765 million liters of hydraulic oil were sold (National Petroleum Refineries Association, 1991). The depletion of petroleum reserves on one side and the increasing demand for petroleum products on the other has stimulated the search for alternative sources of hydrocarbons. Petroleum continues to be the main source for hydraulic and lubricating oils and the alternatives are very limited. As the indigenous crudes are not suitable for the production of high quality lube oil base stocks, the requirements are met by importing suitable crudes. Therefore, it has become absolutely essential to identify alternative sources for hydraulic and lubricating oil base stocks (Bisht et al., 1989).

Most used lubricating oils can be recycled, however, less than 5% of the used lubricating oil is re-refined, while over 95% is dumped into sewers or waterways, spread on roads, or burned as fuel. The present methods of disposing of used oil can create major environmental hazards, as well as waste about 42,000 barrels of lubricating oil every day, which is three times as valuable as ordinary fuel oil (Domenici, 1981).

A 1983 Federal Environmental Protection Agency study reported that American industry,

automobiles, trucks and construction equipment use at least 2.3 billion gallons of oil per year. Of that 2.3 billion, more than half returns to the nation's waste stream as waste oil. The sheer volume of the use of these fluids implies dramatic things about the effect that improperly managed waste oil can and does have on the environment. State and federal environmental legislation has increased significantly over the past few decades, and the potential impact of waste oil, particularly used waste oil, has not gone unnoticed (Shipley and Boyd, 1991). The use of environmentally acceptable hydraulic fluids in mobile machines is becoming more prevalent worldwide as a way to reduce environmental pollution.

The oil in a hydraulic system serves as the power transmission medium. It is also the lubricant and coolant. Selection of the proper oil is important. Hydraulic fluids are rated on their viscosity and anti-wear properties. Anti-wear additives are a group of chemical compounds with low chemical activity under heat and pressure. These fluids are generally referred to in hydraulic oil applications as AW. A biodegradable and nontoxic antiwear hydraulic fluid has been developed based on a selected vegetable oil and additive system. This oil is designated "Environmental Awareness" (EA).

9. One important issue to the development of a Biodiesel industry is acceptance of the fuel by manufacturers of diesel engines and in particular how use of these fuels would affect the manufacturer's engine warranty. A workshop was organized to bring together Biodiesel users, research workers, representatives of the National Biodiesel Board and other interested parties to explore the current status of Biodiesel, its effect on engine warranties and what issues remain to be resolved before Biodiesel can be thought of as a legitimate fuel for diesel engines. The workshop format included brief "state-of-the-art" presentations by researchers, NBB, DOE and Biodiesel users, followed by group sessions which developed a statement of where we are now with engine warranties and a statement of issues that need to be resolved to bring Biodiesel under full warranty coverage equivalent to diesel.

Many tests have shown these fuels to have characteristics as good as, or superior to, common diesel fuel. In spite of these excellent fuel characteristics many hurdles remain before these fuels will be available for general use.

10. A second biodiesel workshop was held in 1996. The workshop entitled "Commercialization of Biodiesel: Environmental and Health Benefits" brought together specialist knowledgeable in toxicity, air pollution and other environmental benefits of biodiesel. This workshop followed the same format as the first conference. A summary on the current knowledge related to environment and health and additional research needs were developed at the conference.

ESTER OF RAPESEED USED AS A BIODIESEL FUEL IN A 1994 DODGE 4X2 PICKUP

A 1994 Dodge 2500 turbocharged and intercooled diesel pickup fueled with 100 percent ethyl ester of rapeseed oil was driven by personnel representing the University of Idaho, Agricultural Engineering Department from Moscow, Idaho and Craig Chase to Los Angeles, CA and back to Moscow and then from Moscow to Ocean City, MD, east of Washington, D.C. and back to Moscow, ID. The truck has passed through 21 different states i.e. Idaho, Oregon, Washington, Utah, Nevada, California, Montana, Wyoming, South Dakota, Nebraska, Missouri, Illinois, Kentucky, Indiana, Wisconsin, Minnesota, Virginia, Maryland, Delaware, Pennsylvania and Ohio. It has also been out of the continental United States to Tijuana, Mexico. These trips and others covered a total of 35,300 miles with 33,700 miles on 100% rapeseed ethyl ester (REE). The truck averaged 18.0 miles per gallon using 1875 gallons of REE. No problems or unusual events were encountered with the truck operation. The truck was completely unmodified as to the engine or fuel system. The fuel required for the trip was all processed in the Agricultural Engineering laboratory at the University of Idaho and was carried on-board as no refueling facilities were available away from Moscow, ID.

Vehicle Preparation

The vehicle tested was a 1994 Dodge pickup with a direct injected, turbocharged and intercooled, 5.9 liter Cummin's diesel engine. The engine is an in-line six cylinder and has a bore and stroke of 4.02 x 4.72 inches respectively; has a compression ratio of 17.5:1; is rated at 175 horsepower at 2500 RPM with a peak torque of 420 ft-lbs at 1500 RPM. The engine was not modified in any way for use with the vegetable oil fuels. The fuel delivery system was modified for convenience of changing fuels between emissions test runs at the LA-MTA emissions test facility and Western States Cat. Fuel delivery and fuel return lines were cut and 3-way, manually operated valves were installed so that a stub line with quick couplers could be installed on one part of the 3-way valves. During normal operation, fuel was delivered and returned to the vehicle fuel tank. During emissions and dynamometer testing the valves were switched to the external lines to which the correct test fuel was connected. For the emissions tests, the fuel filter assembly mounted on the engine was removed and replaced with an aluminum block with internal connecting ports. This change was necessary to minimize the amount of fuel in the system when a fuel switch was required.

The truck had a factory installed 128 L (34 gal) fuel tank. To extend it's range for operation on Biodiesel a 375 L (100 gal) auxiliary tank was installed in the bed. The auxiliary tank had an electric dispensing pump with a volume delivered meter for transferring fuel into the vehicle tank. A canopy was added to the truck for security purpose of the auxiliary fuel tank. The pickup was lettered for identification and exhibits.

Fuel Used

All of the fuel used in this test was produced at the Agricultural Engineering laboratory at the University of Idaho using recipes and techniques developed at the laboratory. Rapeseed oil was expelled using a small screw press from seed purchased from a local company. The seed was cleaned and bagged and then was expelled in a plant capable of 40 kg/h of seed throughput. The oil was filtered and then esterified using ethanol and potassium hydroxide in a small 300 gallon Biodiesel reactor. The ethyl ester fuel production process utilizes 70% stoichiometric excess ethanol (absolute, 100% pure), or a molar ratio of 5.1:1 ethanol to oil ratio. The total free fatty acids are determined and neutralized with the calculated addition of catalyst. Based on the amount of input oil by weight, 1.3% potassium hydroxide (KOH) is used plus the amount to neutralize the free fatty acids. The following equations were used for the quantities processed:

$$\text{EtOH} = 0.2738 \times \text{Oil} \qquad \text{KOH} = \text{Oil}/85$$

Where; Oil = desired amount of oil, in liters
 EtOH = amount of ethanol needed, in liters
 KOH = amount of potassium hydroxide required, in kg

The catalyst is dissolved into the alcohol by vigorous stirring in a small reactor. The oil is transferred into the Biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil and the final mixture stirred vigorously for two hours. A successful reaction produces two liquid phases: ester and crude glycerol. Crude glycerol, the heavier liquid will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within two hours after stirring is stopped. Complete settling can take as long as 20 hours. After settling is complete, water is added at a rate of 5.5% by volume of the oil and then stirred for five minutes and the glycerol allowed to settle again. After settling is complete, the glycerol is drained and the ester layer remains. Washing the ester is a two-step process which is carried out with extreme care. A water wash solution at the rate of 28% by volume of oil and 1 gram of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28% by volume of oil for the final washing.

The REE was characterized by evaluating the parameters required in ASAE EP552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed at Phoenix Chemical Labs, Chicago Illinois. The HPLC and titration analysis for total and free glycerol, percent of oil esterified, free fatty acids, and mono-, di-, and triglycerides were performed by

Diversified Labs Inc., Chantilly, Virginia. Table 1-1 is a brief summary of the fuel properties for REE and number two diesel fuel (2-D).

TABLE 1-1.
PROPERTIES OF ETHYL ESTER and DIESEL CONTROL FUEL

| | <u>100% REE</u> | <u>100% 2-D</u> |
|---------------------------|-----------------|-----------------|
| Gross Heat of combustion, | 40.51 | 45.42 |
| MJ/kg (Btu/lb) | (17,415) | (19,526) |
| Flash point, °C(°F) | 124 (255) | 82(180) |
| Cloud point, °C(°F) | -2 (29) | -14 (6) |
| Pour point, °C(°F) | -10 (14) | -21 (-5) |
| Viscosity cSt @ 40 °C | 6.17 | 2.98 |
| Sulfur (% wt) | 0.014 | 0.036 |
| Specific Gravity, 60/60 | 0.876 | 0.8495 |
| Cetane number | 59.7 | 49.2 |

Details of Travel

The western leg of the trip began March 9, 1994. The starting point was in Moscow, ID. The estimated 3,800 km (2,400 miles) of the trip required approximately 570 L (150 gal) of fuel. In addition, fuel was required for the emission tests at LA-MTA so nearly 1,134 L (300 gal) of fuel was on-board during the trip. A log with stop-over points, miles travelled and liters (gallons) of fuel used for each leg of the trip was as follows:

March 9 - Moscow, ID to Jordan Valley, OR; 403 miles; 19.4 gallons of fuel

March 10 - Jordan Valley, OR to Victorville, CA; 498 miles; 28.0 gallons of fuel

March 11 - Victorville, CA to the Pacific Ocean at Santa Monica Beach; 352 miles; 18.2 gallons of fuel

March 12 - 16 - Testing at LA-MTA

March 16 - Los Angeles to Carson City, NV; 452 miles; 22.5 gallons of fuel

March 17 - Carson City, NV to Moscow, ID; 751 miles; 41.5 gallons of fuel

Total travel distance 2456 miles; 129.6 total gallons used; 18.9 average miles per gallon.

The eastern leg of the run was carried on between June 14 and July 3, 1994. For the estimated 6000 miles of the trip approximately 300 gallons of fuel were required. The vehicle started with the main tank full, the auxiliary tank full, four-55 gallon drums of fuel, and one-5 gallon emergency supply. This was a total of about 360 gallons of fuel weighing over 2600 pounds. Approximately 20 gallons remained at the conclusion of the trip. The log for the eastern leg of the trip was as follows:

June 12 - Moscow, ID to Kadoka, SD; 1088 miles; 54.9 gallons of fuel

June 13 - Kadoka, SD to Kansas City, KS; 714 miles; 40.3 gallons of fuel

June 14 - on display at the ASAE Liquid Fuels Conference in Kansas City, MO

June 16 - miscellaneous travel in Missouri; 183 miles; 11.8 gallons of fuel

June 22 - Kansas City, MO to Columbia, MO; 130 miles; 7.5 gallons of fuel
June 22 - Columbia, MO to Verona, VR; 871 miles; 43.0 gallons of fuel
June 23 - Verona, VR to Washington, D.C.; 252 miles; 13.8 gallons of fuel
June 24 - on display at DOE (Forrestal Building) and the capital mall in Washington, D.C.
June 25 - Washington, D. C. to the Atlantic Ocean at Rehoboth Beach, DE to Ocean City, MD to Toledo, OH; 773 miles; 41.7 gallons of fuel
June 26 - Toledo, OH to Milwaukee, WI; 381 miles; 16.7 gallons of fuel
June 28 - 30 on display at the "Fueling the Future - A Clean Air Transportation and Engine Trade Show," Milwaukee, WI
July 1 - Milwaukee, WI to Rapid City, SD; 899 miles; 51.9 gallons of fuel
July 2-3 - Rapid City, SD to Moscow, ID; 995 miles; 56.5 gallons of fuel
July 7 - dynamometer test at Spokane Western States Cat facility

Total travel distance 6286 miles; 338.2 total gallons used; 18.6 average miles per gallon.

Combined total travel distance 8742 miles; 467.8 total gallons used; 18.7 average miles per gallon.

Unique Characteristics of the Run

1. The total distance travelled was 8742 miles with one fueling location in Moscow, ID.
2. All of the fuel used in the test was 100 percent ethyl ester of rapeseed oil produced in the Agricultural Engineering Department Laboratory at the University of Idaho.
3. All of the fuel was carried on-board and was on-board the vehicle when it left Moscow, ID. No fuel was shipped and/or delivered to other locations.
4. The vehicle ran normally with no engine or fueling system modifications.
5. No diesel fuel was used on the trip, none was carried or purchased and at no time was it felt necessary to attempt to use diesel fuel.
6. The vehicle was driven at normal highway speeds and no attempt was made to avoid any particular situation. Traffic included heavy city traffic, freeways, tollways, etc. On two different days the vehicle travelled over 995 miles.

Dynamometer Tests

After an initial breakin of 1,400 miles, the pickup was tested on a dynamometer tested. Western States Cat in Spokane, WA contributed the use of their Superflow 601 chassis dynamometer facility. The dynamometer was computer controlled and provided a printout of the horsepower to the wheels, torque, fuel consumption, fuel temperature, inlet air temperature, coolant temperature, exhaust temperature, engine blow by, engine rpm, and turbo boost pressure. An opacity meter provided a measure of the amount of smoke in the

exhaust. A full throttle torque test was performed with a predetermined set of engine RPM's programmed into the computer to obtain repetitive data. Data was collected at 150 RPM increments from 1450 RPM to 2950 RPM. The pickup was dynamometer tested at each interval on 100% REE and 100% 2-D with both fuels being tested in triplicate. Table 1-2 is a summary of the horsepower, fuel economy and percent opacity at given RPM's.

Table 1-2. Summary of dynamometer tests.

| Mileage | Fuel Type | Horsepower @2500 RPM | Fuel Efficiency @ 2500 RPM (lb/hp-hr) | Percent Opacity Snap Idle Test |
|---------|-----------|----------------------|---------------------------------------|--------------------------------|
| 1,400 | 100% 2-D | 145 | 0.471 | 21.5 |
| | 100% REE | 145 | 0.5105 | 18.4 |
| 7,520 | 100% 2-D | 145 | 0.4787 | 26.1 |
| | 100% REE | 141 | 0.5205 | 15.5 |
| 16,500 | 100% 2-D | 146 | 0.4653 | 27 |
| | 100% REE | 142 | 0.5107 | 17 |
| 26,200 | 100% 2-D | 146 | 0.4813 | 23.5 |
| | 100% REE | 140 | 0.5213 | 15.8 |
| 35,550 | 100% 1-D | 155 | 0.4555 | 19.8 |
| | 100% REE | 152 | 0.4875 | 14 |

Performance Parameters

After each dynamometer test the injectors were removed from the engine to check for carbon deposits using the procedure described in "A Rapid Engine Test to Measure Injector Fouling in Diesel Engines Using Vegetable Oil Fuels". There was very little carbon buildup on the tip of the injectors, either visually or by calculating the area of the coked injector from one test interval to the next.

The engine cylinder compression was tested and the injector valve opening pressure was also checked. There was no change in the cylinder compression from the beginning of the test to the end at 35,550 miles. The injector valve opening pressures varied from 4000 psi to 3900 psi during the duration of testing.

The Dodge pickup, Cummins engine, has direct access to the combustion chamber and cylinder walls through the injector bore in the cylinder head. A fiber optic borescope was used for this engine to visually inspect the amount of carbon build up on the piston crown and valve heads and to check for any abnormal cylinder wear. There was no significant visual change in the combustion chamber for the duration of testing. At 35,550 miles there were a

few very light scratches appearing on the thrust side of the cylinder walls, which is normal for the accumulated miles. There did not appear to be any excess amount of carbon deposits on the piston crowns or the cylinder heads and valves.

Seven individuals have operated this vehicle and did not notice any change in vehicle operation or other abnormalities during the course of the test. The pickup was operated in all seasons with varying loads from empty to gross vehicle weight to pulling a trailer weighing 8300 pounds.

Engine Oil Analysis

Engine oil samples were taken at each oil change which was every 4,000 miles. Chevron Delo Multi grade SAE 15W-40 heavy duty engine oil was used as the engine lubricating oil. The oil samples were analyzed at a commercial oil analysis laboratory for wear metals, and physical tests were performed, including antifreeze, fuel dilution, water, and viscosity. An infrared analysis for soot, sulfur, nitration, and oxidation of the engine oil was also conducted. The reportable limits for each metal were supplied by the oil analysis lab. Western States Cat analyzed the lube oil for the first 20,000 miles and Cleveland Technical Center for the remainder of the testing.

COMMERCIAL PROCESS FEASIBILITY ANALYSIS AND BENCH SCALE PROCESS SYSTEM DESIGN

CONCEPT AND CONFIGURATION

The transesterification of vegetable oil is accomplished by mixing the oil with ethanol, in the presence of a catalyst (KOH). This mixing process is completed in a tank called a reactor. During this process, glycerol is produced and will be drained from the bottom of the reactor. The ethyl ester fuel then requires washing processes to further purify it.

This process has been designed as a batch process, with mixing and washing processes performed during the day and settling occurring overnight. The duration of the entire batch process may be as much as five days. The first three days require active mixing and washing operations, the fourth day allows for additional settling time and the fifth day allows for storage of the fuel and the cleaning of the reactors. A sketch of the Configuration is provided in Figure 1.

The process incorporates five modular reactors. Each 500 gallon batch will require a maximum of five days. The processes of the five reactors may be staggered, to produce 500 gallons of fuel each day, or the processes of the reactors may be run simultaneously to produce 2,500 gallons each week.

Some of the reasons five modular reactors were chosen over one large reactor include:

- Better agitation
- Ease of draining
- Ease of cleaning
- Ease of visual inspection
- Minimize losses if one batch is interrupted

The rapeseed oil, ethanol and KOH required for the process are stored in large tanks near the reactors. The oil and ethanol may be pumped into the reactors and the KOH will be placed in the reactors manually.

Due to the corrosive nature of KOH, brass, aluminum and steel are unacceptable material for the reactor. The reactor tanks will be constructed from stainless steel and elevated four feet from the floor so the byproducts of each phase of the process may be gravity fed which eliminates the need for pumping.

OPERATIONAL REQUIREMENTS

The supply of rapeseed oil, ethanol and KOH will need to be replaced periodically. The storage tank for the rapeseed oil has a capacity of 3,800 gallons, which is enough for 6 days of operation. The storage tank for the ethanol holds 2,300 gallons, which is sufficient for 16

days. These tanks will need to be filled accordingly.

The operational requirements for the five day parallel process of each reactor are outlined as follows:

Day 1: 684 gallons of ethanol are pumped into the alcohol-catalyst mixing tank and 29.5 pounds of KOH are added and mixed until the KOH is dissolved. 137 gallons of the ethanol-catalyst mixture is transferred into each of the biodiesel reactor tanks. 500 gallons of rapeseed oil will be transferred to the biodiesel reactor and agitated for 3 hours. The solution will be allowed to settle overnight to allow sufficient time for a complete phase separation of the esters and the glycerol.

Day 2: The glycerol byproduct will be drained from the bottom of the reactor. Glycerol is a thick brown layer which is soluble in water and easily distinguished from the ester. The ester layer is a light-yellow and not soluble in water. The glycerol contains most of the potassium hydroxide, is quite alkaline and should be handled with care. The glycerol mixture may be sold at this point. An aqueous wash solution will be added to the reactor. The solution will then be stirred during the day and allowed to settle overnight.

Day 3: The aqueous wash solution and the impurities accrued during the washing will be drained from the bottom of the reactor. This mixture will be sent through the water treatment facility. Water, at one-third the total volume, will be added to the reactor. This solution will be mixed by stirring for 8 hours and then allowed to settle overnight.

Day 4: Occasionally additional time is needed for all of the water to settle out of the fuel. This day will simply provide additional settling time if necessary.

Day 5: The reactor will have the water drained from the bottom of the reactor. The water which is drained will be used for the day 2 washing procedure. The remaining fuel will need to be pumped, using a portable pump, into the storage tank or sold. The reactor will then be cleaned for the next batch.

Two laborers would be sufficient to accomplish the mixing and water addition activities during the first few hours of each days operation. After the first two to three hours the process may be accomplished with a minimum of supervision.

COST

The cost of accomplishing this process will include building, equipment, labor and material cost. These costs are outlined below.

Building Cost

The building is roughly 3,400 square feet. At \$50 per square foot, the building cost would be \$170,000.

Equipment List

A list of the necessary equipment is given below.

| <u>Equipment</u> | <u>Size</u> | <u>Cost each</u> | <u>Quantity</u> |
|---------------------------------|-------------|------------------|-----------------|
| Material Platform | | \$3,100 | 1 |
| Reactor w/stand | 700 gal | \$2,600 | 6 |
| Agitator | 3 hp | \$3,000 | 5 |
| Oil Storage Tank (Polyethylene) | 5,000 gal | \$2,750 | 1 |
| Ethanol Storage Tank | 2,300 gal | \$1,200 | 1 |
| Ethyl Ester Storage Tank | 5,000 gal | \$2,750 | 2 |
| Crude Glycerol Storage Tank | 5,000 gal | \$2,750 | 2 |
| Centrifugal Pump | 1 hp | \$1,200 | 7 |
| PVC Piping (SCH 40) | 1" | \$0.24/ft | 75 ft |
| PVC Piping | 1.5" | \$0.24/ft | 75 ft |
| SS Ball Valves | 1" | \$56.00 | 5 |
| SS Ball Valves | 1.5" | \$114.45 | 5 |
| PVC Tees | 1" | \$0.48 | 4 |
| PVC Tees | 1.5" | \$1.38 | 4 |
| PVC Elbows | 1" | \$0.58 | 5 |
| PVC Elbows | 1.5" | \$1.58 | 5 |
| Air Compressor | 10 hp | \$2050 | 1 |
| Steel Pipe (SCH 40) | 1/2" | | |
| Steel Elbow | 1/2" | \$0.63 | 8 |
| Steel Tees | 1/2" | \$0.82 | 4 |
| Steel End Plug | 1/2" | \$0.46 | 1 |
| Coupler Assemblies | 1/4" | \$4.48 | 5 |
| Combination filter/regulator | 1/4" | \$56.45 | 5 |
| Flexible Air Hose | 1/4" | \$20.25/50 ft | 1 |
| Lock-on Barb Fittings | 1/4" | \$0.96/pkg | 1 |

The total materials cost is \$60,500.

If installation cost of the equipment is assumed to be 40% of the equipment cost, then the total installation cost would be \$24,200.

Labor Cost

It appears that one laborer working for three hours and one supervisor working for the eight hours will be able to accomplish the process.

Laborer: 3 hours at \$15/hr

Supervisor: 8 hours at \$25/hr

Material Cost

Rapeseed Oil \$2.19/gal

Ethanol \$1.05/gal

KOH \$1.56/lb

PERFORMANCE AND SYSTEM THROUGHPUT

The process design detailed in this paper is for a 100,000 gallon per year plant to produce Ethyl Ester rapeseed fuel. It is assumed that the raw rapeseed oil is purchased as oil which eliminates the need for presses, seed handling equipment and meal disposal.

The plant is designed for 500 gallons per day of operation using 200 days per year (Fig 2-1). A batch system using five 700 gallon reactors with their own mixers is conceptualized. This system can be operated in parallel, with each step in the process carried out in each reactor simultaneously, or the operation may be staggered with a new batch started and a batch finishing each operating day.

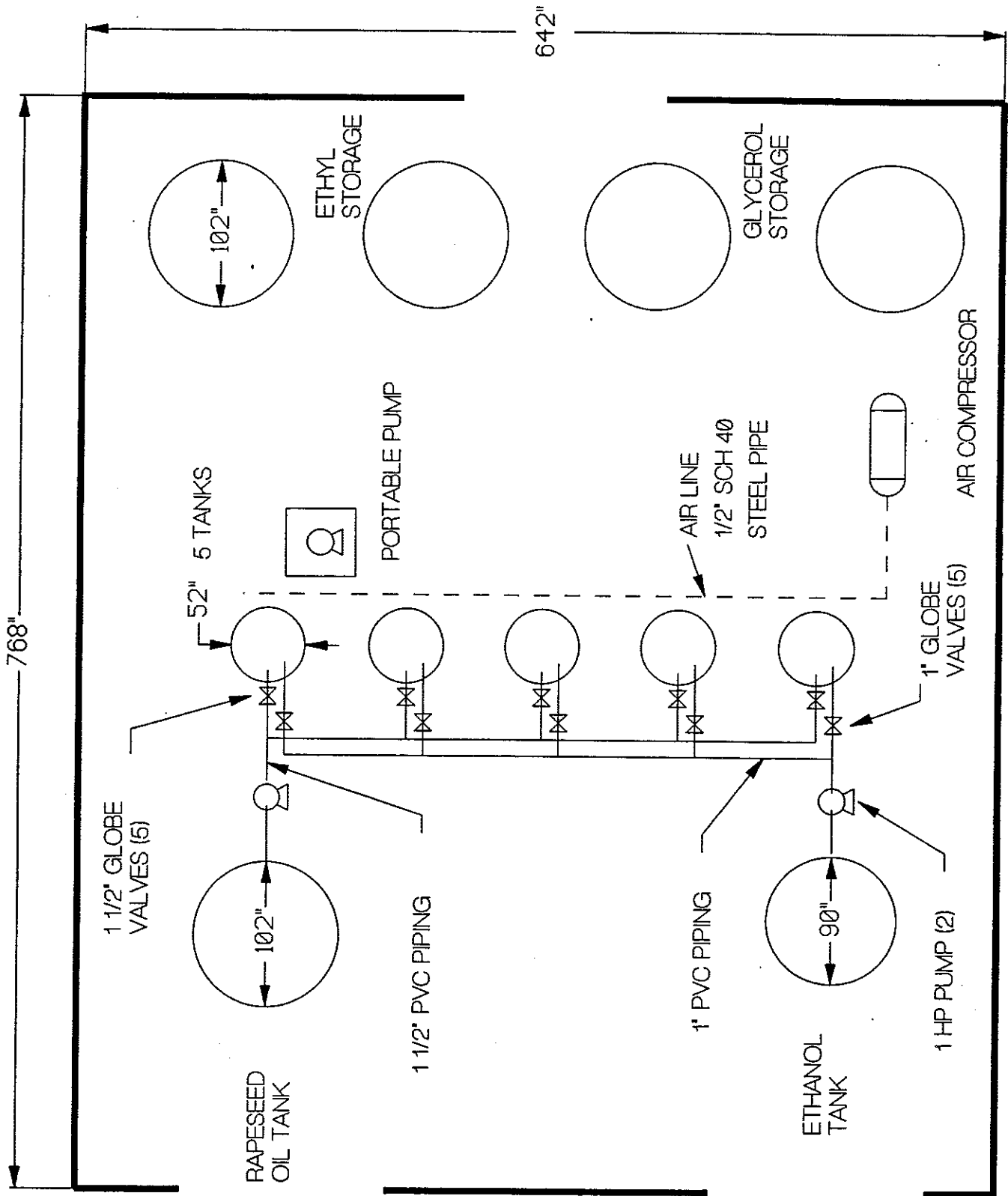
The system of reactors provides flexibility in operation, allows complete conversion, washing and settling in each reactor and assumes that the plant won't be shut down if a difficult batch occupies one of the reactors as could happen with one large reactor.

Plant capacity can be easily expanded by operating more days per year, condensing the cycle or adding reactors.

Storage capacity is available for 10 days supply of raw rapeseed oil and for 16 days supply of ethanol storage. KOH will be delivered in bulk containers in one ton lots which will provide 40 days supply.

Two, 5,000 gallon ethyl ester tanks and two 5,000 gallon crude glycerol tanks are recommended giving some capacity for separation of product and providing for on-site storage of each.

Figure 2-1. Plant layout.



ENVIRONMENTAL SENSITIVITIES AND BENEFITS

Ethyl ester of rapeseed oil used as a fuel is made from renewable ethanol and rapeseed oil. The resulting product is biodegradable, has a high flash point and has been shown in emission tests to reduce HC and CO emissions. NOx and PM emissions depend on engine design.

The esterification process using ethanol has little effect on the environment. The glycerol can be sold as is or purified. The wastewater from this plant is approximately 175 gallons per day which should have little or no impact on local sanitation facilities. Ethanol is not a Resource Conservation & Recovery ACT (RCRA) hazardous waste. The high number of dilutions and any residual catalyst that is present in the washwater need to be considered if this waste were to be processed commercially. The Moscow City Waste Treatment plant has given approval for direct disposal of the wastewater into their plant.

PROJECT ECONOMICS

Fixed Costs

| | |
|-----------|-----------|
| Building | \$170,000 |
| Equipment | \$ 60,500 |

| | |
|---------------------------|----------|
| Annual Cost (8% interest) | \$63,804 |
| Insurance and Taxes (2%) | |

| \$/Per Gallon |
|---------------|
| \$0.64 |
| \$0.05 |

Variable Costs

| | |
|---|------------------|
| Oil@\$0.06/lb to \$0.29/lb | \$0.46 to \$2.23 |
| Ethanol@\$1.05/gal | \$0.34 |
| KOH@\$1.56/lb | \$0.15 |
| Labor@\$245/day | \$0.49 |
| Maintenance and repairs (3% of fixed Costs) | \$0.02 |
| Utilities | \$0.04 |

| | |
|-------|------------------|
| Total | \$2.19 to \$3.96 |
|-------|------------------|

Potential Income

| |
|---------------------------|
| Sale of Ethyl Ester Fuels |
| Sale of Crude Glycerol |

A capitol recovery factor was used for 5 years and 8%. There is no estimation of the potential income from the final product.

PRODUCING BIODIESEL FROM CANOLA IN THE INLAND NORTHWEST: AN ECONOMIC FEASIBILITY STUDY

PROBLEM STATEMENT

The problem dealt with in this report consists of two parts:

1. Can rapeseed and canola be produced economically in eastern Washington and northern Idaho?
2. Under what conditions could their oils be used as a feedstock for biodiesel used in urban bus systems?

The study area is that served by the Spokane Transit Authority, and our data are partially based on a test period in which a biodiesel blend was used in several buses. Production costs were estimated for a simulated plant used to process the oil. The canola seed market price was used for feedstock cost. This cost, added to the costs of extracting the oil and processing the oil into biodiesel, determined the estimated cost of producing biodiesel for the Spokane Transit Authority.

CANOLA AND BIODIESEL PRODUCTION

Canola Production Costs in the Inland Northwest

Several studies have assessed production costs for rapeseed and canola in the Inland Northwest. Estimated costs have ranged from about 10 cents to nearly 20 cents per pound (Melfi and Withers [1993], Smathers and Withers [1993], Smathers and Foltz [1993], Hinman et al [1991]).

Variation in production cost per pound has resulted from different in climate and soil conditions, from different production practices, and from comparing winter canola with spring canola. Estimated typical yield for spring canola was 1,300 pounds per acre (Smathers and Foltz, 1993) and for winter canola was about 2,000 pounds per acre (Smathers and Withers, 1993). In these studies, winter canola was seeded in late summer on fallow land, while spring seeded canola did not require fallow. Fallow costs were included in the winter canola crop estimate. The cost per pound of seed produced was 15 cents for winter canola and 19 cents for spring canola. In these estimates, all costs except management and risk were charged to the crop. Hinman et al. (1991) estimated costs a little lower, 10 cents to 12 cents per pound, in Lincoln and Adams Counties of eastern Washington in a wheat, barley, fallow, canola rotation.

Canola Markets

Once canola seed has been produced, it can be sold on the domestic market or exported. Oil and meal are produced by crushing the seed. Canola oil competes with soybean, sunflower, peanut, and other vegetable oils. U.S. canola also competes with Canadian canola. As soybean oil is most widely used in the United States, canola oil prices are somewhat tied to soybean oil prices. In other words, canola oil prices tend to rise and fall with soybean oil prices. The same can be said for canola meal as it tends to follow soybean meal prices. Canola can be exported as whole seed or as oil and meal. Schermerhorn (1986) concluded that Japan would be the major importer of whole rapeseed and that U.S. access to this market would be difficult because of production in Canada, France, and Denmark. Eastern European countries could also be players in the Japanese market. However, domestic consumption of canola oil far exceeds our current production.

Vegetable Oil as a Fuel

Considerable work has been done on using vegetable oil as a fuel for combustion engines. Peterson (1986) found that power output, torque, and brake thermal efficiency in engines fueled with vegetable oil were equal to or very close to those using diesel. However, engine deposits, coking, and other problems resulted from long-term use.

Engine problems associated with vegetable oil fuel can be eliminated by modifying the oil into vegetable oil esters called biodiesel. Ethanol or methanol can be used for this purpose. Methanol is derived from petroleum, while ethanol is a renewable resource produced from grains and other farm products.

Peterson et al. (1992) found that ethanol and methanol are quite similar in their effects on engine performance. Ethyl esters have a slightly higher viscosity than methyl esters, however, and the cloud and pour points are lower. These properties could reduce ethyl ester usability in cold weather. Fuel consumption is the same with either fuel. Ethyl esters are lower in smoke opacity and have lower exhaust temperature, lower injector coking, and fewer combustion chamber deposits.

When comparing the two esters (biodiesel fuels) with diesel (2-D), Peterson et. al. found that the gross heat units of biodiesel were 9 to 13 percent lower than those of 2-D. The viscosities of biodiesel were almost twice that of 2-D, and 2-D had lower cloud and pour points than biodiesel. Biodiesel fuels produced lower power and torque than 2-D. Injector coking was similar for both ethyl ester and 2-D, but the methyl ester showed a slightly higher coking index. The smoke opacities of biodiesel were one-third that of 2-D, and the exhaust temperature of biodiesel was always at least 50°C lower than 2-D (Peterson et al., 1992).

Van Dyne and Raymer (1992) first looked at the environmental implications of biodiesel and found that the two most important factors in biodiesel's future use may be its low levels of exhaust emissions and its biodegradability. These factors may override cost considerations and performance concerns in certain niche markets such as wetlands, wilderness areas,

national forests, oceans, and other environmentally sensitive areas. Biodiesel is lower than diesel fuel in three out of four categories listed in the 1993 European Economic Community emissions limits.

Biodiesel Production Costs

Caringal (1989) performed an economic analysis of rapeseed methyl ester and found that the cost could be broken down into the following parts: raw material cost (91.52 percent), operating cost (3.12 percent), and capital cost (5.337 percent). Due to this breakdown, Caringal determined that rapeseed methyl ester is not sensitive to either operating or capital costs because the raw materials made up the majority of the costs.

Weber (1993) determined that both feedstock and meal prices are extremely important in the cost of biodiesel. He concluded that economic competitiveness of a cooperative plant depends enormously on localized variables. Areas that offer low electrical rates, existing facilities, and large oilseed acreage would be good locations. Weber also found that without farm program benefits to minor oilseeds such as canola and soybeans were the most economic feedstocks for a biodiesel facility.

Bam (1991) compared the economic viability of rapeseed ethyl ester with that of rapeseed methyl ester. He assumed that the process for making ethyl ester is essentially the same as that used for making methyl ester, so only the difference in the cost of the alcohol was considered. He found that the break-even price of the ethyl ester was \$2.00 per gallon as compared to \$1.85 per gallon for methyl ester.

These studies and reports indicate that biodiesel can be used as a substitute for diesel fuel but is more expensive to produce than diesel fuel. Up to the present, the high cost of production has prevented biodiesel from becoming a more widely used alternative fuel. In Europe, where petrodiesel is more expensive than in the United States, biodiesel has had substantial use.

A calculation of oil cost must also consider the value of meal and glycerine. When oil is extracted from canola, a protein meal is produced that can substitute for soybean meal in livestock rations. Glycerine is a by-product of biodiesel production from producing biodiesel. These by-products help to offset the cost of biodiesel production.

THE COST OF CANOLA FOR PROCESSING

In northern Idaho, canola was introduced as an alternative crop to peas and barley. These are crops grown in rotation with winter wheat, which is the major crop in the area. Farmers grow as much wheat as they can within the limits of rotation requirements and government programs. This means about one-half of the crop acres are seeded to wheat each year with the other half producing peas, barley, and, in some cases, lentils. It was hoped that canola would be more profitable than these traditional crops.

Crop budgets prepared by the University of Idaho Cooperative Extension System were used as a basis for estimating the profitability of canola as compared with peas and feed barley (Table 3-1). All crops had a small return over variable costs, but when fixed costs were added, all had a negative return to risk and management. Canola experienced a loss per acre slightly greater than barley and was at an even greater disadvantage with peas. Higher prices or larger yields will be required to make canola a profitable crop. In some cases, where canola could be produced on program acres where deficiency payments could be received along with canola income, it was profitable. Also a few growers produced farm yields considerably above average for the area and enjoyed a positive net return.

The recent market price of 13 cents per pound of canola seed was used to estimate fuel costs even though this was below estimated total production costs. It was assumed that an adequate supply of seed would be available of the processor at this price.

Table 3-1. Estimated economic costs and returns for selected crops northern Idaho, 1993.

| | Canola | Peas | Feed Barley |
|--|-----------|-----------|-------------|
| Yield per acre | 1,300 lb | 1,700 lb | 1.5 ton |
| Price per unit | \$0.13 | \$0.09 | \$91.00 |
| Gross receipts per acre | \$169.00 | \$148.75 | \$136.50 |
| Total variable costs | \$149.37 | \$131.91 | \$128.55 |
| Return above variable costs | \$19.63 | \$16.84 | \$7.95 |
| Total fixed costs | \$106.18 | \$91.28 | \$89.10 |
| Total costs | \$255.55 | \$223.19 | \$217.65 |
| Return to risk and management | \$(86.55) | \$(74.44) | \$(81.15) |
| Price needed to cover all costs | \$0.20 | \$0.13 | \$145.10 |
| Yield per acre needed to cover all costs | 1,966 lb | 2,551 lb | 2.39 ton |

FEASIBILITY OF RAPESEED OIL AS A FEEDSTOCK FOR BIODIESEL

All three varieties of rapeseed (spring canola, winter canola, and winter rapeseed) grown in the study area could be used for biodiesel because of their high oil content. The largest portion of the cost to produce biodiesel is the feedstock cost. The cost of producing feedstock has been the major obstacle to economic feasibility of biodiesel.

The Clean Air Act of 1990 established stricter emissions regulations for urban transit systems (Caro, 1994). Urban transit directors may have to find ways to reduce emissions either with cleaner engine operation or with pollution reducing fuels. Some alternative fuels competing with biodiesel include compressed natural gas, electricity, ethanol, methanol, and others. The expense of converting buses to use other alternative fuels or of purchasing new fleets to meet the federal emissions standards imposes a financial hardship for urban transit systems.

Biodiesel can be used in existing diesel engines without expensive conversion changes. One merely changes from diesel fuel to biodiesel. Therefore, Spokane Transit Authority and other transit systems have been looking into biodiesel as a viable alternative to diesel fuel. The Spokane Transit Authority system was chosen for this feasibility study as it serves the urban center of the northern Idaho and eastern Washington region, and has tested biodiesel blended with diesel fuel.

Spokane Transit Authority Fuel Use

Spokane Transit Authority (STA) is the urban transit system for Spokane, Washington and the surrounding area in Spokane County. STA serves a 371 square mile area that has a population of about 331,000 people. STA operates several services including 36 bus routes, paratransit services for persons with disabilities, car pool and vanpool matching, as well as transportation consulting services (Spokane Transit Authority, 1993).

Eighteen buses were used for a biodiesel experiment from September 1993 to February 1994. These buses ran on a blend of 70 percent diesel and 30 percent biodiesel. The biodiesel used soybean oil as a feedstock and was supplied by the Iowa Soybean Association. At the end of the six month experiment, STA reported reduced fumes, lower particulate levels, and increased fuel economy for the buses using the blend.

At the time of this study, STA utilized 157 coaches each of which used about 1,100 gallons of diesel per month (Caro, 1994). This is a total of 172,700 gallons of diesel required per month or 2,072,400 gallons per year for the fleet of coaches alone. Considering that Spokane is a major center in the Inland Pacific Northwest, it would be reasonable to look at area rapeseed/canola producers as a source of fuel for the STA.

Plant Site Analysis

A linear programming model was used to select an optimal plant site based on the transportation cost of moving seed and the three co-products of meal, biodiesel, and glycerine to and from the plant. Regional trucking firms were contacted for custom hauling rates between possible plant sites, canola producing areas, and product markets.

Six possible plant sites were selected. The sites include five seed-producing areas (Moscow and Craigmont Idaho, Steptoe, Ritzville, and Dayton Washington) and Spokane, Washington. The five cities were chosen as possible sites because they are located in canola or rapeseed producing areas and are accessible to Spokane by major highways. Spokane was chosen as a possible site since it was the target market for both biodiesel and glycerine (Figure 3-1).

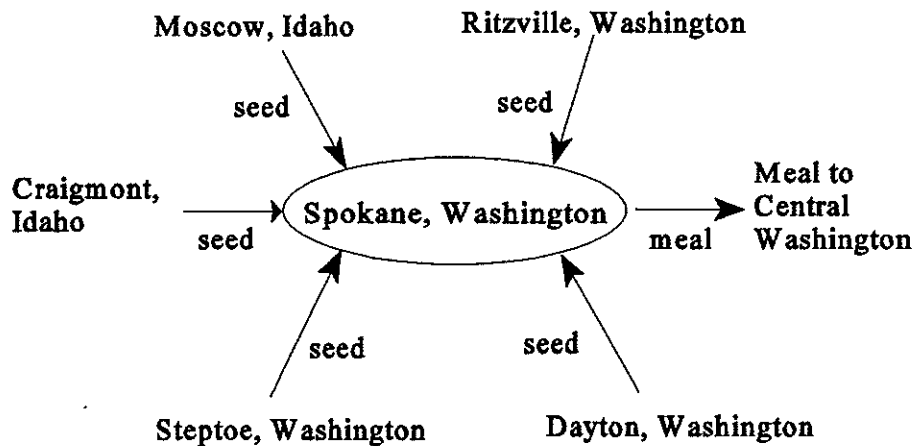


Figure 3-1. Seed and meal flows with Spokane, Washington as the processing location. Spokane is also the market for products except meal, which is shipped to central Washington for livestock feed. Possible destinations for meal include one or more of the following cities: Pascoe, Yakima, Ellensburg, and Moses Lake.

The meal co-product was to be hauled back to the seed producing areas or to one of four cities in central Washington. The four cities considered as potential meal markets were Pascoe, Yakima, Ellensburg, and Moses Lake, Washington. Each of these cities are major trading centers for the surrounding counties, and there are many livestock enterprises in each area. Canola meal can be fed to any livestock species in the area.

Custom hauling rates for seed and meal transportation were based on belly dump trucks capable of hauling 70,000 pounds or more of seed. The rates for glycerine were based on a minimum tanker truck load of 48,000 pounds. The plant was estimated to be able to produce one truck load of glycerine every 2 weeks (Northwest Agricultural Cooperative Association, 1994).

The transport cost of shipping the meal to market was subtracted from the total value of meal produced per day. The base model assumed that the meal was to be shipped to the seed producing areas. Base model calculations revealed that the optimum plant site was Steptoe, Washington. Transport costs at this location totaled \$942.69 per day. The second best location for the biodiesel plant was Spokane, Washington with transport costs of \$1,141.64 per day.

The alternate meal transport site model utilized the same assumptions except that all meal produced by the plant would be shipped to one of four central Washington cities. The model again chose Steptoe, Washington as the plant site with all meal produced being shipped to Moses Lake, Washington (Figure 3-2). The total cost for shipping meal with this option was \$1,066.03 per day. The total cost for custom hauling meal from Spokane, the second plant site choice, again to Moses Lake was \$1,092.42 per day.

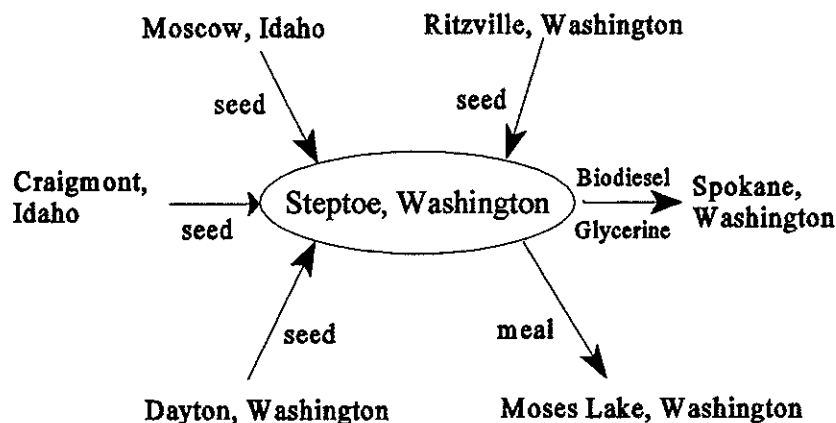


Figure 3-2. Seed, meal, biodiesel, and glycerine flows with Steptoe, Washington as the processing site and Spokane as the product market for biodiesel and glycerine. Meal is shipped to Moses Lake to be used as livestock feed.

Based on these models, the Steptoe plant site was chosen as the least-cost location for the biodiesel plant. Moses Lake was chosen as the destination for the meal.

COST TO PRODUCE BIODIESEL

Canola Procurement Costs

As explained previously, it was assumed that all of the seed needed to supply the market could be purchased for 13 cents per pound at the local storage sites. The structure needed to store the canola seed and meal for the extraction plant was an underutilized grain elevator at the processing site. A grain elevator was considered to be a reasonable site because necessary equipment such as augers, bins, conveyors, scales, and loading areas were all available. Local grain cooperatives owned these grain elevators. The assumption made for this study was that the biodiesel plant was operated by one of these grain cooperatives using an elevator owned by the cooperative. A per bushel rental fee was assumed to be paid for storage.

A plant with a capacity of 75 metric tons of seed per day would be large enough to produce adequate biodiesel for the target area. It was assumed that the plant would process an average of 71.43 metric tons of seed per day for 300 days per year for a total of 21,429 metric tons of seed processed per year. Assuming a typical 1,000-acre farm producing 100 acres of spring canola per year and further that the average yield was 1,300 pounds per acre, it would take 36,330 acres of canola per year, or about 364 farms to supply the market.

Oil yield estimates were based on a 40 percent oil content in the seed and an extraction rate of 91 percent of the oil. An acre producing 1,300 pounds of seed would contribute about 473 pounds of oil and 827 pounds of canola meal. Table 3-2 gives a breakdown of the costs required to extract the oil and produce biodiesel from canola oil.

Table 3-2. Estimated annual biodiesel production costs and cost per gallon.

| | (\$) | (%) |
|---|-------------------|-------|
| Procurement cost | | |
| Canola seed @ 13 cents/pound | 6,139,702 | |
| Transport cost | 129,936 | |
| Elevator rental cost | 22,890 | |
| Storage cost | 161,235 | |
| Total procurement costs | 6,453,763 | 70.1 |
| Extraction costs | | |
| Depreciation expense | 62,500 | |
| Equipment loan payment | 219,263 | |
| Electricity | 21,276 | |
| Water | 473 | |
| Labor | 144,000 | |
| Repairs | 62,500 | |
| Total extraction costs | 510,012 | 5.5 |
| Transesterification costs | | |
| Depreciation expense | 157,292 | |
| Equipment loan payment | 219,564 | |
| Electricity | 16,640 | |
| Water | 357 | |
| Waste Water | 468 | |
| Labor | 187,200 | |
| Repairs | 17,391 | |
| Materials | 695,336 | |
| Transport cost | 55,637 | |
| Total transesterification costs | 1,349,885 | 14.7 |
| Overhead costs | | |
| Insurance | 106,481 | |
| Sales and administration | 36,000 | |
| Operating loan payment | 631,130 | |
| Total overhead costs | 773,611 | 8.4 |
| Opportunity cost of equity capital | 115,684 | 1.3 |
| Total biodiesel cost | 9,202,955 | 100.0 |
| Credits | | |
| Net meal value | 2,349,761 | |
| Net glycerine value | 904,493 | |
| Net biodiesel cost | 5,948,701 | |
| Net cost of biodiesel per gallon | 2.56 | |
| Note: Annual acres required | 36,330 acres | |
| Annual canola seed required | 47,228,481 pounds | |
| Annual canola oil production | 17,191,167 pounds | |
| Annual biodiesel production | 2,327,000 gallons | |

Extraction Costs

Two companies were contacted about extraction plant costs. Each of these companies is prominent in the extraction equipment supplier industry. They supplied written bids on equipment used, costs, utilities, and installation.

The detailed extraction process in Figure 3-3 was taken from information provided by Anderson International Company. The end products are filtered oil and oil meal.

A separate building was needed to house the extraction and transesterification systems since they involve the use of alcohol, heating elements, and steam and could not be located in the preexisting grain elevator. It was assumed that an 8,000-square foot building would be adequate and would cost \$51.39 per square foot. This cost includes required piping, electrical installation, central air-conditioning, fire alarms, and sprinkler system. This building would be used for both oil extraction and transesterification of the fuel.

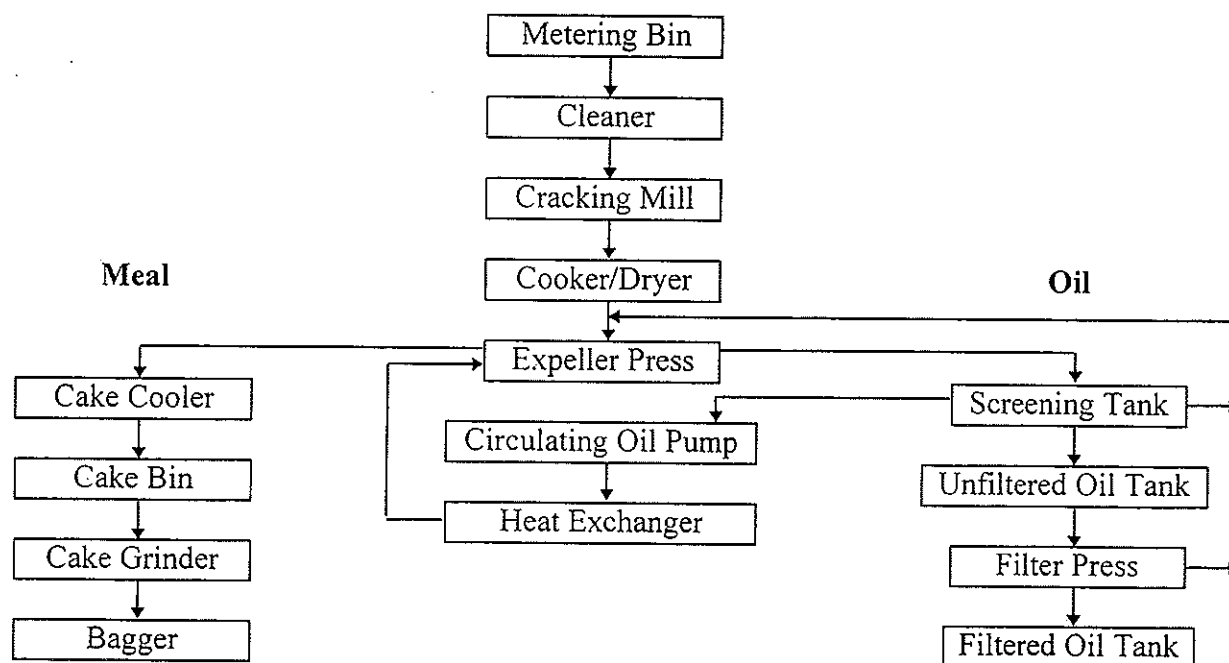


Figure 3-3. Flow chart of extraction process. Seed is brought to the mill, cleaned, and prepared for extraction. After oil is removed from the seed, the oil is filtered and then ready for processing into biodiesel and glycerine. Meal is diverted, cooled, ground for more uniform product, and stored in bulk or put into bags.

Extraction Plant Installation Costs

Installation costs include all costs required to get the capital equipment running to its capacity. Both companies stated that the installation costs for an extraction plant equal roughly the cost of the equipment. The equipment cost was \$1,250,000, making the finished plant cost about \$2,500,000 (Anderson International Co. 1993; French Oil Mill Machinery Co. 1993).

Utilities Costs

Electricity requirements for the extraction process were estimated at 325.14 kWh per day based on written bids provided by the manufacturers. This includes power for all the equipment used in the extraction plant. The plant also has a steam boiler that would require 1,447.74 kWh per day. The rate of 4 cents per kWh was quoted by Washington Water Power and was used to calculate the electricity cost per day.

The heat exchangers utilize 100 gallons of water per minute to help cool the oil after it has been extracted. The water is recycled through a cooling tower with only about a 3 percent loss due to evaporation and drift. This estimate of water loss results in the extraction plant requiring 4,320 gallons per day to replace the lost water. Steptoe water users were charged \$13 for the first 5,000 gallons used each month. From 5,000 to 10,000 gallons the rate was 55 cents per 1,000 gallons, and above 10,000 gallons the rate was 30 cents per 1,000 gallons. (Steptoe Water and Sewer District 1994). The extraction water cost was estimated by multiplying the total plant water usage by the percentage of water used in the extraction process.

Labor Costs

Labor requirements for this size of an extraction plant are minimal because of the automation of the plant. Only two people were needed per shift at a semi-skilled labor rate of \$10 per hour. This rate included a base wage plus a percentage for Social Security, Medicare, unemployment insurance, and other employment expenses.

Maintenance and Repair Costs

Because maintenance costs were not included in the written bids, an estimate of 5 percent of the capital costs was used. This rate was based on a telephone conversation with a representative of French Oil Mill Machinery Co. (French Oil Mill Machinery Co. 1993).

Canola Meal Adjustment

Canola meal value was subtracted from total costs of producing biodiesel in order to estimate the net cost. The market price for canola meal was based on prices paid in the Portland, Oregon, market. Canola meal prices tend to follow soybean meal prices according to available price data for recent past years.

Canola meal has about three-fourths the protein of soybean meal, and the Portland price for canola meal was about 70 percent of the Portland soybean meal price. This relationship was fairly constant for the nine years of available price data (Figure 3-4). Other areas of the nation may have a different relationship between soybean and canola meal depending on demand and proximity to the source.

In the absence of a canola meal price for areas of the Pacific Northwest, one can estimate its value to be about 70 percent of the soybean meal value.

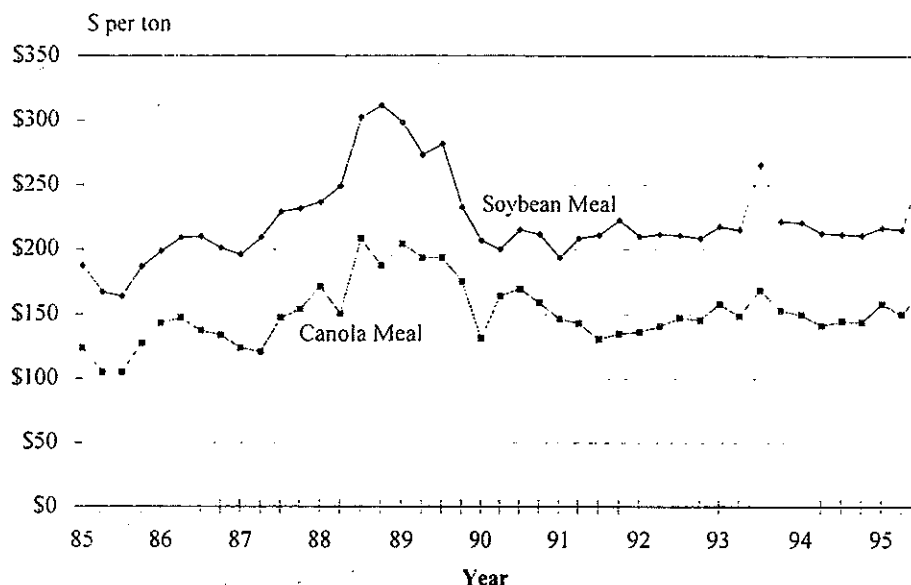


Figure 3-4. Price of feed meals, Portland, Oregon, 1985-95. (Price quotes for January, April, June, and October of each year. Only the first two quarters were available for 1995.) Source: USDA 1985-94.

The Transesterification Process

Once the feedstock has been crushed and the oil extracted, the transesterification of the oil into biodiesel takes place. Transesterification is the process of reacting a triglyceride, such as one of the vegetable oils, with an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters.

The processing plant was set up to manufacture a canola methyl ester rather than an ethyl ester, since methanol has historically been the lower priced alcohol. Two catalysts commonly used in transesterification are sodium hydroxide (NaOH) and potassium hydroxide (KOH). The catalyst chosen in the initial case was KOH.

The transesterification process begins with filtered canola oil from the extraction plant. The oil is added to the reactor from its storage tank. The alcohol and catalyst are combined in a mixing tank and then added to the reactor. After mixing, the ester separates from the glycerol. The raw ester is left in the reactor for washing, and the glycerol is drained off. After washing, the methyl ester is approximately 99 percent pure. The conversion rate of oil to methyl ester was calculated at 98.3 percent (Caringal 1989).

The glycerol phase is flash distilled to vaporize the remaining methanol, which is then condensed and recycled for reuse in the reactor. After the methanol has been recovered, the glycerol phase is vacuum evaporated to recover and refine the glycerol present. The residue that remains after the glycerine has been recovered is discarded. The glycerine recovered has

a glycerol content of 98.2 percent. The glycerol recovery rate at the evaporator was 86.29 percent (Caringal 1989).

Methyl ester was to be stored for delivery to STA in tanks with a capacity of one week's production. Glycerine would also be stored on site since it would require two weeks of production to fill a truck for transportation to market.

The entire transesterification process requires 24 hours to complete. Therefore, the transesterification plant costs were calculated at 24 hours per day, and the volume of methyl ester needed to supply STA would require production for 260 days per year.

The flow chart in Figure 3-5 illustrates the materials used and the products that result from the transesterification process on a daily basis. Recycling of the methanol reduces the consumption of this raw material by 26 percent.

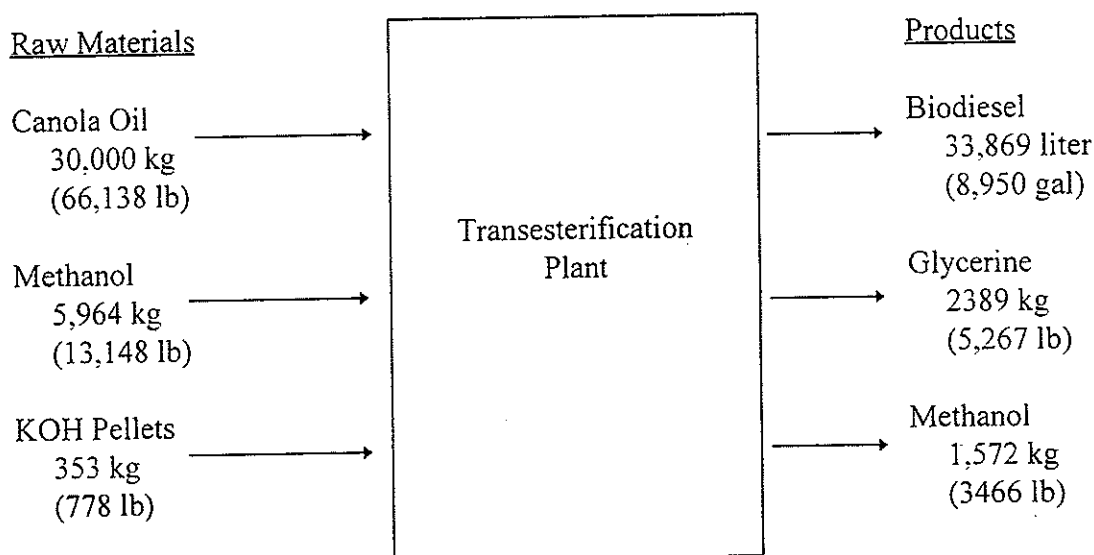


Figure 3-5. Material balance of transesterification process (per day). The methanol recovered is recycled back to the raw materials so the net methanol use per day is 4,392 kg.

Transesterification Equipment Costs

The estimated equipment costs for a transesterification facility that can process 30 metric tons of canola oil per day was \$695,656. Equipment required was estimated using scale-up techniques of Caringal (1989). The cost of the equipment was determined using Caringal's estimate with an adjustment for size and a 3 percent per year adjustment for inflation.

Transesterification installation costs were calculated at 50 percent of the total transesterification equipment cost. Installation costs include freight charges, labor, electrical set-up, spill control dikes around storage tanks, and all other costs necessary to have the plant running at or near capacity.

Transesterification Operating Costs

Electrical costs were based on a total daily usage and were estimated using the scale-up techniques of Caringal (1989).

The water usage of the transesterification process was estimated to be 187,710 gallons per day. However, most of this water was recycled and used in the washing process again. The water usage costs were allocated between the extraction and transesterification processes based on the percentage of total water use by each system. The transesterification process was estimated to use 43 percent of the total water consumed by the plant.

Of the water used, all could be recycled except for about one-third of a gallon for each gallon of fuel produced, which was considered waste water. At a level of 2,983 gallons of waste water produced per day, the plant produces 775,580 gallons per year. The City of Steptoe had a waste water rate of \$39 per month for industrial uses with water requirements at the level of the processing plant.

Labor required for the transesterification process was estimated at three people for each eight-hour shift. Semi-skilled labor was used and was paid \$10 per hour. The labor rate included a base wage plus a percentage for Social Security, Medicare, unemployment insurance, and other overhead expenses. Repairs and maintenance costs for each year were estimated at 2.5 percent of the equipment costs. This was below the rate for the extraction process because the equipment had a higher value and less deterioration.

The price of methanol used in this study was \$1.44 per gallon (Van Waters and Rogers Inc. 1994). This price was based on the market price for methanol with a quantity purchase discount included. The plant uses 1,479 gallons per day, and has the methanol delivered to the plant in truckloads of 9,600 gallons each.

Potassium hydroxide (KOH) pellets were valued at 70 cents per pound (Van Waters and Roger, Inc. 1994). The plant used 778 pounds per day and had the KOH delivered in 400-pound drums once a week.

When NaOH was used as the catalyst, it had a cost of 44 cents per pound (Van Waters and Rogers, Inc. 1994). NaOH beads were used in the same amount as KOH pellets. The plant received the NaOH beads in shipments of 500-pound drums once a week.

Transport costs for shipping biodiesel to Spokane from the plant site in Steptoe totaled \$213.99 per truckload (JJW Trucking Limited 1994). The biodiesel was assumed to be shipped using tanker trucks at the rate of one truckload per day.

Glycerine Co-Product Adjustment

Industry processing methods for crude glycerine include distillation and ion exchange. Caringal (1989) studied two methods for glycerol recovery from the biodiesel process. Method A utilized a series of filtration steps to separate the glycerol from the glycerol phase. Method A yielded a condensate that was 90.1 percent glycerol, not technical grade. Method B used vacuum evaporation to separate the glycerol and resulted in a condensate of 98.2 percent glycerol, which is technical grade. Caringal (1989) recommended vacuum evaporation because of the higher purity and recovery rate of the glycerol and the fewer steps involved in the process. Caringal's vacuum evaporation method appears to be similar to the distillation process widely used in industry. The vacuum evaporation method was assumed for this study because of its high glycerol recovery rate, lower labor requirement, and resulting purified glycerine to be sold at the refined glycerine price.

Glycerine is recovered at the rate of about 5,270 pounds per day. Glycerine prices were based on the prices reported for 96 percent glycerol in the Chemical Marketing Reporter 1985-1994 series. Value of glycerine produced per day of processing was estimated to be \$3,531 using the five-year average glycerine price of 67 cents per pound.

The cost of hauling glycerine to Spokane from the plant site at Steptoe was subtracted from the value of glycerine produced. Transport cost was estimated to average \$52.08 per day including cleaning the truck tanks after delivery. One truckload of glycerine was shipped to Spokane every two weeks and sold to regional chemical companies. Selling crude unprocessed glycerine was not considered in this study as no accessible market was found in the area.

Transesterification Overhead Costs

Insurance costs for the plant were estimated by a local commercial insurance agency. The insurance costs include both property and liability coverage.

Sales and administration of the plant are handled by the plant manager. The manager was to be paid for an eight-hour day at a labor rate of \$15.00 per hour. The labor rate includes a base wage plus a percentage for Social Security, Medicare, unemployment insurance, and other overhead expenses.

A revolving operating loan was needed to cover the first month of cash expenses for the plant. This loan is assumed to be for one year at 8 percent interest.

Other Assumptions for the Cost Analysis

Depreciation expense for the extraction equipment was based on a 40 year useful life using the straight-line method and assuming no salvage value. It was assumed that the cooperative of growers running the biodiesel plant would borrow 90 percent of the capital needed to purchase the equipment. The long-term fixed interest rate loan payment was calculated at 9 percent per year for 30 years with equal amortized payments.

The transesterification equipment had an assumed useful life of seven years, while the building constructed to house the plant has an estimated life of 50 years. Depreciation expense for the transesterification equipment and the building was calculated using the straight-line method assuming no salvage value. As with the extraction equipment, it was assumed that the cooperative would require a loan worth 90 percent of the capital needed to purchase the equipment and the building. The equipment loan was for seven years, and was calculated using an 8.5 percent per annum interest rate and equal total payments. The building had a long-term loan of 30 years with a fixed interest rate of 9 percent per annum and equal total payments of principal and interest. The operating costs were calculated as described in the transesterification cost analysis section.

Cost Allocation

The cost of producing canola seed was, by far, the largest single cost of producing biodiesel so shown on (Table 2). At 70 percent of total costs, it is obvious that as the price of canola seed fluctuates, it will greatly impact the price per gallon of biodiesel fuel.

Transesterification accounted for nearly 15 percent of the total cost. More than half of this was for materials. Overhead costs made up 8.4 percent of the total.

The co-product credits played a large role in the reduction of these total costs. The canola meal adjustment offset 26 percent of total costs, while the glycerine adjustment offset 10 percent of total costs. Combined, the two co-product credits offset 36 percent of total costs, leaving the sale of biodiesel to recover only 64 percent of the total.

SENSITIVITY ANALYSIS

Canola Seed

The cost of canola seed makes up a large portion of the total cost of biodiesel, so the price of the seed could have great impacts on the cost per gallon. The cost estimate was used to do a sensitivity analysis of how price changes in canola would impact biodiesel's cost per gallon. At a price of 9 cents per pound of seed, the cost of biodiesel was \$1.69 per gallon. At 15 cents per pound the cost per gallon of biodiesel was \$2.91 per gallon. On average, a one cent per pound increase in the price of canola seed increased the price per gallon of biodiesel by 20 cents.

Meal

The meal adjustment accounted for 26 percent of total costs, reflecting the importance of the meal sales price to the cost of biodiesel per gallon. When the price of meal increases by \$10 per ton the cost of biodiesel decreases around 6 cents per gallon. As has been shown, canola meal prices closely follow the soybean meal price and can be expected to fluctuate in a similar way. Large changes in the price of meal can significantly affect the net cost of biodiesel.

Glycerine

The glycerine adjustment accounted for 10 percent of total costs. Since glycerine prices are quite volatile, the cooperative will need to develop a market strategy to obtain the best possible price. A price sensitivity analysis showed that as glycerine prices increase 5 cents per pound the cost biodiesel decreased by about 3 cents.

Diesel - Biodiesel Blend

The estimated cost of \$2.56 per gallon to produce biodiesel assumes 100 percent biodiesel used to power the buses. A more likely scenario would be a blend of biodiesel with diesel fuel. For example, an 80-20 blend of diesel and biodiesel was found to reduce air pollution substantially and its cost would be about the following:

$$(0.8)(0.90) = 0.72$$

$$(0.2)(2.56) = 0.51$$

\$ 1.23 per gallon

This price is higher than straight diesel but may be justified in areas where pollution reduction is critical. If the blend were used instead of total biodiesel, the amount of biodiesel required by STA would be reduced. In this case, a larger market would be required to use the production from the proposed processing plant. An alternative would be to sell canola oil on the market except for a reduced amount used in a smaller transesterification facility. Another alternative would be to buy canola or other vegetable oils from a larger extraction plant located in another area and process the biodiesel locally.

SUMMARY AND CONCLUSIONS

A limited acreage of industrial winter rapeseed has been grown for several decades in the Palouse region of Idaho and Washington. Recently canola types of rapeseed have been introduced into the areas as an alternative to barley, peas, and other crops grown in rotation with wheat. Unlike industrial rapeseed, canola produces an edible oil and a good quality protein meal for livestock. Canola competes with other edible vegetable oils such as soybean, cottonseed and others.

Vegetable oil can also be used as feedstock for biodiesel. With this in mind, this study estimated the cost of producing biodiesel in eastern Washington and northern Idaho using locally grown canola. Studies of canola production costs and returns have shown that returns can cover all economic costs only if excellent yields are obtained. In this study, estimated

economic costs of producing spring canola seed amounted to about 20 cents per pound based on a yield of 1,300 pounds per acre. The biodiesel cost estimates used a price of 13 cents per pound to more nearly reflect the market price for canola seed.

Costs were estimated for extracting oil from the seed and for processing the oil into biodiesel. Seed procurement cost, including seed at 13 cents per pound, transport, and storage, was 70 percent of the final cost of biodiesel. Oil extraction was another 5.5 percent of the cost. The other 24.5 percent of costs were for transesterification of the oil, transportation of the oil, transportation, equity capital, and overhead.

The estimated cost of a gallon of biodiesel was \$2.56 when canola seed cost 13 cents per pound. When the price of canola were raised to 15 cents, the estimated cost of each gallon of biodiesel was \$2.91. When the price of canola was dropped to 9 cents per pound, the estimated cost of one gallon of biodiesel was only \$1.69. Clearly, seed cost is a big factor on the final price of biodiesel.

Biodiesel blends afford most of the advantages of biodiesel at a much lower cost than straight biodiesel. With the cost of diesel fuel at 90 cents per gallon and the cost of biodiesel is \$2.56 per gallon, a gallon of blended fuel composed of 20 percent biodiesel and 80 percent diesel would cost about \$1.23.

While canola produces an adequate quality of biodiesel, a canola based biodiesel is expensive in comparison with diesel. Therefore, except for specialized uses, a less expensive feedstock will be needed to make biodiesel a competitive fuel. There may be specific circumstances where it would be feasible to use a blended canola fuel, however, such as in environmentally sensitive areas, including congested urban areas. The Spokane Transit Authority, however, decided in 1994 that the cost of its diesel-biodiesel blend exceeded the benefits, and decided against its further use in buses for the near future. For the present, at least, the vegetable oil market will be the preferred market for canola. Industrial rapeseed, on the other hand, must compete in the more limited industrial oils market.

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EMA 200 HOUR TESTS

MATERIALS AND METHODS

Equipment

Three Yanmar 3TN75E-S diesel engines (3-cylinder, 4-stroke, naturally aspirated, direct injection) were used as the test engines. Each has a bore and stroke equal to 75 mm, a displacement of 994 cc, a compression ratio of 17.6:1 and a one-hour power rating of 15 kW at 3000 RPM. These engines were chosen because their design is typical of most diesel engines used in agriculture today.

Three test stands, designed and built at the University of Idaho were used to load and monitor the test engines. Each stand uses a hydraulic dynamometer which consists of a Hydreco gear pump (cradled for torque measurement) coupled directly to the engine clutch shaft. A Sperry-Vickers electronically modulated relief valve (EMRV) was used to control the pressure on the pump and thus the load applied to the engine. A constant volume flowmeter, which measures the time for a known volume of fuel to be consumed, and a magnetic pickup, which measures engine speed at the clutch shaft have been incorporated into each stand. Throttle control was provided by a DC gearhead motor linked to the throttle shaft of each engine's fuel injection pump. Each test stand can be controlled either manually from the stand or remotely with a data acquisition and control system.

The data acquisition and control system consists of a microcomputer and a Hewlett Packard 3497 data acquisition control unit. The system capabilities include control of engine speed and load as well as measurement of engine torque, speed, power output, fuel consumption, and temperatures (exhaust, crankcase oil, fuel, and hydraulic oil).

Diesel exhaust quality is usually expressed in terms of the opacity of the exhaust smoke. A Telonic Berkley model 200 portable opacity meter was connected to the data acquisition unit and collected data at the 50 hour torque test intervals. The opacity meter consists of a light source positioned on one side of the exhaust stream and a photo resistor mounted on the opposite side. The meter provides an output voltage ranging from 0 to 1.00 volts. One hundred percent opacity (1.0 volt) corresponds to no light transmission whereas 0 percent opacity corresponds to complete light transmission.

Load Cycle

The standard EMA test was designed to initiate durability problems associated with the use of alternative fuels in a relatively short period of time. Thus the load cycle is quite severe. The standard test utilizes four engine load cycles (1 set) over a three hour period. The standard test calls for five consecutive sets (15 hours of continuous operation) followed by a nine hour (minimum) period during which the engines are shut down and allowed to reach ambient

temperature. In order to accommodate the schedules of the lab staff, this study used a shortened version of the standard test which consisted of 3 consecutive sets (9 hours of continuous operation). This was continued until 200 hours were logged on each engine.

The four conditions are described as follows:

1. Rated condition (60 minute): Operating at full throttle, a load is applied until engine speed decreases to the manufacturer specified rated speed.
2. Maximum torque (60 minute): Operating at full throttle, a load is applied until the engine speed decreases to the speed of rated torque as described by the manufacturer.
3. High idle (30 minute): the load is set at 25 percent of maximum torque and the throttle is varied to achieve an engine speed of 90 percent of rated speed.
4. Low idle (30 minute): At no load the throttle is varied to achieve the manufacturers recommended curb idle.

The following data (averaged over the duration of the cycle) were measured and collected for each load cycle of every set:

| | |
|------------------|---------------------------|
| Engine speed | Crankcase oil temperature |
| Torque | Exhaust gas temperature |
| Power output | Fuel temperature |
| Fuel consumption | Ambient temperature |

Lubricating Oil

A 55-gallon drum of Chevron Delo Multigrade SAE 15W-40 heavy duty motor oil was procured at the beginning of the test. The engine oil and filter were changed at 100 hour intervals and an oil analysis was performed at 50 hour intervals for each engine.

PROCEDURES

The 200 hour test cycle described above was run to evaluate the engine durability effects of long term usage. The tests were performed on three identical engines simultaneously and controlled by the microcomputer based data acquisition and control system.

Prior to the test, the engines were completely rebuilt. New pistons, rings and valves were installed and the cylinder heads were glass bead cleaned to remove all carbon build-up in the intake and exhaust ports. Following the rebuild, the engines were subjected to a short break in period on 100% 2-D as recommended by the manufacturer before beginning the described test.

At 100 hour intervals the engine oil and filter were changed and oil samples were taken from each engine's crankcase and analyzed by a commercial lab for wear metal concentrations and viscosity changes. At 50 hour intervals, the test was halted to run the following tests with each engine running on its respective test fuel:

Constant throttle - variable speed torque tests
Injector performance check
Cylinder compression check
Opacity check

At each of these 50 hour intervals the injectors were removed, photographed and digitized to provide a quantitative record of injector coking. The results of the injector digitizing method are reported as a relative coking number. This number is obtained by, first, digitizing a clean injector photograph and using its projected area as a reference. Then each used injector is photographed from two positions, 90 degrees apart, and both profiles are digitized. The areas are then corrected through use of a scale factor to compensate for variations in the photograph printing process. The profile which gives the maximum corrected area is selected and subtracted from the corrected area of the clean injector.

All engine service and maintenance was performed as specified in the manufacturers service manual. No modifications were made to any three of the engines for testing the Biofuels.

PART I

EMA Tests with RME, REE, and 2-D

Fuels

The fuels used in this study were 100% Phillips 0.05 sulfur diesel fuel (2-D), 100% ethyl ester of rapeseed oil (REE), and 100% methyl ester of rapeseed oil (RME). The rapeseed was Dwarf Essex variety and was expelled and processed using the facilities of the University of Idaho's Department of Biological and Agricultural Engineering. The fuel properties were determined by University of Idaho technicians and a commercial lab and are displayed in Table 4-1.

RESULTS AND DISCUSSION

Fuel Consumption

The engine fueled on 2-D consumed 630 liters (166 gallons) of fuel, the REE fueled engine consumed 742 liters (196 gallons) of fuel, and the RME fueled engine consumed 780 liters (206 gallons) of fuel. The differences in fuel consumption reflects the differences in heat of combustion and density of the individual fuels and are affected by variations in settings between engines.

Table 4-1. Fuel Characterization Data

| | 2-D | REE | RME |
|----------------------------------|--------|--------|--------|
| Fuel Specific Properties | | | |
| Specific Gravity, 60/60 | 0.8495 | 0.876 | 0.8802 |
| Viscosity, cSt @ 40°C | 2.98 | 6.17 | 5.65 |
| Cloud Point, °C | -12 | -2 | 0 |
| Pour Point, °C | -25 | -15 | -15 |
| Flash Point, °C | 87 | 185 | 175 |
| Boiling Point, °C | 191 | 273 | 347 |
| Water and Sediment, % Vol. | <0.005 | <0.005 | <0.005 |
| Carbon Residue, % mass | 0.16 | 0.06 | 0.08 |
| Ash, % mass | 0.002 | 0.002 | 0.002 |
| Sulfur, Wt% | 0.036 | 0.014 | 0.012 |
| Cetane Number | 48.2 | 64.9 | 61.8 |
| Heat of Combustion, Gross, MJ/kg | 45.42 | 40.51 | 40.54 |
| Copper Corrosion | 1A | 1A | 1A |
| Karl Fischer Water, ppm | 38 | 761 | 757 |
| Particulate Matter, mg/L | | | |
| Total | 0.9 | 1.9 | 1 |
| Non-Combustible | <0.1 | 0.9 | <0.1 |
| Elemental Analysis | | | |
| Nitrogen, ppm | | 11 | 6 |
| Carbon, % | 86.67 | 76.83 | 78.7 |
| Hydrogen, % | 12.98 | 11.8 | 12.66 |
| Oxygen, % (by difference) | | 11.36 | 9.22 |
| Iodine Number | 8.6 | 99.7 | 91.9 |
| Ester Specific Properties | | | |
| Percent Esterified | | 94.75 | 98.02 |
| Acid Value | | 0.097 | 0.128 |
| Free Glycerol, %wt | | 0.72 | 0.4 |
| Total Glycerol, %wt | | 0.93 | 0.86 |
| Free Fatty Acids, %wt | | 0.58 | 0.57 |
| Monoglycerides, %wt | | 0.58 | 0 |
| Diglycerides, %wt | | 1.33 | 1.35 |
| Triglycerides, %wt | | 2.17 | 0.45 |
| Alcohol Content, % mass | | <1 | <1 |
| Catalyst, microgram/gram | | 12 | 11 |
| Fatty Acid Composition, % | | | |
| Palmitic (16:0) | | 2.6 | 2.2 |
| Stearic (18:0) | | 0.9 | 0.9 |
| Oleic (18:1) | | 12.8 | 12.6 |
| Linoleic (18:2) | | 11.9 | 12.1 |
| Linolenic (18:3) | | 7.7 | 8 |
| Eicosenoic (20:1) | | 7.3 | 7.4 |
| Behenic (22:0) | | 0.7 | 0.7 |
| Erucic (22:1) | | 49.5 | 49.8 |

Engine Performance

The observed performance trend, shown in Figure 4-1, shows the change in power relative to output at zero hours for each 50 hour interval. Relative power change is shown instead of actual power to compensate for the difference in engines.

Cylinder compression varied from 2.65 MPa (385 psi) to 3.10 MPa (450 psi) between cylinders and engines, but varied only 40 psi for the same cylinder during the test. The fuel injector valve opening pressure (psi) varied from 20.34 MPa (2,950 psi) to 21.37 MPa (3,100 psi) for all the fuel injectors. Individual injector valve opening pressure varied only 344 kPa (50 psi) for the duration of testing. Engine blowby was measured at each 50 hour interval with no difference from beginning to end for each of the three engines.

Oil Analysis

All engines show a decrease in engine oil viscosity compared to new lubricating oil. A slight increase in engine oil viscosity, compared to RME and REE, was observed with the diesel fueled engine. The engine oil viscosity versus time data is shown in Figure 4-2, and the total base number (TBN) versus time is shown in Figure 4-3. The TBN indicates the potential of the oil to neutralize strong acids as the mineral acids derived from sulfur, chlorine, and bromine. Decreases in TBN are associated with corrosion of engine parts and increases in varnish deposits.

Engine wear was evaluated on the basis of the concentrations of three wear metals in the lubricating oil. The metals, and their primary source, used as the wear basis are as follows:

- 1) Iron - cylinder, camshaft, valve train, gear wear
- 2) Aluminum - piston and bearing wear
- 3) Silicon - anti-foam additive, ingested dirt

Wear metal concentration results are shown in Figures 4-4 through 4-6. All the engine oil analysis were within the allowable limits.

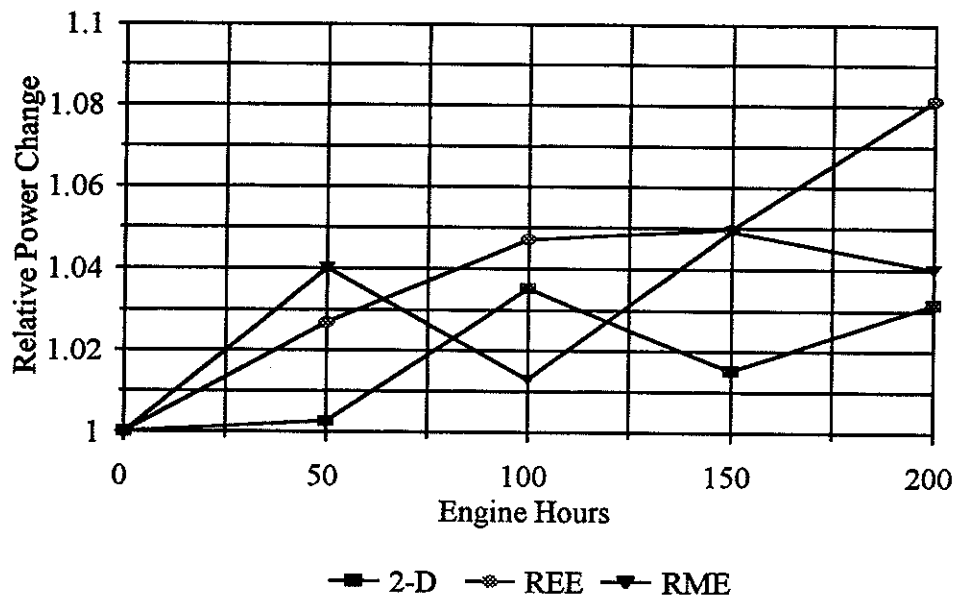


Figure 4-1. Engine Power Change Relative to the Engine Power at 0 Hours.

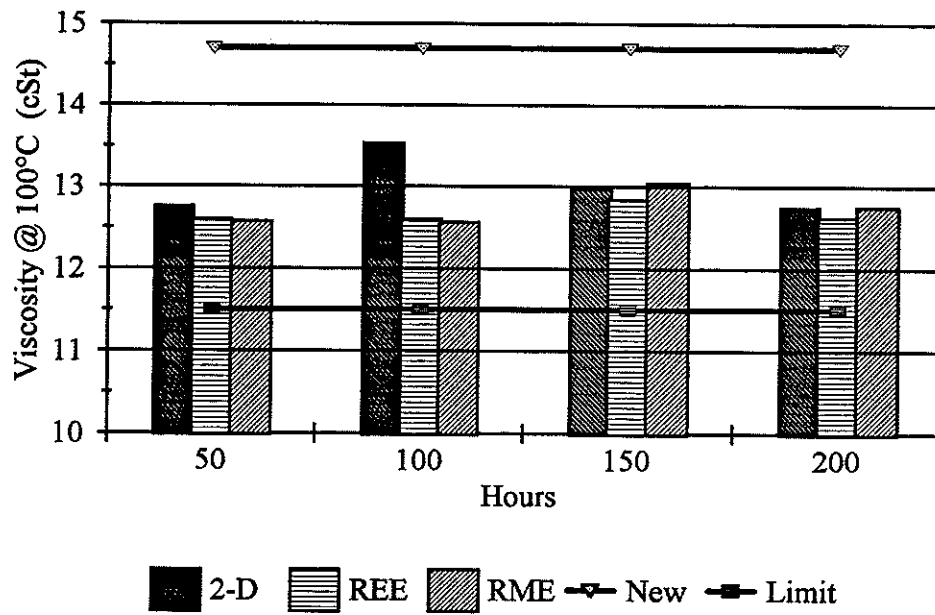


Figure 4-2. Engine Oil Viscosity vs Time.

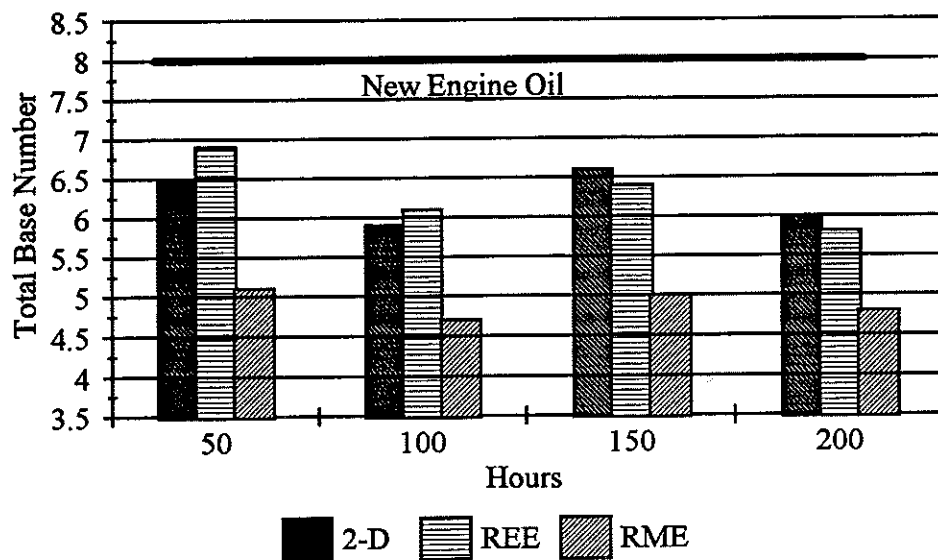


Figure 4-3. Engine Oil Total Base Number vs Time.

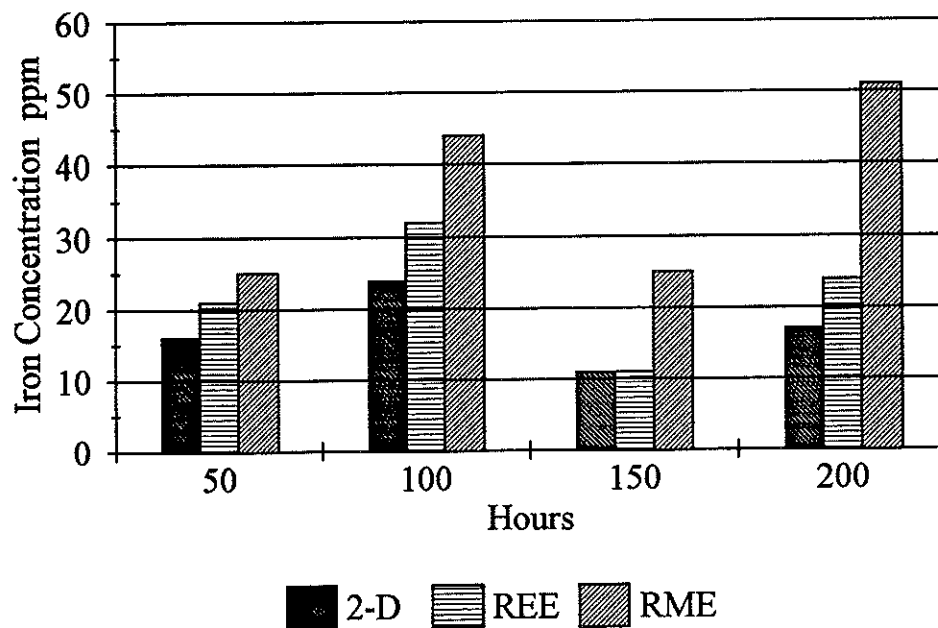


Figure 4-4. Engine Oil Iron Concentration vs Time.

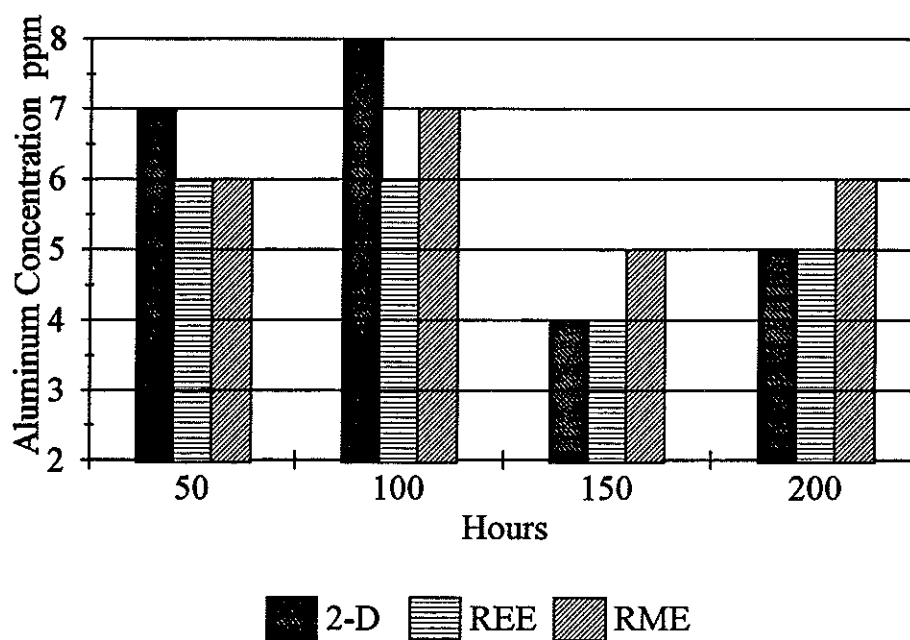


Figure 4-5. Engine Oil Aluminum Concentration vs Time.

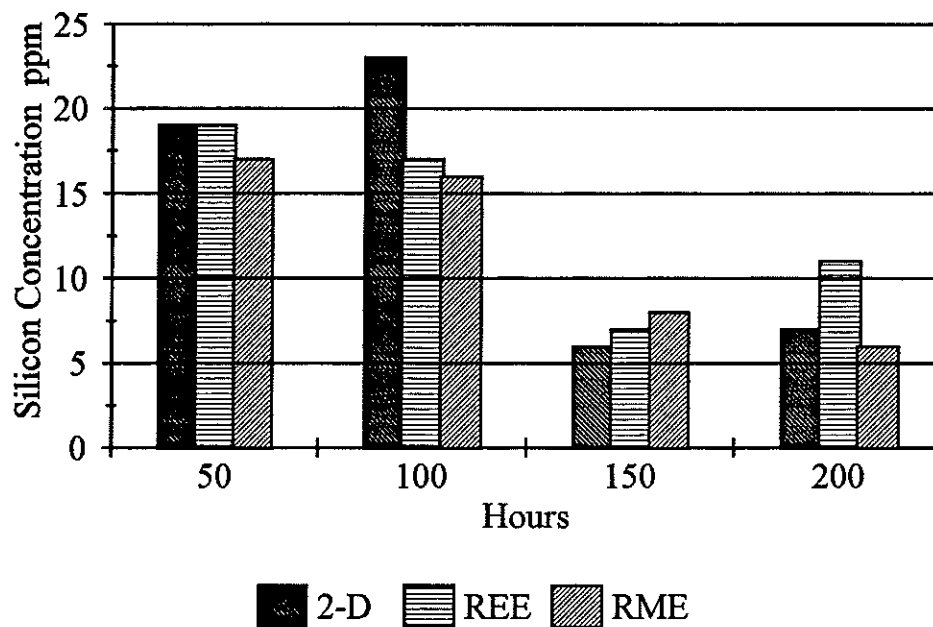


Figure 4-6. Engine Oil Silicon Concentration vs Time.

Injector Coking

The coking results from the quantitative digitizing method are presented in Figure 4-7. At the conclusion of the test the injectors were disassembled and inspected for internal deposits. The lift needles of the injectors operated on these fuels were clean and showed no wear and discoloration.

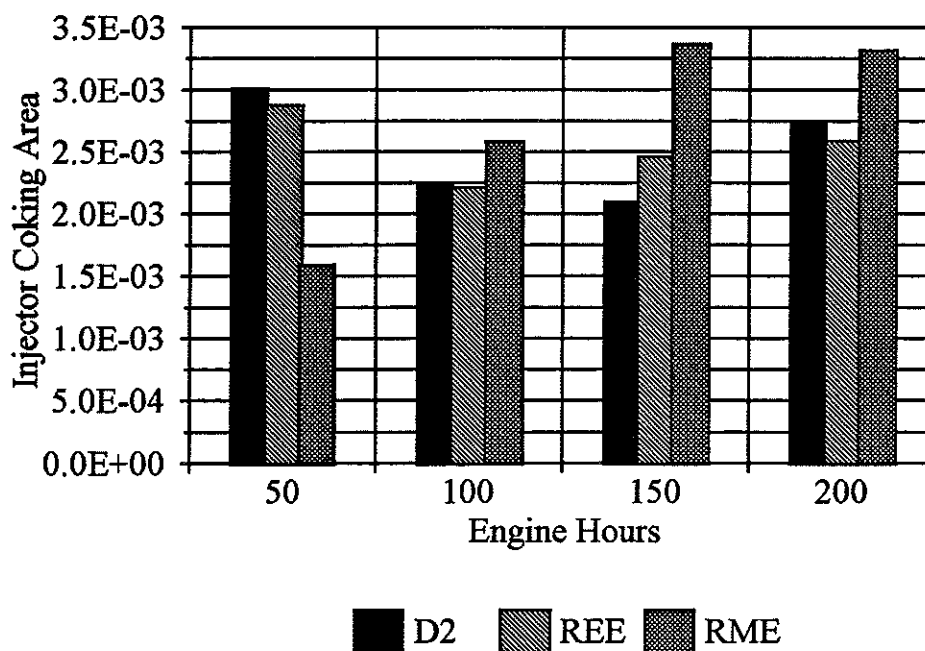


Figure 4-7. Injector Coking vs Time.

Engine Inspection

Following the 200 hour EMA test, the three engines were disassembled and inspected.

Engine fueled with 2-D fuel. The oil in the bottom of the oil pan was dark in color but there were no large particles or foreign material. The engine oil pickup screen was free from debris. The cylinder walls look good with no visible or measurable wear. All the valve seats in the cylinder head were clean and shiny. A small amount of carbon build up was present in the exhaust ports, and the intake ports were clean. The intake valve faces were clean and the stem area had a slight amount of hard carbon deposits. The exhaust valve faces were fairly clean. The piston ring lands were very clean. The tops of the pistons had minimal amounts of carbon build up and grayish in color. The rod and main bearings had no visible wear with very small scratches on the lower halves. There was no measurable wear in the engine components that move. The overall condition of this is engine is normal for a 200 hour EMA test.

Engine fueled with 100 percent REE. The oil in the bottom of the oil pan was dark in color but there were no large particles or foreign material. The engine oil pickup screen was free from debris. The cylinder walls look good with no visible or measurable wear. All the valve seats in the cylinder head were clean and shiny. A small amount of carbon build up was present in the exhaust ports, more so than the diesel fueled engine, and the intake ports were clean. The intake valve faces were clean and the stem area had a slight amount of gummy carbon deposits. The exhaust valve faces were dull. The top piston ring lands had carbon build up one-eighth the circumference. The tops of the pistons had minimal amounts of carbon build up. The rod and main bearings had no visible wear. There was no measurable wear in the engine components that move. The overall condition of this engine is normal for a 200 hour EMA test.

Engine fueled with 100 percent RME. The oil in the bottom of the oil pan was dark in color but there were no large particles or foreign material. The engine oil pickup screen was free from debris. The cylinder walls look good with no visible or measurable wear. All the valve seats in the cylinder head were clean and shiny. A small amount of carbon build up was present in the exhaust ports and the intake ports were clean. The intake valve faces were clean and the stem area had a slight amount of hard carbon deposits. The exhaust valve faces were fairly clean and the carbon on the heads of the valves were orange in color. The top piston ring lands on number one and two pistons had carbon in them about one half way around, number three piston top ring land had a small area of carbon build up. The second and third ring lands were clean. The tops of the pistons had minimal amounts of carbon build up. The rod and main bearings had no visible wear. There was no measurable wear in the engine components that move. The overall condition of this engine is normal for a 200 hour EMA test.

Weights and Measurements

Table 4-2 is the change in weight relative to 2-D for the given engine components.

Table 4-2. Engine Component Change in Weights Relative to 2-D

| | | 2-D | REE | RME |
|---------------|--------|------|------|------|
| Piston Rings | Top | 1.00 | 0.24 | 0.11 |
| | Second | 1.00 | 0.15 | 0.12 |
| | Oil | 1.00 | 0.13 | 0.10 |
| Piston | | 1.00 | 1.33 | 1.25 |
| Intake Valve | | 1.00 | 0.92 | 1.43 |
| Exhaust Valve | | 1.00 | 0.44 | 0.40 |

CONCLUSIONS

There were no modifications to the engine for testing the biodiesel fuels. The EMA 200 hour test demonstrated that these fuels are suitable alternatives to diesel fuel and further testing is appropriate. Results of the engine oil analysis for the Biodiesel fuels were similar to the diesel fueled engine. There was no cylinder wall to piston scuffing with any of the fuels. All the piston rings for the three different fuels were clean and free. The crankshaft bearings in each engine showed normal wear with no measurable difference in the crank journals. The injector pressures did not vary more than 50 psi during the course of testing. The injector needles moved freely at the end of the test. Injector coking varied for each fuel throughout the test series but on the whole the REE was comparable to 2-D and RME was 1.3 times that of 2-D.

The top piston ring for the REE fueled engine had 86 percent less wear, by weight, and 89 percent less for the RME fueled engine than the 2-D fueled engine. The REE and RME pistons, the three averaged together, had 33 percent more and 25 percent more weight respectively than the average of the 2-D pistons. The intake valve averages by weight were 8 percent less for REE and 25 percent more for RME compared to 2-D. The exhaust valves for the RME and REE fueled engines had 60 percent less weight compared to the 2-D fueled engine.

Fuel characterization data showed some similarities and differences between REE and RME and diesel fuel. a) Specific weight is higher for Biodiesel, heat of combustion is 8 percent lower, and viscosities are 2 times that of 2-D. b) Pour points for REE and RME are 10 and 5 degrees celsius higher than diesel. c) Sulfur content is 40 percent less for REE and RME than 2-D.

PART II

EMA Tests with Hydrogenated Soy Ethyl Ester and Diesel Fuel

Idaho produces approximately 120 million cwt of potatoes from over 152,000 ha. Nearly 60% of these are processed, the vast majority being made into french fried potatoes. These operations use mainly hydrogenated soybean oil, some beef tallow and some canola. It is estimated that there are several million pounds of waste vegetable oil from these operations each year. Additional waste frying oil is available from smaller processors, off-grade oil seeds and restaurants.

One of these processors, produces over two billion pounds of frozen potatoes per year at plants in Oregon, Idaho and North Dakota. This company built an ethanol plant in the late 1980's, which uses potato waste as the feedstock. One plant provides an opportunity for a Biodiesel facility using waste vegetable oil and ethanol to produce hydrogenated soy ethyl esters (HySEE). The market value of waste frying oils is about \$0.11 per liter (\$0.40 per gallon). Ethanol has a plant value of about \$0.28 per liter (\$1.05 per gallon). It is projected that this facility could produce Biodiesel at only slightly over \$0.25 per liter (\$1.00 per gallon) making it economically comparable to diesel fuel.

Fuels

This study examines long term engine tests with HySEE and blends with diesel fuel. The three fuels used for this study were 100% Hydrogenated Ethyl Ester (HySEE), 80% HySEE - 20% number one diesel fuel, and 20% HySEE - 80% number 2 diesel fuel. For comparative purposes 100% 2-D data is included with these three fuels from EMA test 14. Even though the three engines are identical the performance is not. Due to the variability in power and fuel consumption from engine to engine and only one replication for each fuel, one needs to reference the paper by Peterson et al. (1994) "Processing, Characterization and Performance of Eight Fuels from Lipids" for a comparison of performance variables.

RESULTS AND DISCUSSION

Fuel Consumption

The engine fueled on HySEE consumed 747 liters (197 gallons), the 80HySEE fueled engine consumed 651 liters (172 gallons), the 20HySEE fueled engine consumed 681 liters (180 gallons) of fuel, and the 2-D fueled engine consumed 630 liters (166 gallons) of fuel. The differences in fuel consumption reflects the differences in heat of combustion and density of the individual fuels and are affected by variations in settings between engines. A complete listing of fuel properties is given in Table 4-3.

Table 4-3. Fuel Characterization Data

| | HySEE | 80HySEE | 20HySEE | 2-D |
|----------------------------------|--------|---------|---------|--------|
| Fuel Specific Properties | | | | |
| Specific Gravity, 60/60 | 0.872 | 0.862 | 0.867 | 0.8495 |
| Viscosity, cSt @ 40°C | 5.68 | 4.31 | 3.49 | 2.98 |
| Cloud Point, °C | 9 | 7 | -6 | -12 |
| Pour Point, °C | 6 | 3 | -8 | -25 |
| Flash Point, °C | 180 | 79 | 72 | 76 |
| Boiling Point, °C | 310 | 178 | 182 | 191 |
| Water and Sediment, % Vol. | <0.005 | <0.005 | <0.005 | <0.005 |
| Carbon Residue, % mass | 0.04 | 0.04 | 0.05 | 0.16 |
| Ash, % mass | 0.001 | 0.001 | 0.001 | 0.002 |
| Sulfur, Wt% | <0.005 | <0.005 | 0.028 | 0.036 |
| Cetane Number | 61 | | | 48.2 |
| Heat of Combustion, Gross, MJ/kg | 39.69 | 40.86 | 43.84 | 45.42 |
| Copper Corrosion | 1A | 1A | 1A | 1A |
| Karl Fischer Water, ppm | 1075 | 815 | 172 | 38 |
| Particulate Matter, mg/L | | | | |
| Total | 0.99 | 0.54 | 0.68 | 0.9 |
| Non-Combustible | 0.06 | 0.21 | 0.14 | <0.1 |
| Elemental Analysis | | | | |
| Carbon, % | 78.56 | 78.28 | 83.75 | 86.67 |
| Hydrogen, % | 13.09 | 13.32 | 13.12 | 12.98 |
| Oxygen, % (by difference) | 8.35 | 8.40 | 3.10 | |
| Iodine Number | 69.3 | 54.9 | 28.7 | 8.6 |
| Ester Specific Properties | | | | |
| Percent Esterified | 91.65 | | | |
| Acid Value | 0. | | | |
| Free Glycerol, %wt | 0.18 | | | |
| Total Glycerol, %wt | 6.06 | | | |
| Free Fatty Acids, %wt | 0.42 | | | |
| Monoglycerides, %wt | 1.97 | | | |
| Diglycerides, %wt | 3.98 | | | |
| Triglycerides, %wt | 1.33 | | | |
| Alcohol Content, % mass | <1 | | | |
| Fatty Acid Composition, % | | | | |
| Palmitic (16:0) | 10.3 | | | |
| Stearic (18:0) | 15.0 | | | |
| Oleic (18:1) | 24.6 | | | |
| Linoleic (18:2) | 48.6 | | | |
| Behenic (22:0) | 0.7 | | | |

Engine Performance

The observed performance trend, shown in Figure 4-8, shows the change in power relative to output at zero hours for each 50 hour interval. Relative power change is shown instead of actual power to compensate for the difference in engines. The relative power from start to end for 2-D was 1.03, 1.02 for HySEE, 1.01 for 20HySEE and 1.007 for 80HySEE. The maximum power for each of the engines stayed fairly constant throughout the 200 hour test.

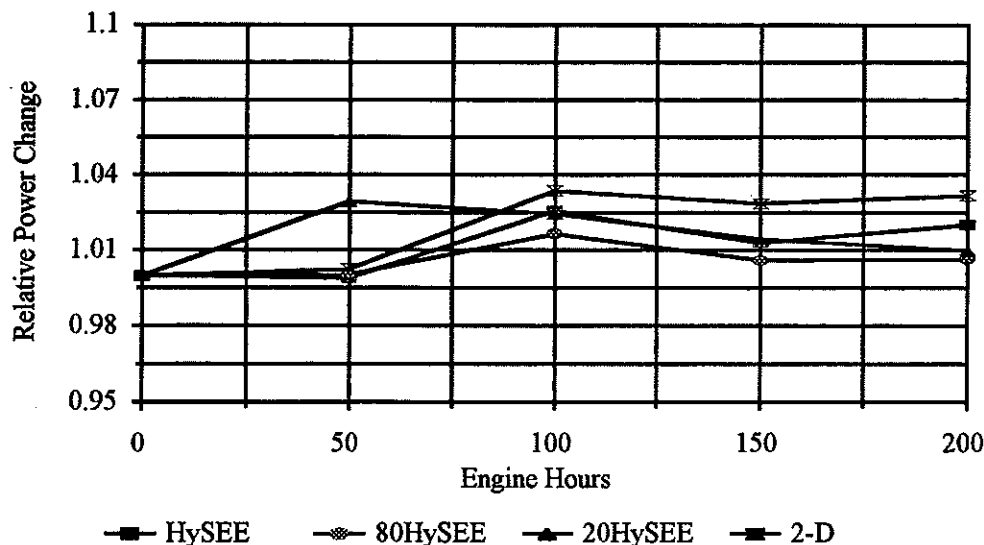


Figure 4-8. Engine power change relative to the engine power at 0 hours.

Cylinder compression varied from 2.65 MPa (385 psi) to 3.00 MPa (420 psi) between cylinders and engines, but varied only 30 psi for the same cylinder during the test. The fuel injector valve opening pressure (VOP) varied from 19.65 MPa (2,850 psi) to 21.00 MPa (3,050 psi) for all the fuel injectors. Individual injector valve opening pressure varied only 344 kPa (50 psi) for the duration of testing. Engine blowby was measured at each 50 hour interval with no difference from beginning to end for each of the three engines. Percent opacity using the snap idle test was 20.1% for HySEE, 11.5% for 80HySEE, and 30.8% for 20HySEE.

Oil Analysis

All engines show a decrease in engine oil viscosity compared to new lubricating oil. The HySEE fueled engine had a viscosity less than the allowable limit at the 100-hour interval but not at the 200 hour interval. The engine oil viscosity versus time data is shown in Figure 4-9, and the total base number (TBN) versus time is shown in Figure 4-10. The TBN indicates the potential of the oil to neutralize strong acids as the mineral acids derived from sulfur, chlorine, and bromine. Decreases in TBN are associated with corrosion of engine parts and increases in varnish deposits.

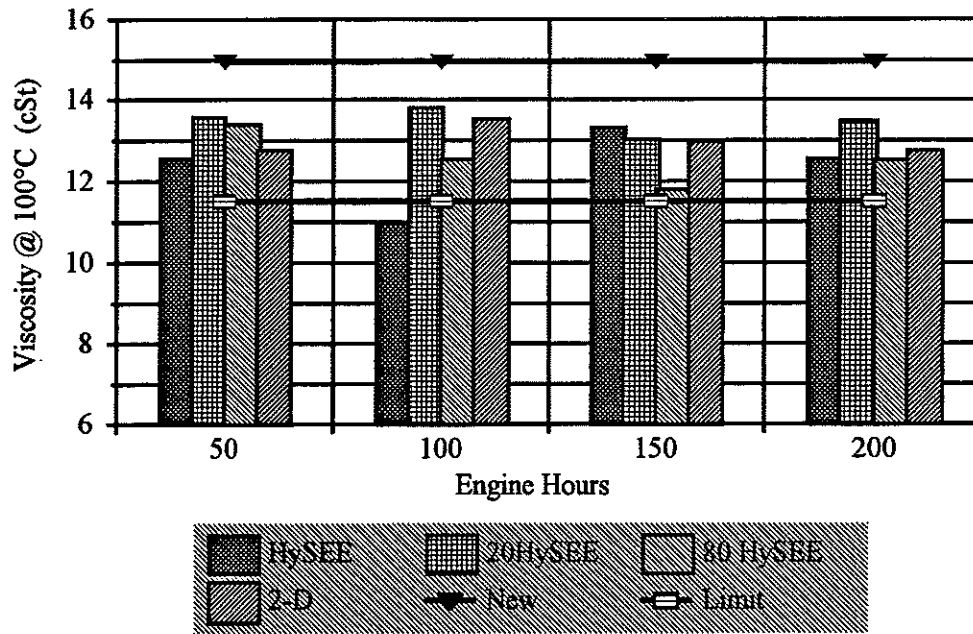


Figure 4-9. Engine oil viscosity vs time. The engine oil was changed at 100 hours.

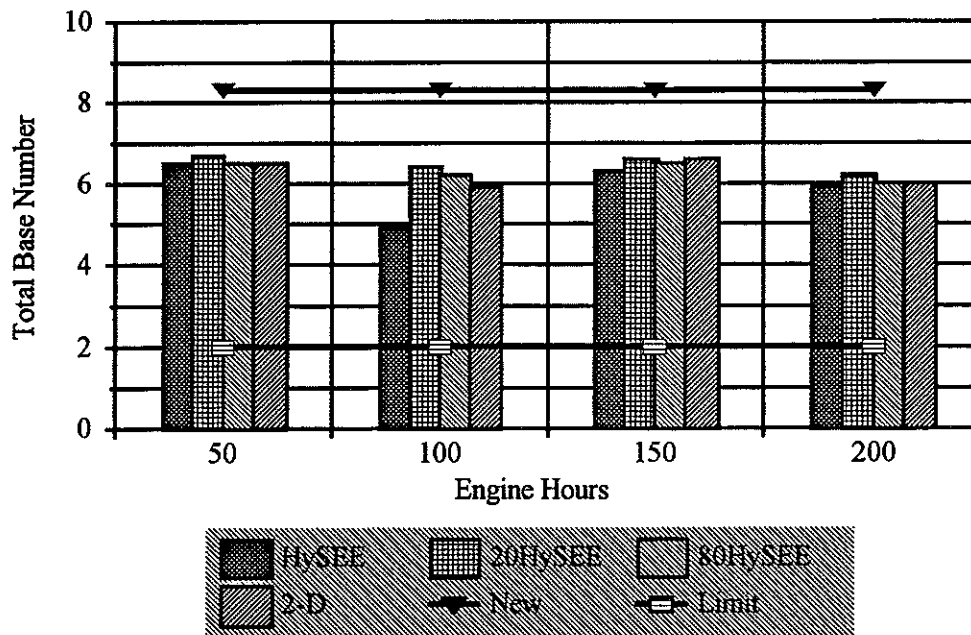


Figure 4-10. Engine oil total base number vs time. The engine oil was changed at 100 hours.

Engine wear was evaluated on the basis of the concentrations of three wear metals in the lubricating oil. The metals, and their primary source, used as the wear basis are as follows:

- 1) Iron - cylinder, camshaft, valve train, gear wear
- 2) Aluminum - piston and bearing wear
- 3) Silicon - anti-foam additive, ingested dirt

Wear metal concentration results are shown in Figures 4-11 through 4-13. All the engine oil analysis were within the allowable limits with the exception of 2-D at 100 hours. Wear and viscosity limits were reported by Cleveland Technical Center, Spokane, Washington.

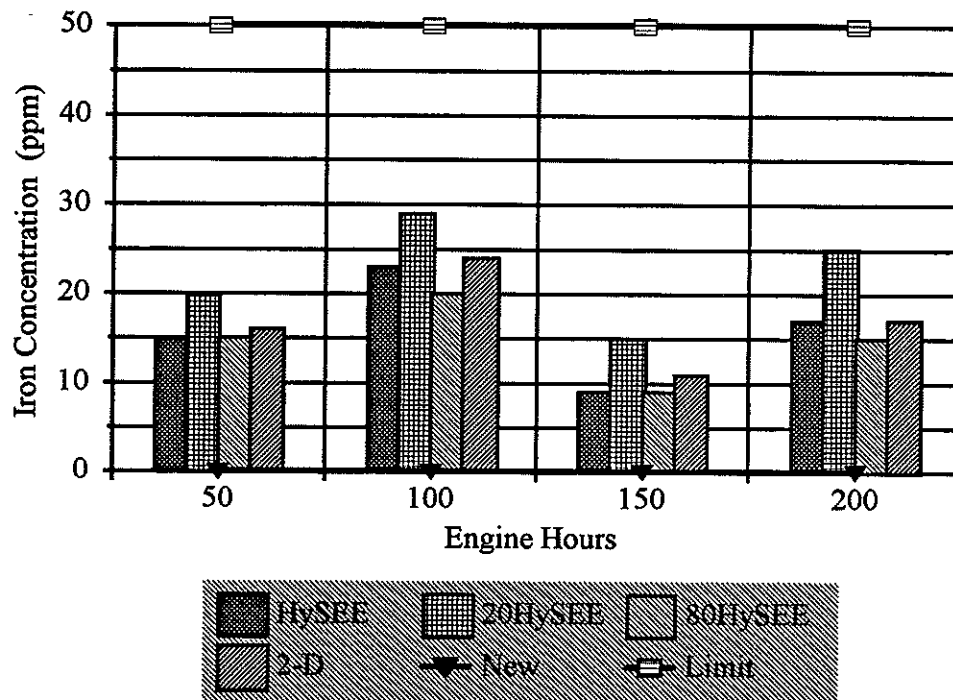


Figure 4-11. Engine oil iron concentration vs time. The engine oil was changed at 100 hours.

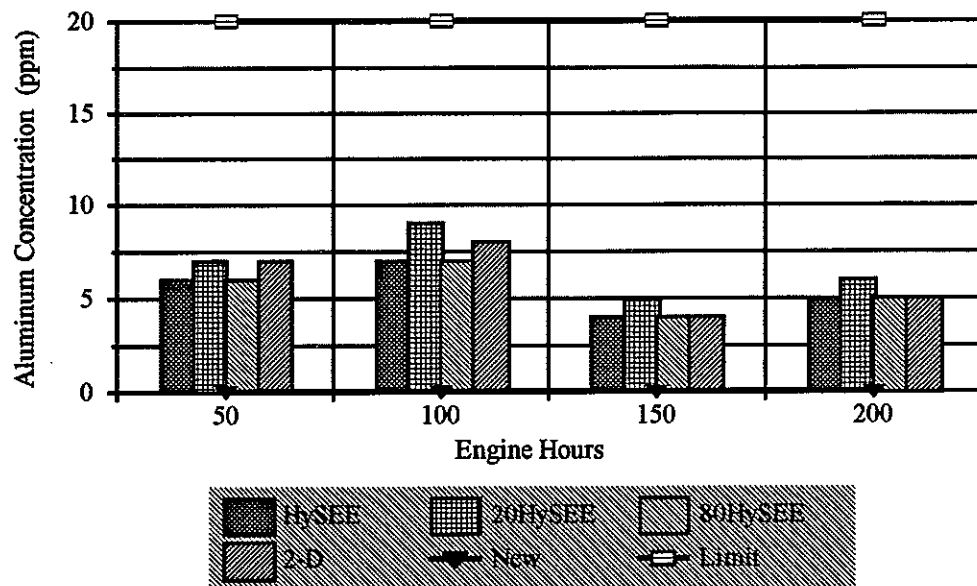


Figure 4-12. Engine oil aluminum concentration vs time. The engine oil was changed at 100 hours.

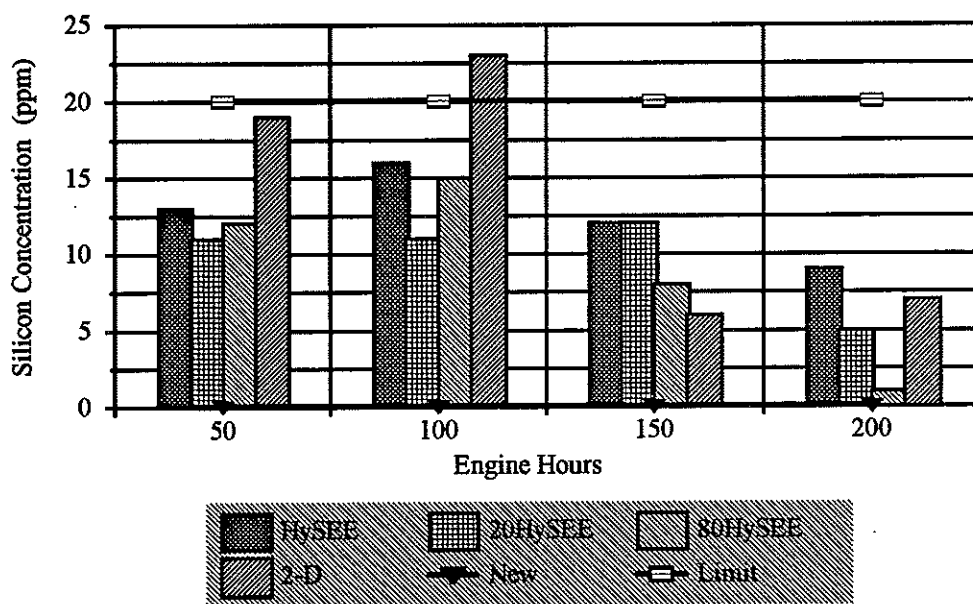


Figure 4-13. Engine oil silicon concentration vs time. The engine oil was changed at 100 hours.

Injector Coking

The coking results from the machine vision method are presented in Figure 4-14. At the conclusion of the test the injectors were disassembled and inspected for internal deposits. The lift needles of the injectors operated on these fuels were clean and showed no wear or discoloration.

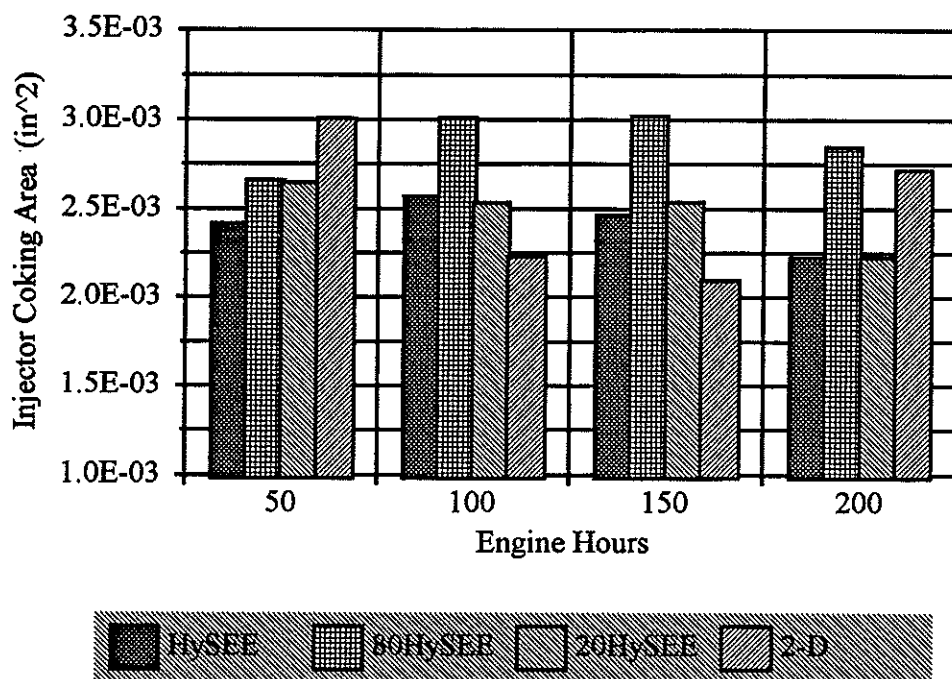


Figure 4-14. Injector coking vs time.

Engine Inspection

Following the 200 hour EMA test, the three engines were disassembled and inspected.

100% 2-D

The oil in the bottom of the oil pan was dark in color but there were no large particles or foreign material. The engine oil pickup screen was free from debris. The cylinder walls look good with no visible or measurable wear. All the valve seats in the cylinder head were clean and shiny. A small amount of carbon build up was present in the exhaust ports, and the intake ports were clean. The intake valve faces were clean. The stem area had a slight amount of hard carbon deposits. The exhaust valve faces were fairly clean. The piston ring lands were very clean. The tops of the pistons had minimal amounts of carbon build up grayish in color. The rod and main bearings had no visible wear with very small scratches on the lower halves. There was no measurable wear in the engine components that move. The overall condition of this engine was normal for a 200 hour EMA test.

80%HySEE - 20% I-D

The remaining oil in the oil pan was black but did not have any foreign material. The oil pickup screen was free from debris. The visual appearance of the camshaft and lifters was normal. The main and rod bearings had normal wear without any scratches. The crankshaft was identical to the bearings. The piston ring wear patterns were uniform for each of the cylinders. Piston #1 was a new piston with carbon build up from the top of the piston to the first ring land approximately 3/4 around. The top ring land was clean and free of carbon. The area between the first and second rings had carbon build up about 1/8 the circumference of the piston. The second ring land had a slight build up of carbon identical to the previously mentioned area. The oil ring land was clean and free of carbon build up, as was the area between the second ring and the oil ring. The piston skirt was clean and without scratches.

The piston ring wear patterns were uniform for each of the cylinders. Piston #2 had carbon build up from the top of the piston to the first ring land about 3/4 around. The top ring land had carbon build up about 1/2 inch around the circumference. The area between the first and second rings had carbon build up about two inches around the circumference of the piston. The second ring land had a slight build up of carbon identical to the previously mentioned area. The oil ring land was clean and free of carbon build up, as was the area between the second ring and the oil ring. The piston skirt was clean and without scratches.

Piston #3 had slightly more carbon build up from the top of the piston to the first ring land, about 3/4 around the circumference, than the other two pistons. The top ring land had a small amount of carbon in one area. The areas between the first and second rings, the second ring land, the area between the second ring and the oil ring, and the oil ring land was free of carbon build up. The piston skirt was clean and without scratches.

The carbon deposits on the top of each piston was equal and was black with one area that was brownish gray in color.

All the valve seats in the cylinder head were clean and shiny as were the intake valve faces. The exhaust valve faces were shiny black from a small amount of carbon discoloration and the stem area had a thin layer of carbon. The intake valve stems had a slight build up of carbon - more than the exhaust stems. The carbon deposits on the intake valve heads were black and the exhaust valve heads were dark brownish-gray. All the cylinder head intake ports were clean and the exhaust ports had a slight amount of carbon.

100% HySEE

The remaining oil in the oil pan was black but did not have any foreign material. The oil pickup screen was free from debris. The visual appearance of the camshaft and lifters was normal. The main and rod bearings had normal wear without any unusual scratches. The crankshaft was identical to the bearings. The piston ring wear patterns were uniform for each of the cylinders. Piston #1 was a new piston with carbon build up from the top of the piston to the first ring land approximately 3/4 around. The top ring land was clean and free of

carbon. The area between the first and second rings had carbon build up about 1 ½ inch around the circumference of the piston. The second ring land had a slight build up of carbon identical to the previously mentioned area. The oil ring land was clean and free of carbon build up, as was the area between the second ring and the oil ring. The piston skirt was clean and without scratches.

Piston #2 had carbon build up from the top of the piston to the first ring land about ¾ around. The top ring land had carbon build up about ½ the circumference. The area between the first and second rings had carbon build up about three inches around the circumference of the piston. The second ring land had a slight build up of carbon identical to the previously mentioned area. The oil ring land was clean and free of carbon build up, as was the area between the second ring and the oil ring. The piston skirt was clean and without scratches.

Piston #3 had carbon build up from the top of the piston to the first ring land about ¾ around the circumference of the piston. The top ring land had a small amount of carbon in one area. The areas between the first and second rings, the second ring land, the area between the second ring and the oil ring, and the oil ring land was free of carbon build up. The piston skirt was clean and without scratches.

The carbon deposits on the top of each piston was equal and was black with one area that was brownish gray in color.

All the valve seats in the cylinder head were clean and shiny as were the intake valve faces. The exhaust valve faces were shiny black from a small amount of carbon discoloration. The stem area had a thin layer of carbon. The intake valve stems had a slight build up of carbon - more than the exhaust stems. The carbon deposits on the intake valve heads were black and the exhaust valve heads were dark brownish-gray. All the cylinder head intake ports were clean and the exhaust ports had a slight amount of carbon. The overall condition of this engine was normal for a 200 hour EMA test.

20%HySEE - 80% 2-D

The remaining oil in the oil pan was black but did not have any foreign material. The oil pickup screen was free from debris. The visual appearance of the camshaft and lifters was normal. The main and rod bearings had normal wear without any unusual scratches. The crankshaft was identical to the bearings. The piston ring wear patterns were uniform for each of the cylinders. Piston #1 was a new piston and appeared to have antifreeze in the cylinder because the carbon was flaking off, although there was no sodium in the oil analysis. The top ring land had carbon about ½ the circumference of the piston. The area between the first and second rings had carbon build up about 1/3 the circumference of the piston. The second ring land had a slight build up of carbon identical to the previously mentioned area. The oil ring land was clean and free of carbon build up, as was the area between the second ring and the oil ring. The piston skirt was clean and without scratches.

Piston #2 had carbon build up from the top of the piston to the first ring land about 3/4 around. The top ring land had carbon build up about 1/2 inch around the circumference. The area between the first and second rings had carbon build up about two inches around the circumference of the piston. The second ring land had a slight build up of carbon identical to the previously mentioned area. The oil ring land was clean and free of carbon build up, as was the area between the second ring and the oil ring. The piston skirt was clean and without scratches.

Piston #3 had carbon build up from the top of the piston to the first ring land about 3/4 around the circumference of the piston. The top ring land had a small amount of carbon almost 1/2 the circumference and 1/4 down the width of the ring land. The area between the first and second rings had carbon about 1/3 the circumference. The second ring land had a slight build up of carbon identical to the previously mentioned area. The area between the second ring and the oil ring was clean as was the oil ring land. The piston skirt was clean and without scratches. The carbon deposits on top of each piston were equal and black in color.

All the valve seats in the cylinder head were clean as were the intake valve faces. The exhaust valve faces were shiny black from a small amount of carbon discoloration and the stem area had a thin layer of carbon. The intake valve stems had a slight build up of carbon - more than the exhaust stems. The carbon deposits on the intake valve heads and exhaust valve heads were black. All the cylinder head intake ports were clean and the exhaust ports had a slight amount of carbon. The overall condition of this engine was normal for a 200 hour EMA test.

Visually ranking these engines - 100%HySEE was the cleanest, 80%HySEE/20%D1 second cleanest, and 20%HySEE/80%2-D was cleaner than the 100%2-D engine.

Weights and Measurements

Table 4-4 is the change in weight relative to 2-D for the given engine components.

Table 4-4. Engine Component Change in Weights Relative to 2-D

| | | Diesel | HySEE | 80HySEE | 20HySEE |
|---------------|--------|--------|-------|---------|---------|
| Piston Rings | Top | 1.00 | Incr* | 0.20 | 0.69 |
| | Second | 1.00 | Incr* | 0.06 | 0.20 |
| | Oil | 1.00 | 0.12 | 0.08 | 0.08 |
| Piston | | 1.00 | 1.12 | 1.15 | 1.06 |
| Intake Valve | | 1.00 | 0.44 | 0.34 | 1.15 |
| Exhaust Valve | | 1.00 | 0.08 | 0.19 | 0.16 |

* Incr is an increase in weight for piston rings which is theoretically not possible since the carbon was removed from the rings before weighing.

Ranking the three engines for this 200 hour test using relative weights from table 2 as the indicator; the engine fueled with HySEE was ranked highest (less wear and carbon build up than 2-D) with 80HySEE following and 20HySEE as the lowest. This coincides with the visual ranking reported earlier.

CONCLUSIONS

There was no engine or engine part modifications before or during the tests. The EMA 200 hour test demonstrated that these fuels are suitable alternatives to diesel fuel and further testing is appropriate. Engine oil analysis for the HySEE fuels were similar to the diesel fueled engine. There was no cylinder wall to piston scuffing with any of the fuels. All the piston rings for the three different fuels were clean and free. The crankshaft bearings in each engine showed normal wear with no measurable difference in the crank journals. The injector pressures did not vary more than 50 psi during the course of testing. The injector needles moved freely at the end of the test. Injector coking varied for each fuel throughout the test series. HySEE and 20HySEE had fewer carbon deposits while 80HySEE had more deposits than did the diesel fueled engine.

The HySEE, 80HySEE and 20HySEE pistons, three pistons for each engine averaged together, had a weight increase of 12%, 15% and 6% respectively compared to the average of the 2-D pistons. The carbon deposits on the intake valves were 44% less for HySEE, 34% less for 80HySEE and 15% more for 20HySEE compared to 2-D. The exhaust valves for the HySEE < 80HySEE and 20HySEE fueled engines had a decrease in carbon deposits of 8%, 19% and 16% compared to the 2-D fueled engine.

A complete set of fuel characteristics are presented. Fuel characterization data show some similarities and differences between HySEE and diesel fuel. a) Specific weight is higher for Biodiesel, heat of combustion is 8% lower, and viscosities are 2 times that of 2-D. b) Pour point for HySEE is 17°C higher than diesel. c) Sulfur content is 40% less for HySEE than 2-D.

All the fuels had a performance which surpassed the requirements of the EMA standard.

BIODIESEL TESTING IN TWO ON-ROAD PICKUPS

Past research has focused on the development and testing of Biodiesel in controlled environments. The objective of this project was to determine if Biodiesel is a viable transportation fuel using two Biodiesel fueled on-the-road pickups. Specific objectives for achieving this goal were to:

- Operate two pickups for 80,000 kilometers with a blend of 20 percent rapeseed methyl ester (RME), 80 percent number two diesel (2-D) [20RME] in one, and a blend of 20 percent raw rapeseed oil /80 percent 2-D (20RAW) fuel in the other.
- Design an on-board fuel mixing system to maximize the travel range for each pickup and, at the same time, keep the fuel from congealing.
- From dynamometer testing, both chassis and steady state, determine the percent difference in power, opacity, and fuel economy compared to that of 2-D.
- Conduct pending ASAE fuel standard tests for 20RME, 20RAW, number two diesel, and 100% RME.

LITERATURE REVIEW

Initial studies at the University of Idaho used 100 percent raw vegetable oil resulting in incomplete combustion, causing severe engine deposits, ring sticking, injector coking, contamination to the engine oil, and, inevitably, to engine failure (Peterson et al., 1983). Vegetable oils are highly unsaturated making them more susceptible to gum formation, causing carbon buildup in the combustion chamber and around the injector nozzle tips. Vegetable oils have a viscosity 11 to 17 times higher than that of diesel fuel, which causes droplets produced by the fuel injector to be much larger than those produced when using diesel fuel. As a result, less oil comes in contact with oxygen, the unburned fuel spray impinges on the cylinder wall washing away the lubricating oil film, and causes thickening of the crankcase oil.

After these first tests, the vegetable oil was modified through a process called transesterification. Transesterification is a process which involves reacting vegetable oil with an alcohol in the presence of a catalyst to produce an ester and glycerine layer. Ester viscosities are reduced to a more suitable level for use as a fuel.

Even today, after a decade of research and development with esterified fuels, there is the misconception by the general public that the engine failure and excessive injector coking originally reported with raw vegetable oil has not been solved. With this background, the literature review will focus mainly on esterified fuels with a major emphasis on power, opacity, and emissions reported from tests performed with Biodiesel.

Schumacher et al., (1993) have fueled two Dodge diesel pickups, one a 1991 and one a 1992, with 100 percent soydiesel. They added a fuel tank to the bed of each pickup and installed stainless steel heat exchangers for cold weather operation. The soydiesel fuel tanks and fuel lines were insulated. Two 110-volt thermostatically controlled flat mat heating pads were placed beneath the soydiesel tank for heating during cold weather when the vehicle was not in use. The 1991 pickup accumulated approximately 48,000 kilometers (km) and the 1992 pickup approximately 32,000 km. Fueling these pickups with soydiesel increased engine power by 3 percent (1991 engine) and reduced power by 6 percent (1992 engine). Engine oil analysis indicated that the engines were wearing at a normal rate. Visible exhaust smoke was reduced as much as 86 percent when the diesel engine was fueled with 100 percent soydiesel. Transient emissions tests were done in an EPA certified laboratory. Carbon monoxide emissions were reduced by one percent, hydrocarbon emissions were reduced by 48 percent, and particulate matter emissions were increased by 13 percent when the engine was fueled with soydiesel.

Holmberg and Peeples (1994) summarized the work done for the National Biodiesel Board (formally the National SoyDiesel Development Board). Biodiesel has accumulated nearly eight million miles in demonstrations involving more than 1,500 vehicles in fleets across the country, particularly in urban buses. Biodiesel has been used successfully as a motor fuel in many types of equipment from watercraft to locomotives. The results of numerous studies and demonstrations show the performance of Biodiesel to be substantially similar to, if not better than, diesel. They predict that as a renewable fuel with a very positive energy balance, Biodiesel will be a major contributor to the stabilization of greenhouse emissions. They also report that by using state-of-the art engine technology, Biodiesel reduced EPA-regulated emissions of PM, CO, THC, and NOx. Actual emissions tests do not verify their optimism that Biodiesel will reduce both NOx and PM.

Pischinger et al. (1982) reports on tests with the Volkswagen 1.6 liter diesel indirect injection engine installed in a VW Passat passenger car or a delivery van. In Volkswagen's rigid durability test program for diesel engines, the diesel engine was fueled with 100 percent methyl ester of soybean (MESO) oil. It was dynamometer tested for 1,418 hours operating about 70 percent of the time at maximum power and 20 percent at maximum torque. Values of torque, power, smoke levels, and cylinder compression remained within the normal variations expected for this test. Engine wear of the bearings, piston rings, cylinder bores, and valve train remained within the VW specifications. Differences in emissions and fuel consumption of the Passat diesel when comparing diesel fuel and MESO fuel were measured on a chassis dynamometer. A city driving cycle and a warm engine were used in the test. They reported that CO was 40 percent less, NOx increased 2.7 percent, and fuel consumption was increased 6 percent compared to diesel fuel.

Mittelbach and Tritthart (1988) tested a Volkswagen diesel Rabbit powered by a 1.6 liter four cylinder, 4-stroke, direct injection engine with a 50/50 volume blend of methyl ester of used frying oil. A total of 100 liters of ester fuel was consumed. They reported that "no changes in

operation whatsoever could be observed. The smoke emissions were extremely low and only a faint smell of burnt fat was detected. No volumetric fuel consumption was observed. They reported that "in our test the fuel consumption was almost the same as when using diesel fuel." They stated "about a 10% power loss with ester fuel can be expected with unchanged fuel delivery of the injection pump. However, because particulate emissions are halved when using ester fuel, a higher fuel input for the ester fuel may be tolerated by the engine without excessive full load smoke. So the engine power may become comparable for both fuels without any deteriorating effects on emissions." In their vehicle testing, they reported that a diesel Volkswagen Passat had run 26,500 km, and a Volkswagen van 5,200 km with MESO. It was difficult to identify any difference between the MESO fueled vehicles compared to identical diesel fueled vehicles.

Shafer (1994) from Mercedes-Benz Germany, reports on the use of methyl esters of soybean oil, rapeseed oil, and palm oil. The testing was performed in Germany and Malaysia in trucks, busses and industrial engines. Shafer concludes that if the fuel (RME and PME) is of high quality, the fuel injection system can remain unchanged and no excess nozzle coking will be found: too high glyceride content causes nozzle coking. The black smoke emission is reduced by at least 50 percent and the disagreeable odor can be reduced by installing an oxidation catalyst. He also states that engine oil dilution is within relatively tight limits and no sludge is apparent with a suitable lubricating oil.

Closing Comments - Numerous feedstocks for Biodiesel exist, including rapeseed, tallow, soybean, canola, peanut, sunflower, cottonseed, safflower, coconut, palm, and used cooking oils with which methyl or ethyl esters may be produced. Biodiesel reduces smoke by up to 80 percent, decreases power by 6 percent, and increases fuel consumption 4 percent, due to the heat content of Biodiesel being about 11 percent less than 2-D. It also decreases HC by as much as 50 percent, CO by as much as 40 percent, and increases NOx almost inversely to PM by as much as 10 percent. Injector coking is slightly greater for Biodiesel, with the carbon deposits being harder than diesel deposits.

Fuel properties suggested by ASTM D-975 were reported in most of the papers reviewed, but no ester specific properties were reported such as percent ester of the fuel, percent glycerol, and alcohol content. The percent of fuel that is ester is one factor that determines the quality of the fuel. The percent of Biodiesel which is ester, along with the viscosity, determines the rate at which carbon deposits are formed in the engine combustion chamber (Peterson et al., 1994). Unmodified triglycerides caused polymerization in the piston ring lands of earlier studies.

MATERIALS AND METHODS

Two blends of Biodiesel and number two diesel fuel (2-D) were studied using two diesel powered pickups at the University of Idaho. During the past decade researchers at the University of Idaho have shown that methyl ester of rapeseed is comparable to 2-D. This study was to verify the use of blends of Biodiesel in on-road vehicles.

Fuels

The feedstock for both fuels in this study is winter rapeseed, Dwarf Essex variety, expelled at the University of Idaho Department of Agricultural Engineering Farm Scale Processing Facility. One blend of fuel was 20 percent raw rapeseed oil and 80 percent 2-D. The other was a 20 percent blend of rapeseed methyl ester (RME), produced at the farm scale processing facility, and 80 percent 2-D. The RME was processed using equipment and techniques scaled up and modified from prior research at the University of Idaho [10]. The abbreviations used to denote the different fuels are as follows:

| | |
|-------|---|
| RAW | 100 percent raw rapeseed oil from the oil expeller and filtered |
| 20RAW | 20 percent RAW and 80 percent 2-D |
| RME | 100 percent methyl ester of rapeseed |
| 20RME | 20 percent RME and 80 percent 2-D |
| 2-D | 100 percent number two diesel fuel |

The fuels were characterized by evaluating the parameters required in ASAE EP552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed at Phoenix Chemical Labs, Chicago Illinois. The HPLC and titration analysis for total and free glycerol, percent of oil esterified, free fatty acids, and mono-, di-, and triglycerides were performed by Diversified Labs Inc., Chantilly, Virginia.

On-road Vehicles

1992 Dodge - The first pickup was a Dodge* 3/4-ton powered by a Cummins 5.9 liter turbocharged, intercooled, direct injected, diesel engine. The engine is an in-line six cylinder and has a bore and stroke of 102.0 x 120.0 mm, respectively; has a compression ratio of 17.5:1; is rated at 119 kW at 2,500 RPM; with a peak torque of 542 N-m at 1750 RPM. It was equipped with a Bosch VE distributor type fuel injection pump. This pickup was operated on 20RME.

*The use of manufacturer's names or trade products does not represent an endorsement of the product nor discrimination toward similar products which are not named.

1992 Ford - The second pickup was a Ford, powered by a Navistar 7.3 liter, naturally aspirated, precombustion chambered V-8 diesel engine. The engine has a bore and stroke of 104 x 104 mm, respectively; has a compression ratio of 21.5:1; is rated at 134 kW at 3,300 RPM; with a peak torque of 467 N-m at 1400 RPM. It was equipped with a Stanadyne rotary type fuel injection pump. A blend of 20 RAW was selected for this pickup because of the precombustion chambered engine.

Check Vehicles - Three other pickups were used as check vehicles. Two were equipped with 5.9 liter direct injection engines, and the other used a 7.3 liter engine with a precombustion chamber. These vehicles were privately owned and were operated on 100 percent diesel fuel to serve as a comparison. Oil samples and analyses were performed at each owner's discretion and analyzed by the same laboratory as the Biodiesel pickups. When possible, these vehicles were dynamometer tested at the same facility as the Biodiesel pickups.

Fuel Mixing System

The fuel delivery systems in the Biodiesel pickups were modified to provide for on-board mixing of the fuel. On-board mixing greatly extends the range of the vehicles compared to the original equipment. A 210 liter insulated fuel tank was added to the bed of each vehicle to store the Biodiesel fuel. A 5.7 liter mixing chamber was mounted to the frame of

each vehicle with the diesel and Biodiesel fuel lines routed to this chamber (Fig 5-1). Each fuel supply was transferred from the tanks to the combining chamber with 12 volt electric fuel pumps. The combining chamber was constructed from mild steel and designed to incorporate four floats. The bottom float was a normally open, polypropylene float and stem mounted horizontally in the chamber 44 mm from the bottom. This float operated a low fuel warning light in the operator's cab, which warned the operator that the fueling

circuit was not functioning. The second float was also a normally open polypropylene float and stem mounted horizontally in the chamber. When the fuel drops below this float a relay turns on the diesel fuel pump. Diesel fuel is then transferred into the chamber until the third float deactivates the relay and shuts off the diesel fuel pump. The third float simultaneously activates the Biodiesel fuel pump and fills the chamber until the 20/80 blend is obtained. A fourth float, made of Buna-N and a brass stem, was mounted vertically in the top of the tank and can be adjusted to give the correct blend. The adjustment was preset in the laboratory before being mounted in the frame of the vehicle. Based on a 20 percent blend of Biodiesel /

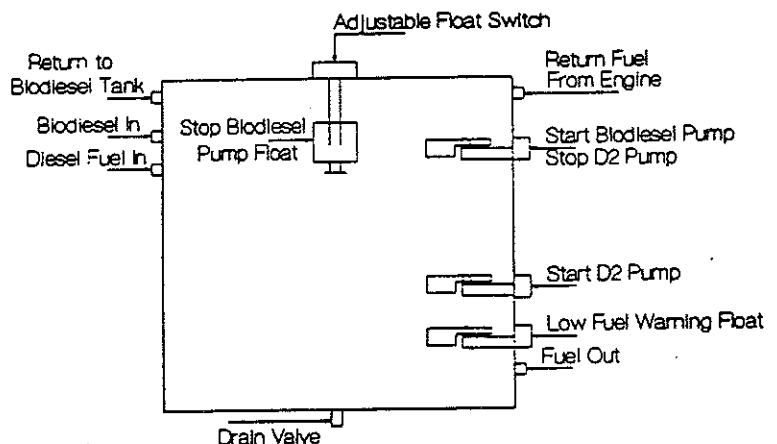


Figure 5-1. Fuel Combining Chamber.

80 percent diesel and 7.5 km/L fuel consumption, on-board mixing increased the travel distance from 965 km to 4,800 km before requiring a Biodiesel fill up.

During the first 32,000 km of operation of the Dodge pickup, rust began to form in the Biodiesel tank and was transferred to the fuel filter. The fuel filter required replacing every 4,800 km due to plugging and loss of engine power. The mild steel 210 liter tank and combining chamber were replaced with stainless steel tanks of similar design on the Dodge pickup only. New 12-volt positive displacement fuel pumps were installed for the Biodiesel fuel and a 12-volt shut-off solenoid valve was placed in line with the pump on both vehicles.

Fuel Heating System

During cold weather operation the Biodiesel fuels need to be kept above the pour point, which is higher than normal diesel fuel. Engine coolant was used to warm the fuel in the Biodiesel fuel tanks. A stainless steel in-line fuel warmer was installed horizontally into the 210 liter Biodiesel fuel tank. A thermostat with an adjustable set point was set at 13°C and closed on rise to operate the coolant pump. The coolant lines were 15.9 mm silicon heater hose, which was routed alongside the fuel supply and return lines and laid beside the fuel combining chamber and Biodiesel fuel pump. They were insulated to help keep the fuel lines and the fuel in the combining chamber above the pour point when the vehicle was not in operation. While the pickup was not operating, a 110-volt thermostatically controlled engine pre-heater was used to keep the engine coolant at 38°C. The thermostat was installed on the inlet side of the heater. It sensed the temperature of the coolant at the inlet to the heater and kept the coolant at the preset temperature range.

Since the coolant pump operates on 12-volts, a 10 amp DC power supply was used to convert standard 120-volt AC power into regulated 12-volt DC power. A 12-volt, 25 amp DC power relay was used to switch the power source when 120-volts AC was required. A shut off valve was added prior to the coolant pump for flow control purposes.

Other Modifications

While the engines of the test vehicles were unmodified, the vehicles themselves were modified for convenience of running the test. For example, it is known that esters will deteriorate rubber components over a period of time, so the rubber fuel lines were replaced with viton hose. A low coolant indicator was installed and a red light in the cab was used to warn the operator of low coolant. An hour meter, operated by engine oil pressure, was also added. A Biodiesel fuel tank gauge gave an indication of the fuel level in the Biodiesel tank. Additional ammeters and indicator lights indicated whether or not the fuel mixing system was working properly. Each pickup was equipped with a log book to keep daily and long-term records. Also, a maintenance record book was kept for each vehicle, which included the oil samples, dynamometer test data sheets, and any other scheduled or unscheduled maintenance.

Dynamometer Testing

Both pickups had a break-in period and were dynamometer tested before the Biodiesel fuel mixing system was incorporated. Each pickup was dynamometer tested every 16,000 km at Western States Caterpillar in Spokane, Washington. During each dynamometer test, the vehicle was tested with the following: once with the 20/80 mix and again with 100 percent diesel. In addition, the Dodge pickup also was dynamometer tested with 100 percent RME. A full throttle torque test was performed with a predetermined set of engine RPM's programmed into the computer to obtain repetitive data. The Ford pickup was dynamometer tested from 1,400 to 3,400 RPM in increments of 200 RPM. Engine RPM's for the Dodge were 1,600 to 2,650 RPM in 150 RPM increments. A computer recorded vehicle power, vehicle speed, fuel economy, engine RPM, opacity, torque, engine oil pressure, fuel pressure and temperature, exhaust temperature, inlet air temperature, and coolant temperature. The Dodge pickup also had intake manifold pressure and engine blowby measured.

Performance Parameters

After each dynamometer test the injectors were removed from the engine to check for carbon deposits using the procedure described in "A Rapid Engine Test to Measure Injector Fouling in Diesel Engines Using Vegetable Oil Fuels" (Korus et al., 1985). The cylinder compression was tested and the injector valve opening pressure was also checked. The Dodge pickup, Cummins engine, has direct access to the combustion chamber and cylinder walls through the injector bore in the cylinder head. A fiber optic borescope was used for this engine to visually inspect the amount of carbon build up on the piston crown and valve heads and to check for any abnormal cylinder wear.

Oil samples were taken at each oil change, which was 4,800 km for the Biodiesel pickups, and at the convenience of the owners of the control vehicles. The oil samples were analyzed at a commercial oil analysis laboratory for wear metals, and physical tests were performed, including antifreeze, fuel dilution, water, and viscosity. An infrared analysis for soot, sulfur, nitration, and oxidation of the engine oil was also conducted. The reportable limits for each metal were supplied by the oil analysis lab.

RESULTS AND DISCUSSION

Fuels

A complete summary of the fuel characterization data is listed in Table 5-1 for each fuel used in this study. Important observations on a few of the parameters are listed below.

Viscosity - The RAW fuel had a viscosity 15.7 times greater than 2-D at 40°C, while RME was only 1.8 times greater than 2-D. The 20RME had a similar viscosity as 2-D.

Cloud and Pour Point - The pour point for 2-D was -23°C and -15°C to -17°C for Biodiesel and blends. RME had a cloud point of 0°C and 2-D was -12°C, the RAW and blends were within 1°C of 2-D.

Sulfur - 2-D (not low sulfur diesel) had 18 times more sulfur than RME and 10.5 times more than RAW.

Heat of Combustion - The gross heat of combustion for 2-D is 5.6 percent greater than RME fuel and 11 percent greater than RAW oil on a mass basis.

Flash Point - A flash point of 74°C was measured for 2-D while the RME was measured at 179°C and RAW at 274°C. The higher flash points of Biodiesel indicate that it is safer to use, store, and handle based on fire safety concerns.

Table 5-1. Fuel Characterization Data

| | RAW | 20RAW | RME | 20RME | 2-D |
|----------------------------------|-------|--------|--------|--------|--------|
| Fuel Specific Properties | | | | | |
| Specific Gravity, 60/60 | 0.91 | 0.872 | 0.8802 | 0.854 | 0.8495 |
| Viscosity, cSt @ 40°C | 46.7 | 5.39 | 5.65 | 3.1 | 2.98 |
| Cloud Point, °C | -13 | -13 | 0 | -12 | -12 |
| Pour Point, °C | -15 | -17 | -15 | -15 | -23 |
| Flash Point, °C | 274 | 160 | 179 | 82 | 74 |
| Boiling Point, °C | 311 | 181 | 347 | 194 | 191 |
| Water and Sediment, % vol. | 0.01 | <0.005 | <0.005 | <0.005 | <0.005 |
| Carbon Residue, % mass | 0.27 | 0.13 | 0.08 | 0.06 | 0.16 |
| Ash, % mass | 0.007 | 0.002 | 0.002 | 0.00 | 0.002 |
| Sulfur, wt% | 0.021 | 0.039 | 0.012 | 0.035 | 0.036 |
| Cetane Number | 42.6 | 55.4 | 61.8 | 51.4 | 49.2 |
| Heat of Combustion, Gross, MJ/kg | 40.4 | 44.08 | 42.88 | 44.54 | 45.4 |
| Copper Corrosion | 1A | 1A | 1A | 1A | 1A |
| Karl Fischer Water, ppm | 449 | 187 | 847 | 153 | 38 |
| Particulate Matter, mg/L | | | | | |
| Total | 8.53 | 1.29 | 1.1 | 1.1 | 0.9 |
| Non-Combustible | 1.7 | 0.4 | <0.1 | <0.1 | <0.1 |
| Elemental Analysis | | | | | |
| Nitrogen, ppm | 8.8 | 89 | 10 | | |
| Carbon, % | 79.48 | 85.44 | 81.5 | 84.76 | 86.67 |
| Hydrogen, % | 11.81 | 12.89 | 11.72 | 12.89 | 12.98 |
| Oxygen, % (by difference) | 8.17 | 1.67 | 6.76 | 2.35 | 0.33 |
| Iodine Number | 87.5 | 26 | 97.4 | 24.5 | 8.6 |
| Ester Specific Properties | | | | | |
| Percent Esterified | | | 98.02 | | |
| Acid Value | | | 0.128 | | |
| Free Glycerol, %wt | | | 0.4 | | |
| Total Glycerol, %wt | | | 0.86 | | |
| Free Fatty Acids, %wt | 1.45 | | 0.57 | | |
| Monoglycerides, %wt | 0.61 | | 0 | | |
| Diglycerides, %wt | 1.25 | | 1.35 | | |
| Triglycerides, %wt | 96.39 | | 0.45 | | |
| Alcohol Content, % mass | | | <1.0 | | |
| Catalyst, microgram/gram | | | 11 | | |
| Fatty Acid Composition, % | | | | | |
| Palmitic (16:0) | 2.7 | | 2.2 | | |
| Stearic (18:0) | 1 | | 0.9 | | |
| Oleic (18:1) | 13.9 | | 12.6 | | |
| Linoleic (18:2) | 11.7 | | 12.1 | | |
| Linolenic (18:3) | 7.4 | | 8 | | |
| Eicosenoic (20:1) | 8.5 | | 7.4 | | |
| Behenic (22:0) | 0.6 | | 0.7 | | |
| Erucic (22:1) | 48.9 | | 49.8 | | |

On-road Vehicles

The addition of the fuel tanks and heating system added approximately 230 kilograms to the total mass of the vehicle, with the Biodiesel tank filled to capacity. There was no noticeable change in power, acceleration or fuel economy with the added mass.

1992 Dodge - The Dodge pickup accumulated 89,150 total kilometers, with 85,950 km on the 20/80 blend. The fuel economy for the first 3,180 km using 100 percent 2-D was 8.55 km/L. The average fuel economy with the blend was 8.3 km/L. The vehicle consumed 6,881 liters of diesel and 2,793 liters of RME, for a blend of 28.8 percent RME and 71.2 percent 2-D. This was 8.8 percent above the target value of the 20 percent blend of RME.

Rust was observed in the steel tanks at 48,280 km and continued to be a problem until the tanks were converted to stainless steel. The rust may have been due to the heating and cooling of the fuel in the tank during the winter, condensing the moisture in the atmospheric air, and/or a very small amount of catalyst in the RME fuel, which is basic and would speed up the oxidation reaction. After converting to stainless steel tanks there was unusual fuel filter plugging during the winter months. A wax-like substance in the fuel filter was analyzed and it was determined to be 50 percent diesel fuel and 50 percent Biodiesel. Fuel filter plugging ceased as the ambient temperature increased during the spring and summer.

1992 Ford - The Ford pickup accumulated 89,160 total kilometers with 85,910 km on the 20/80 blend. The fuel economy for the first 2,680 km using 100 percent 2-D was 7.37 km/L. The average fuel economy with the blend was 6.96 km/L. This truck consumed 9,433 liters of diesel and 2,670 liters of rapeseed oil, for a blend of 22.5 percent RAW and 77.5 percent 2-D. This was 2.4 percent above the target value of the 20 percent blend.

The mixture of rapeseed oil varied from 14 percent to a high of 41 percent (when the pickup would not start.) Fuel economy varied from 5 km/L to 8.3 km/L. During the first 77,700 km of testing, the percent of rapeseed oil was as high as 40. This was higher than the target of 20 percent and caused excessive carbon buildup on the injector tips. The injectors were removed and cleaned at 73,145 km, after which the performance of the pickup noticeably improved.

Fuel Heating System

The fuel heating system on both pickups worked very well through the course of testing. After the initial installation of the heating system, the pickups were parked outside over a period of three days and nights with temperatures below -9°C. The ambient and Biodiesel fuel temperatures were monitored with thermocouples and a data acquisition system for the three day period. As the ambient temperature dropped below -9°C, the Biodiesel fuel maintained a temperature of 12.7 to 15.5°C.

Dynamometer Testing

1992 Dodge - Figure 5-2 is a graphical comparison of the power and smoke density with each of the three fuels tested over a period of five dynamometer tests. On the average, 100 percent RME produced 5 percent less power than 2-D and 20RME produced one percent less than 2-D. Also, smoke density was reduced 26 percent with 100 percent RME, while 20RME was reduced by 10 percent over 2-D.

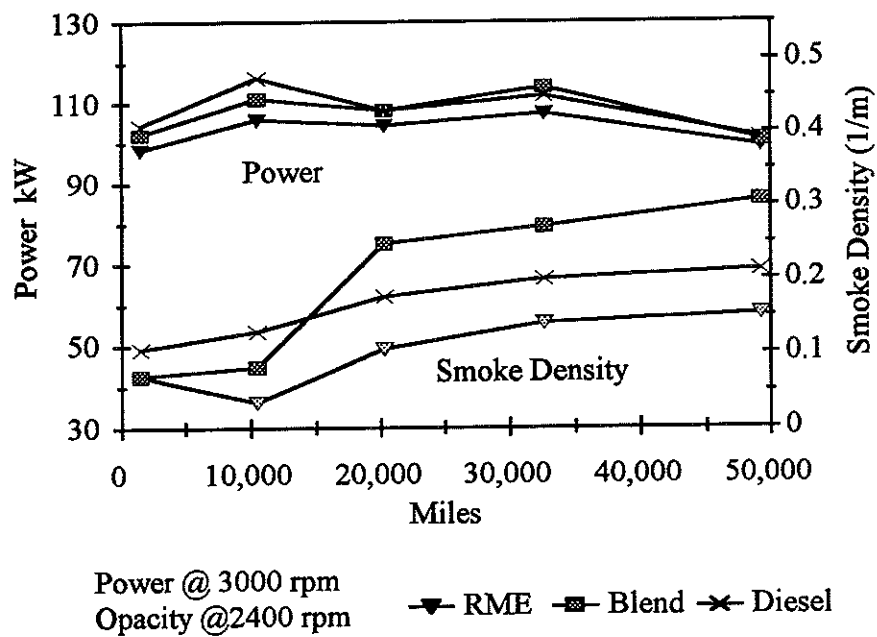


Figure 5-2. Dodge power and smoke density at five dynamometer tests.

1992 Ford - Figure 5-3 is a graphical comparison of the horsepower and smoke density for both fuels tested over a period of five dynamometer tests. The 20RAW produced one percent less power, and 11 percent less smoke compared to 2-D.

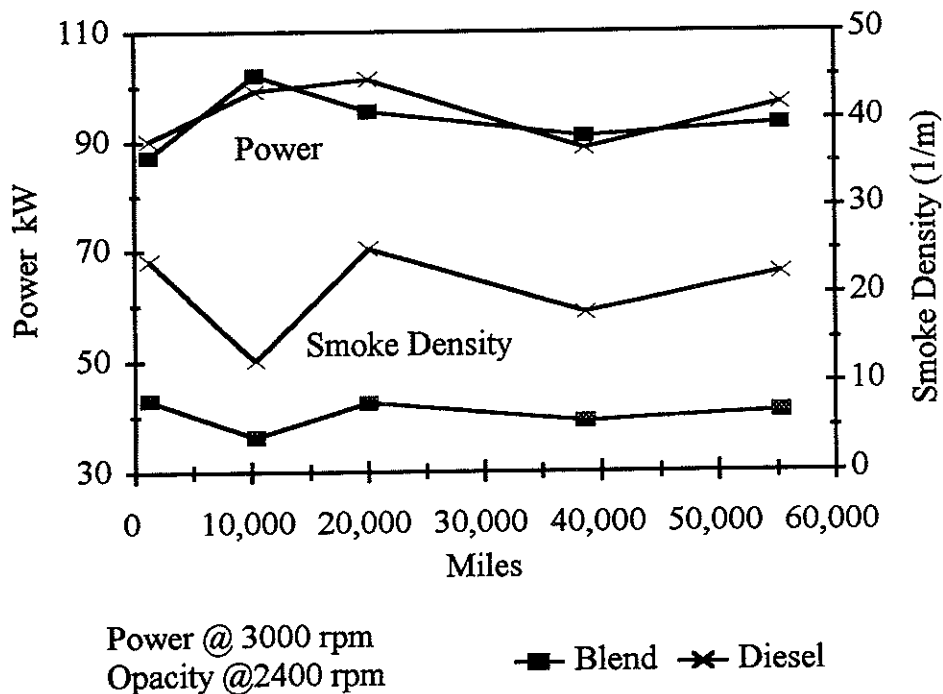


Figure 5-3: Ford power and smoke density at five dynamometer tests

Check Vehicles - The Ford check vehicle was dynamometer tested twice. At 62,235 km, a power rating of 92.5 kW at 3,000 RPM and 11.7 percent opacity for the snap idle test was recorded. The compression was comparable to the Biodiesel and the injector VOP was 1.38

MPa lower. The Dodge check pickups were equipped with automatic transmissions, which are not compatible with the dynamometer.

Engine Oil Analysis

Chevron Delo Multigrade SAE 15W-40 heavy duty engine oil was used. Wear data for the Dodge pickup was at acceptable levels without any significant differences between the sampling reports. The Ford Biodiesel pickup indicated high iron after 45,000 km. The Ford check vehicle also indicated high iron throughout the monitoring period. The high iron concentration in the engine lubricating oil was not an effect of the fuel.

Performance Parameters

Injector coking was measured after each dynamometer test, but a check vehicle operating on 100 percent 2-D was not studied during this testing; therefore, an injector coking index is not available. There was very little carbon buildup on the tip of the fuel injectors, either visually or by calculating the area of the coked injector from one interval to the next for the Dodge.

The Dodge fuel injectors were sticking when tested at the 79,300 km engine performance test because of the fuel filter plugging and rusty fuel being introduced into the injectors. The injectors were cleaned and retested, which resulted in a good spray pattern and the specified valve opening pressure.

The Ford fuel injector tips had a significant amount of carbon buildup both visually and by calculating the area of the coked injector from one interval to the next. The fuel injector tips were cleaned at 73,200 km due to excess carbon buildup that was distorting the fuel spray pattern.

The engine cylinder compression on both the Dodge and Ford was checked at each performance interval. The cylinder compression in the Dodge either stayed the same or decreased only as much as 103 kPa from the beginning of the test to the end. The cylinder compression in the Ford increased in each cylinder as little as 275 kPa, with the exception of cylinder number 5, which decreased by 103 kPa. The average cylinder compression for both pickups was 3.45 MPa.

The average beginning valve opening pressure (VOP) for the Dodge was 24.2 MPa with a standard deviation of 145 kPa. The average ending VOP was 23.7 MPa with a standard deviation of 450 kPa. The average beginning VOP for the Ford pickup was 13.8 MPa with a standard deviation of 117 kPa. The average ending VOP was 13.4 MPa with a standard deviation of 220 kPa. The Ford check vehicle had the VOP checked at 62,230 km. The average VOP was 12.7 MPa with a standard deviation of 317 kPa.

The Dodge internal combustion areas were borescoped at each performance interval. There was no significant visual change from one time to the next. At the end of this study there were a few slight carbon scratches on the thrust side of the cylinder walls of each cylinder,

which is normal for the number of accumulated miles. There did not appear to be any excess amount of carbon buildup on the piston crowns or the cylinder head and valves.

The drivers of the vehicles did not notice any change in vehicle operation or other abnormalities during the course of the test. The Ford averaged 7.35 km/L and the Dodge 8.30 km/L for the 80,500 km. The Ford check vehicle averaged 5.4 km/L and the Dodge 7.06 km/L. These two check vehicles were used for utility type applications with heavy loads while the test vehicles generally were operated empty, which may explain the differences in economy.

On-road performance tests demonstrated that RME and 20RME can be used to successfully fuel a diesel engine. The 20RAW fuel should be limited to pre-combustion chamber engines and may require more frequent fuel injector tip cleaning. The 20RAW fuel has generally not been recommended for general use because of potential engine polymerization and lubrication oil problems.

CONCLUSIONS

At the conclusion of 80,500 km with two pickups operating on 20 percent Biodiesel (raw or RME), there is no indication of abnormal wear or performance. The on-board mixing system, designed and reported on in this paper, was essential only for this experiment. It should be clear, however, that for commercial use the blending would take place at the fuel plant, eliminating the on-board mixing system.

Specific conclusions from the results of this testing are presented below.

- Fuel characterization data show some similarities and differences between RME and 2-D. a) Specific weight is higher for RME, viscosity is 1.8 times that of 2-D at 40°C, and the heat of combustion is 5.6% lower than 2-D. b) Sulfur content for RME is 67% less than 2-D.
- Visually, all injector coking was low with 20RME. The 20RAW injector tips had accumulated excessive deposits and were cleaned at 73,200 km with a noticeable improvement in performance. The Dodge injectors were cleaned at 79,340 km due to rust.
- The fuel heating systems performed acceptably during the test period. The fuel combining systems were updated twice, due to continual adjustments, to achieve the targeted 20 percent blend.
- On the average, RME produced 5 percent less power than 2-D and 20RME produced one percent less power than 2-D. The 20RAW produced one percent less power than 2-D.
- On the average, smoke density was reduced 39 percent with RME, while 20RME increased 18 percent over 2-D. The 2-D had a smoke density 3.1 times that of 20RAW.
- The average fuel economy for RME was 4 percent higher than that of 2-D, 1.8 percent higher for 20RME, and 2.6 percent higher for 20 RAW. The differences in fuel

consumption and power reflect the differences in heat of combustion and density between the two fuels.

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POTENTIAL OF HIGH ERUCIC ACID RAPESEED (BRASSICA NAPUS, VAR. DWARF ESSEX) OIL AS A HYDRAULIC FLUID

The goal of this project was to compare the hydraulic fluid properties of raw rapeseed oil with commercially available hydraulic fluids. The three commercially available fluids that were compared with rapeseed oil were: mineral oil based Hy-TransPlus; PlantoHyd 40N¹, which is rapeseed oil based; and Mobil EAL 224H, also a vegetable oil based product.

The fluids were evaluated by the following tests: Kinematic Viscosity, Viscosity Index, Total Acid Number, Pour Point, Flash Point, Volume Change of Elastomeric Material under static condition, Mist Spray Flammability of hydraulic fluids, wear characteristics, and spectrographic analysis.

LITERATURE REVIEW

Eichenberger (1991) made a very detailed study of the properties of rapeseed oil. He reported that rapeseed oil offers good corrosion protection for hydraulic systems and does not attack sealing materials, varnish or paint. It does not affect the oil performance when mixed with conventional mineral oil. Rapeseed oil is not water soluble. Since rapeseed oil is lighter than water, escaped oil on a water surface can be skimmed off. High temperature stability of rapeseed oil is very critical.

Eichenberger (1991) conducted the CEC-L-33-T-82 test on rapeseed oil and other selected products. This test was developed by Co-ordinating European Council (CEC), for determining the biodegradability of two stroke cycle outboard engine oils in water. A biodegradability of 99% for rapeseed oil, 70 to 99% for polyethylene, 10 to 90% for synthetic ester, and 20% for mineral oil, was reported.

Lubrizol Corporation (1990), has described the basic chemistry of rapeseed oil as follows: rapeseed oil contains three major types of fatty acids, these being Erucic acid (C22:1), Oleic acid (C18:1) and Linoleic acid (C18:2). The percentage of the acids vary in different types of rapeseed oil. Two types of rapeseed oil are currently being marketed, namely Low Erucic Acid Rape (LEAR), and High Erucic Acid Rape (HEAR) oils. LEAR contains typically 0-5% Erucic acid, while HEAR contains 50-60% Erucic acid. HEAR type oils provide good lubricity and oxidation stability (due to the greater presence of the longer C22:1 chain), while LEAR type oils provide good biodegradability and will be more liquid at lower temperatures (due to the increased presence of the shorter C18:1 chain), but have poorer lubricity.

¹Use of trade names is for simplification in identification and does not constitute an endorsement of the product nor discrimination against similar products which are not mentioned.

Cheng et al. (1991) of Mobil Oil Corporation has assessed the biodegradability of hydraulic fluids by the shake flask test and the Co-ordinating European Council (CEC) test. Vegetable oils and a number of synthetic esters met the "ready biodegradability" criterion developed by Mobil, products are considered acceptable if their aquatic toxicity is greater than 1000 ppm, and ready biodegradability is greater than 60% (as measured by conversion to CO₂). None of the formulations containing mineral oil base stocks were able to meet the ready biodegradability criterion, even though 40 to 49% of these materials were converted to CO₂ in 28 days. A range of mineral oil formulations was assessed by the CEC test, values for a typical white oil ranged from 49 to 60%. The polyglycol-based materials also failed to meet the ready biodegradability criterion with 6 to 38% of the test materials being converted to CO₂ in 28 days.

In his U.S. and related international patent application, Jokinen et al. (1988) has claimed that vegetable oils with iodine value between 50 and 130 are ideal for hydraulic fluids. Below 50, fluids have high pour points due to lack of unsaturations, and above 130, oils tend to be oxidatively unstable. It was also pointed out that the fatty acids contained in some vegetable oils are polar in nature and tend to cling to metal surfaces more effectively than mineral oils, providing improved lubricity. Using these criteria as a guide, a biodegradable and nontoxic hydraulic fluid was formulated by Cheng et al. (1991), based on a selected vegetable oil additive system. This oil was designated as Environmental Acceptable (EA) oil A. Two characteristics presented special formulation challenges. First, a vegetable-based antiwear fluid had a high foaming tendency, and secondly, the water tolerance property, which indicates additive stability in the presence of water contamination, was a difficult target to meet. Seal swelling tests on EA oil A showed acceptable compatibility with Buna N and Viton elastomers; and an extended stability study at several temperatures demonstrated satisfactory fluid stability on long term storage.

Since EA oil A gave satisfactory results on the ASTM the D2882 wear test, the test was extended from 100 hours to 200 hours, along with the addition of 1% water at 0 and 100 hours of test operation. The result indicated low cumulative wear as well as small viscosity and total acid number increase for the test duration. EA oil A was evaluated in the HF-O piston test rig. Wear (shoe thickness) measurements and thorough surface examination showed the critical parts to be in exceptionally good condition. In addition to the axial piston pump evaluation, a vane pump test based on the new A.SK-30320 procedure recently developed by Hagglunds-Dension of France, was conducted on EA oil A and a good passing result was obtained. To further assess fluid useful life in critical applications, EA oil A was evaluated in a proprietary hydraulic fluid durability test. An increase in viscosity and total acid number were observed for EA oil A. Despite these increases, the pump operated satisfactorily over 2000 test hours. Turbine Oil Stability Test (TOST) values of less than 75 hours for vegetable oil and less than 500 hours were measured for the ester and polyglycol fluids. The TOST test measures the time for a fluid to incur a total acid value (TAN) increase of 2 NN, passing is 1000 hour. However they are also careful to note that the TOST test relevance to EA oils has not been established.

The vegetable oil used in the development of the EAL oil had a pour point of -20°C (-4°F). In a cold-storage study, a sample of the neat vegetable oil showed onset of solidification in just a few hours at -18°C (-0.4°F). EA oil A, formulated with an optimum treat of an effective pour depressant, was found to stay fluid over three months in storage at -18°C . At 4°C (7.2°F) lower (-22°C , -7.6°F), the first signs of solidification were observed after 14 days.

Cheng et al. (1991) conducted two tests to assess the diesel engine oil (DEO) contamination. A storage stability study involved contaminating the EA fluids by several dosages of a typical DEO, ranging from 5% to 40% under both dry and wet (0.5% water) conditions. Observations were made after the samples were stored at several temperatures for a two-week period. Up to 20% contamination under dry conditions resulted in the mixture being free from deposits. However, under wet conditions, even 5% contamination brought heavy deposits. Several other commercial, environmental acceptable (EA) fluids were also evaluated and gave similar results. A secondary study was based on a dynamic filterability test which was developed to simulate in-service filtration problems relating to water contamination, and extended shutdown for machinery equipped with fine-porosity filters. While an uncontaminated EA fluid clearly passed this test requirement, it was found that a fluid contaminated with 5% of DEO was a definite failure. In comparison, no problems were observed when a typical mineral AW hydraulic fluid was used in place of the DEO in both of the tests cited above. This compatibility study underscored the need for a very thorough flushing procedure, particularly in systems where a DEO was previously installed.

Eichenberger (1991) has reported a Caterpillar field test using bio-oils. The reason for this test was the confrontation with the new regulations by equipment owners. Equipment owners wanted to know if their equipment can operate with bio-oils. Their first step was to select several different machines and the objective was simple; gain practical experience under field conditions. A one year test program was started in cooperation with the dealers in Austria, Germany and Switzerland, the oil suppliers and the machine owners. In addition to regular maintenance procedures, oil sample analysis was added. The test program was successfully completed without any indication of system deficiencies.

Eichenberger (1991) has also reported a 4000 hour field test program, using a medium size wheel loader. With 4045 operating hours, the hydraulic pump (vane type) was removed and inspected. Samples of new and used rapeseed oil were analyzed in the laboratory. The analysis showed that the used oil was still in acceptable condition. Only a minor viscosity change was measured. Pump performance was lower than expected for 4045 hours of operation but not enough that the operator had noticed any difference. This case showed that extension of the regular change period (2000 hours) are possible. Caterpillar's recommendations, however, remain the same and equipment owners were advised to follow the guidelines published for specified mineral oils.

An example of the future trend in hydraulic systems has been reported by Eichenberger (1991). Gravel pit and quarry operations are particularly vulnerable to pollution. A company

operating several pits throughout Switzerland took the initiative to convert all hydraulic systems from mineral oil to biodegradable oil. The equipment fleet involved 101 machines. Some difficulties were expected and in fact some systems behaved differently than others. Equipment maintenance personnel faced some seal problems and reduced pump bearing life. Other unusual measure taken by the company were the reduction of onsite bulk storage of oil and diesel fuel. This example may not be typical or representative, but it may indicate a trend into the future. Other companies are taking similar action to reduce the risk of environmental pollution.

MATERIALS AND METHODS

This study was undertaken to demonstrate the potential of rapeseed oil as a hydraulic fluid. The primary elements and procedures used in this research are in accordance with the American Society for Testing and Materials (ASTM) standards, except where noted.

Selection of Oils

The rapeseed oil used was extracted from Dwarf Essex variety winter rapeseed grown in Nez Perce and Latah county, in northern Idaho. Dwarf Essex is an industrial rapeseed high in erucic acid. The oil was extracted and filtered in the laboratory at the Department of Agricultural Engineering, University of Idaho.

Hy-TransPlus (MS 1207) is a Hydraulic/Transmission fluid, manufactured by Case IH for JI Case, A Tenneco Company, Racine, WI 53404. Mobil EAL 224H hydraulic oil is a nontoxic biodegradable antiwear hydraulic oil having a ISO VG of 32/46. Its trademark is registered to Mobil Oil Corporation, Fairfax, Virginia 22037. PlantoHyd 40N is also a nontoxic biodegradable hydraulic oil. The product container gave the address: Metal Lubricants Co., 17050 Lathrop Avenue, Harvey, Illinois 60426.

Spectrographic Analysis and Pour Point Test

The spectrographic analysis and Pour point tests were conducted at The Oil Analysis Lab Inc., Spokane, Washington. The spectrographic analysis identifies 19 trace elements to determine component wear, airborne dirt and oil additive concentrations.

Test method for Kinematic Viscosity of Transparent and Opaque Liquids

The ASTM standard test procedure D445 was followed for determining the viscosity (ASTM, 1991). A Cannon-Fenske routine viscometer was used to determine the viscosity at both 40°C and 100°C. The viscometer was suspended in a water bath; a temperature controller was used to maintain the bath at a constant temperature. A standard liquid-in-glass thermometer was used for temperature measurement.

Method for Calculating Viscosity Index from Kinematic Viscosity at 40°C and 100°C

After determining the kinematic viscosity of the oil at both 40°C and 100°C by ASTM test method D445, ASTM test procedure D 2270 was followed for calculating the viscosity index (ASTM, 1991).

Test Method for Flash Point by Pensky-Martens Closed Tester

The ASTM standard test procedure D93 was followed for determining the flash point (ASTM, 1991). The apparatus used was a Pensky-Martens closed flash tester, and a standard thermometer for measuring the temperature. In this test the sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

Test method for Acid and Base Number by Color-Indicator Titration

The ASTM standard test procedure D974 was followed for determining the total Acid Number (ASTM, 1991). The apparatus used was a 50 ml buret graduated in 0.1 ml subdivisions. Reagents used were hydrochloric acid solution, methyl orange indicator solution, p-Naphtholbenzein indicator solution, potassium hydroxide solution and titration solvent, a mixture of 500 ml. of toluene, 5 ml. of water and 495 ml. of anhydrous isopropyl alcohol. In this test, the sample was dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end point indicated by the color change of the added p-Naphtholbenzein solution.

Test Method for Volume Change of Elastomeric Materials in Hydraulic Fluids Under Static Conditions

The test was conducted according to the ASTM standard test procedure D3604 (ASTM, 1983). The specimen selected was a Buna N rubber O-ring from a Vickers vane pump, used in wear test. An electric oven, capable of maintaining a temperature of 70°C, was used to maintain the specimen temperature. A 25 ml. beaker was used to immerse the specimen in the test fluid. An electronic balance accurate to 0.0001 of a gram was used to weigh the specimen.

In this test, the specimen is wiped with cheese cloth that has been saturated with anhydrous methanol. Then the specimen is air dried for one hour and weighed both in air and distilled water at room temperature. The specimen is immersed in the test fluid and placed in an oven at 70°C for one week. The specimen is weighed again to calculate the volume change.

Test Method for Mist Spray Flammability of Hydraulic Fluids

This test was conducted according to the ASTM standard test procedure D3119 (ASTM, 1983). A pneumatic type spray gun was used to generate a mist of the test fluid. The ignition source was a natural gas-air laboratory Bunsen burner, capable of being adjusted to give a steady yellow flame. A metal sheet was used to intercept the excess fluid spray that does not

burn or vaporize. The intercepted fluid was collected in a metal pan. The test sample was heated by a hot plate. The temperature of the heated fluid was measured by a thermometer. The spray gun used was not recommended by ASTM, but it met the ASTM specifications.

Figure 6-1 shows the test setup for the mist spray flammability test. The distances between the spray gun, burner and the metal sheet were maintained as specified by the ASTM standards.

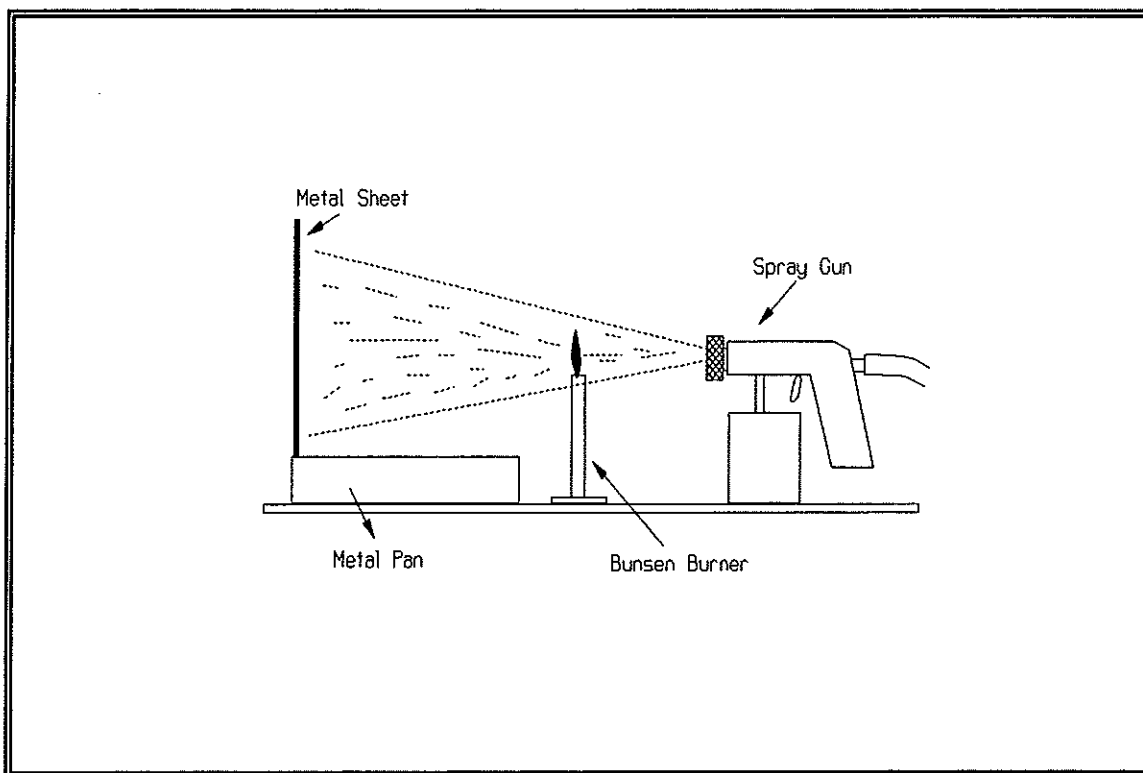


Figure 6-1: Flammability Test Setup

Test Method for Indicating the Wear Characteristics of Petroleum and Non-Petroleum Hydraulic Fluids in a Constant Volume Vane Pump

The ASTM standard test procedure D2882 was followed for conducting the test (ASTM, 1991).

Perez and Brenner (1992) of Lubrizol Corporation, have developed a new constant volume vane pump test for measuring wear characteristics of fluids, which uses Vickers 20VQ5 vane pump. This new test method was compared with various alternate pump tests to evaluate fluids. The results showed that the new method ranked the fluids the same as the existing pump tests, which uses Vickers 104C vane pump. Because the Vickers 104C pump is no longer available from the manufacturer, the Vickers 20VQ5 pump was used in this test.

A Kubota model diesel engine was used to run the Vickers 20VQ5 vane pump. A five gallon reservoir with a 60-mesh finger screen in its outlet was used as a test fluid reservoir. System pressure of 2000 psi was generated by a pressure control valve (Vickers pressure relief valve CT-06 F50 3000 psi). A constant fluid temperature of 65.5°C was maintained with a heat exchanger (Young Heat Exchanger, RFF-314-H05-2P-N), temperature controlled valve (Johnson Penn), fan, radiator, and a water pump. A thermocouple and reader were used to measure temperature. A 25 micron return line filter was used for filtering the oil and a flow meter was used to record the flow rate. Low oil level, high temperature, and high pressure safety systems were used. Figure 6-2 shows a schematic of the test stand that was built at the Department of Agricultural Engineering, University of Idaho, for this project.

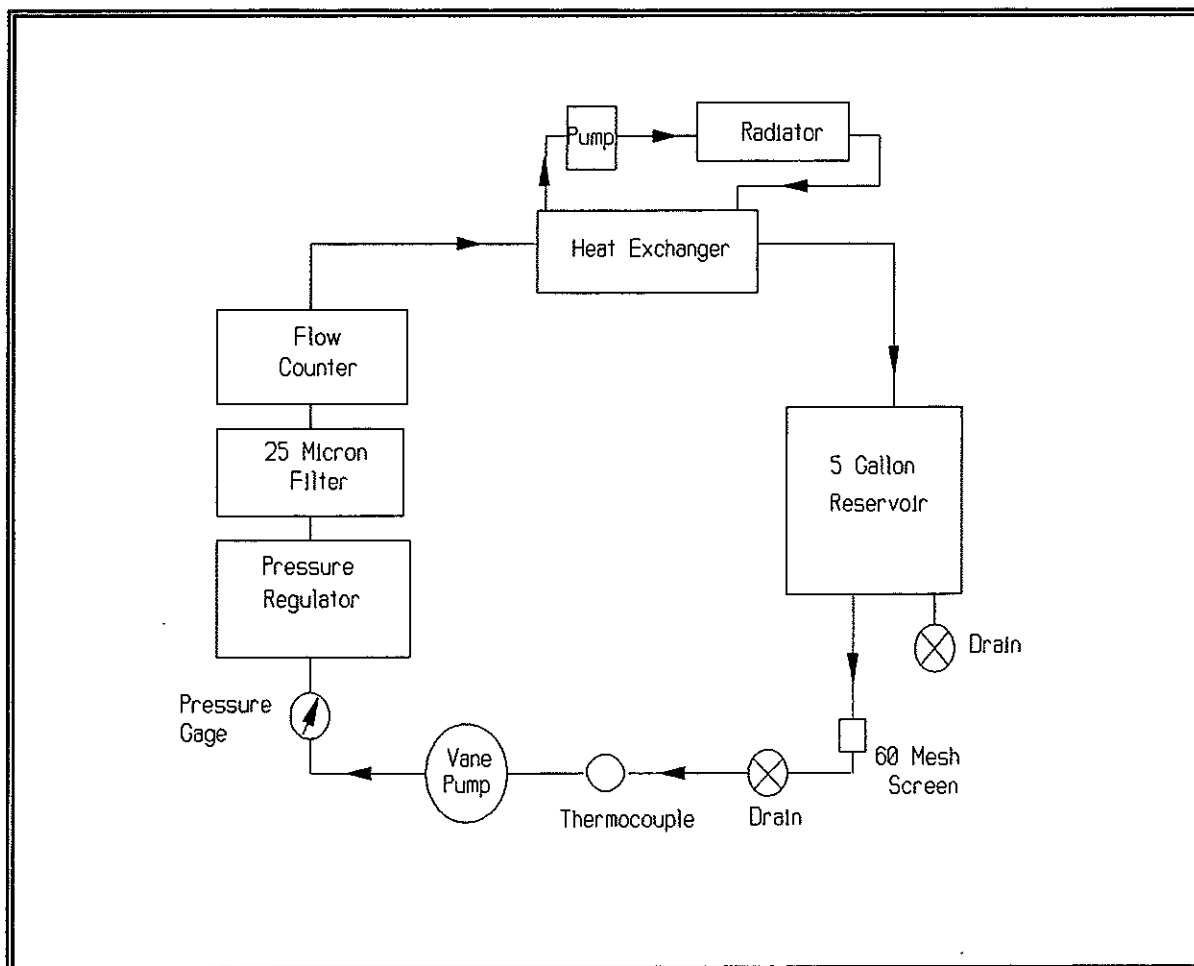


Figure 6-2: Schematic of Wear Test Setup

PRESENTATION OF DATA AND DISCUSSION OF RESULTS

The following section presents the data of the individual tests. In the tables, "New" oil means, the oil before the wear test, and "Used" means the oil after the wear test. All the tests were conducted in the laboratory at the Department of Agricultural Engineering, University of Idaho, except for Spectrographic analysis and Pour point test.

Kinematic Viscosity Test

Figures 6-3 and 6-4 show that rapeseed oil has a higher viscosity than the other three oils, though not much higher than the PlantoHyd 40N. The viscosity of Hy-TransPlus, Mobil EAL, and PlantoHyd 40N decreased after the wear test, but it was opposite with the rapeseed oil. The viscosity of vegetable oils increase due to poor stability and polymerization.

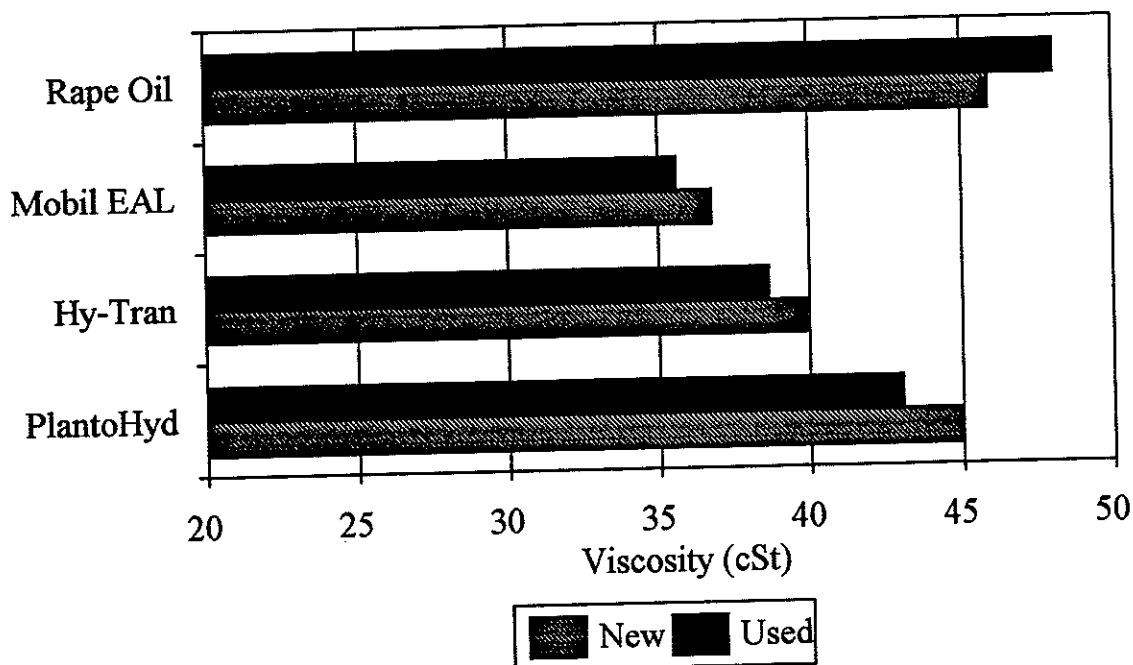


Figure 6-3. Kinematic Viscosity at 40°C

PlantoHyd 40 decreased after the wear test, but it was opposite with the rapeseed oil. The viscosity of vegetable oils increased due to poor stability and polymerization.

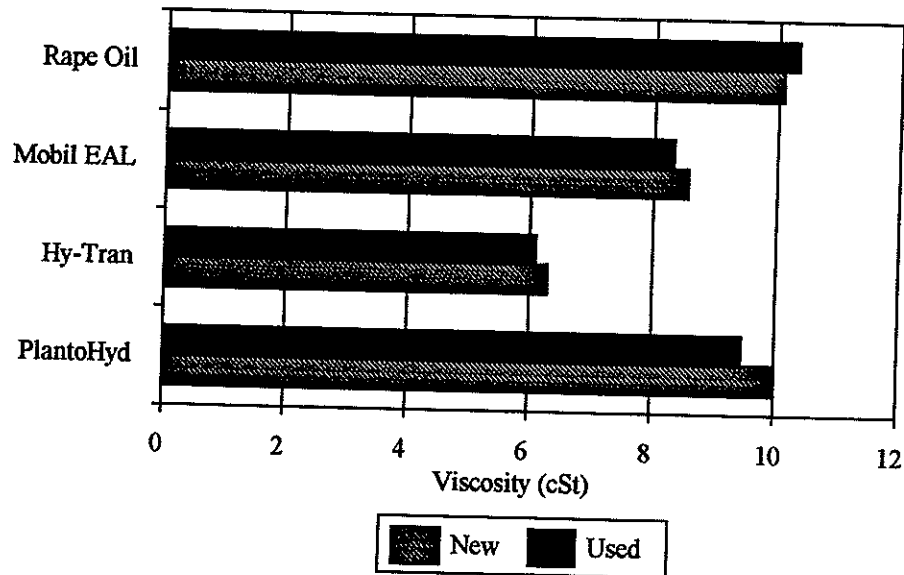


Figure 6-4. Kinematic Viscosity at 100°C

Viscosity Index

Figure 6-5 shows that viscosity index of rapeseed oil is comparable to Mobil EAL and PlantoHyd 40N, and much higher than Hy-TransPlus. The higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The result of this test indicates that rapeseed oil is very stable between the two test temperatures.

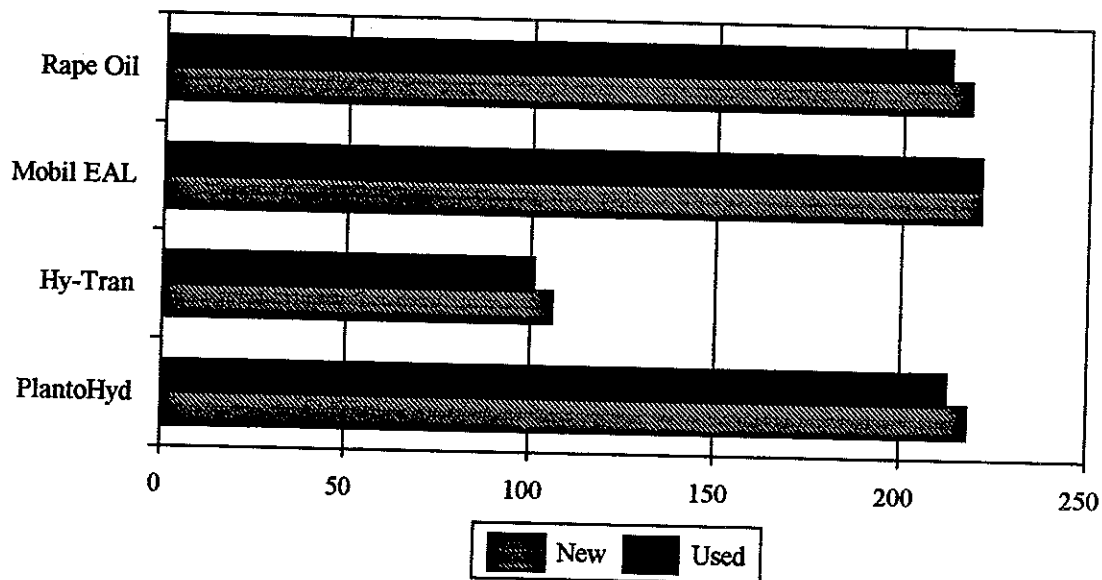


Figure 6-5. Results of Viscosity Index Calculations

Flash Point Test

Figure 6-6 shows that Hy-TransPlus has a lower flash point than rapeseed, Mobil EAL and PlantoHyd 40N hydraulic oils. This test only measures the response of the sample to heat and flame under controlled laboratory conditions. This test shows that rapeseed oil is less hazardous than petroleum based products. Also there is no change in flash point of the oils following the wear test.

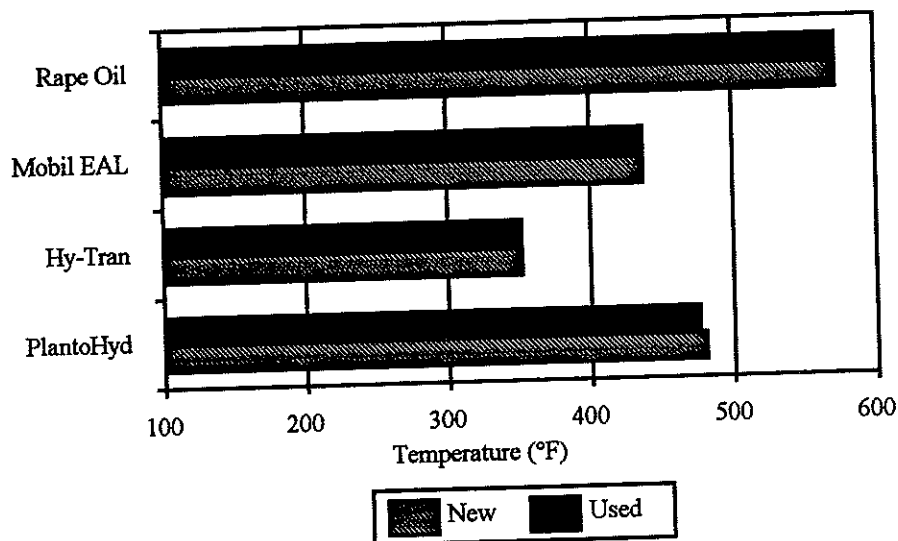


Figure 6-6. Results of the Flash Point Test

Pour Point Test

Figure 6-7 shows that the pour point of rapeseed oil is much higher than Hy-TransPlus, Mobil EAL and PlantoHyd 40N. The pour point of Hy-TransPlus increased slightly after the wear test but that of Mobil EAL, PlantoHyd 40N and rapeseed oil did not change.

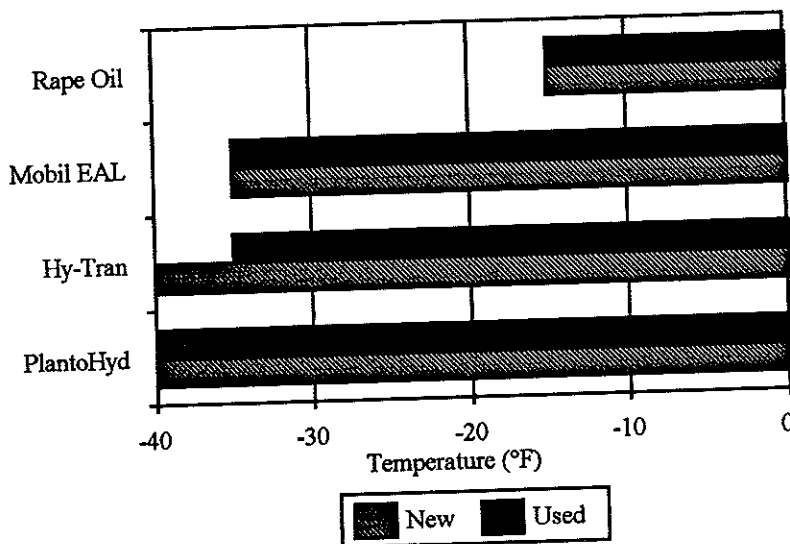


Figure 6-7. Results of the Pour Point Tests

Neutralization Number Test:

Figure 6-8 shows that rapeseed oil is more acidic than Hy-TransPlus, Mobil EAL and PlantoHyd 40N. This could cause a more rapid deterioration of the fluid, bearings, component parts, and seals.

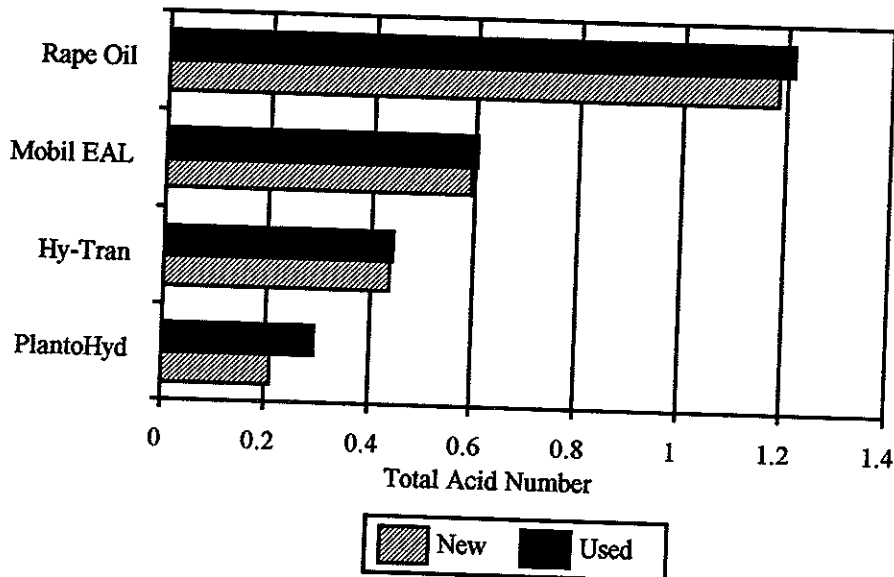


Figure 6-8. Results of Total Acid Number Test

Volume Change of Elastomeric Material test

Figure 6-9 shows that in case of Hy-TransPlus and PlantoHyd 40N, there is a decrease in volume of the elastomer after the wear test. Both Mobil EAL and rapeseed oil showed an increase in the volume, after the wear test.

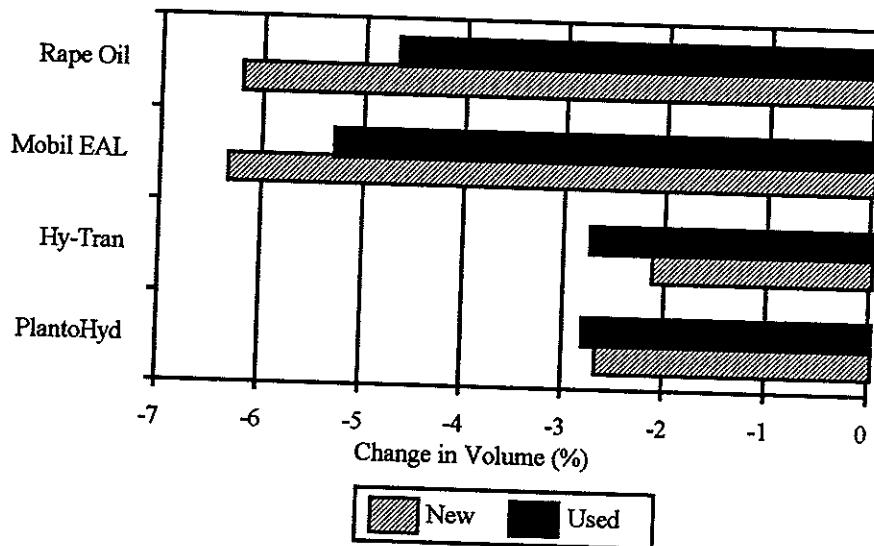


Figure 6-9. Results of Volumetric Expansion Tests

Mist spray Flammability Test

Figure 6-10 shows the rapeseed oil offers better resistance to fire than its counterparts, Hy-TransPlus, Mobil EAL and PlantoHyd 40N hydraulic fluids. Violent fire was observed in Hy-TransPlus, i.e., the entire spray pattern ignited and burnt vigorously, Mobil EAL and PlantoHyd 40N displayed fire at the torch, which means the fluid burned at the area of the ignition source only. Even though they are both vegetable oil based, fire at the torch was observed, where as there was no fire in case of rapeseed oil, this might be due to the additives that are used in the formulation of Mobil EAL and PlantoHyd 40N.

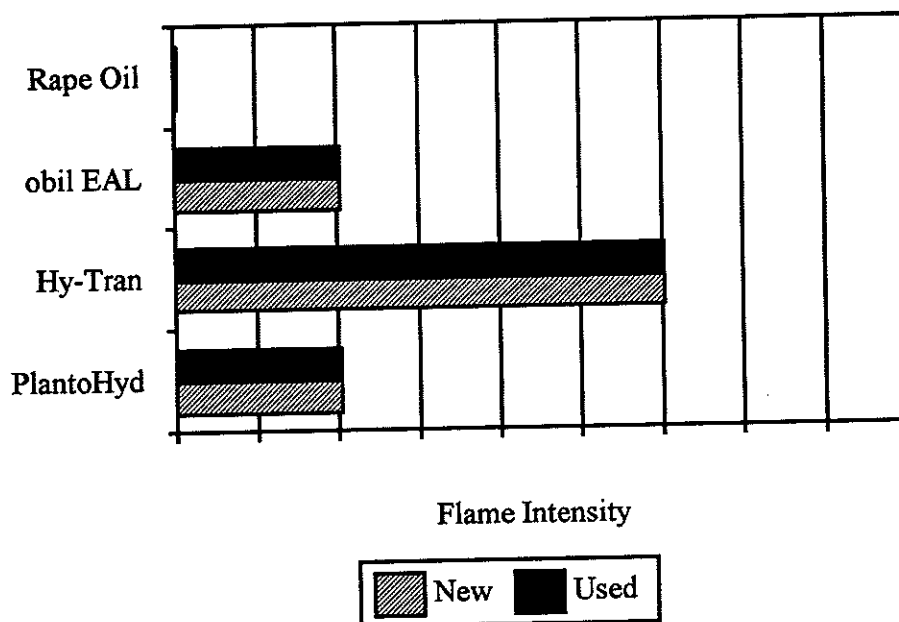


Figure 6-10. Results of Mist Spray Flammability Tests

Wear Test

Figure 6-11 shows that rapeseed oil displayed higher wear, when compared with its counterparts. Perez and Brenner (1992) have conducted similar test on some commercial hydraulic fluids and have reported wear ranging from 7 mg to 329 mg. So, the total weight loss of 18 mg, in rapeseed oil, is well within the acceptable range.

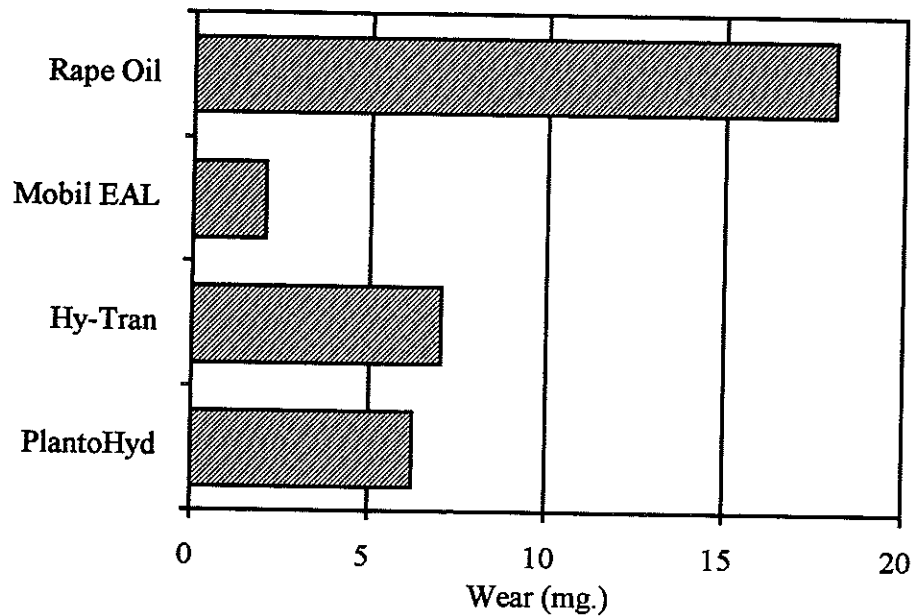


Figure 6-11. Results of the Wear Test

Spectrographic Analysis:

None of the oils were contaminated by water, and there was no trace of oxidation or nitration. Figure 6-14 shows that rapeseed oil has more elements, than Mobil EAL (Figure 6-13), Hy-TransPlus (Figure 6-12) or PlantoHyd 40N (Figure 6-15). The lab report indicated the content of silicon in rapeseed oil as "impending failure". This may be due to fine soil particles residing in the oil following the pressing process of rapeseed. The silicon contents in Hy-TransPlus, Mobil EAL, and PlantoHyd 40N are almost equal and are less than rapeseed oil.

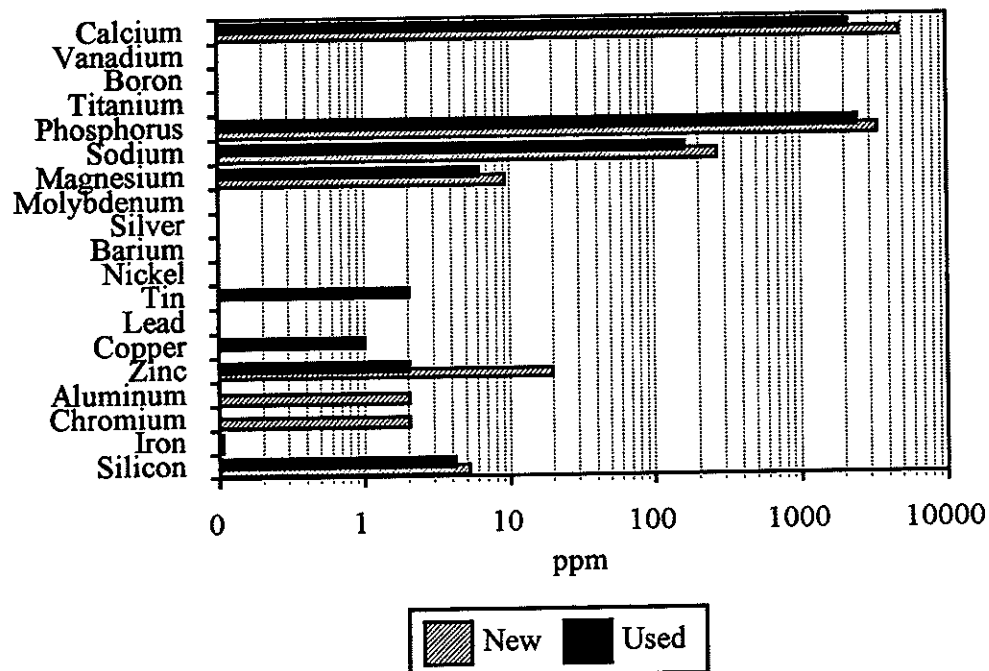


Figure 6-12. Spectrographic Analysis of Hy-Tran

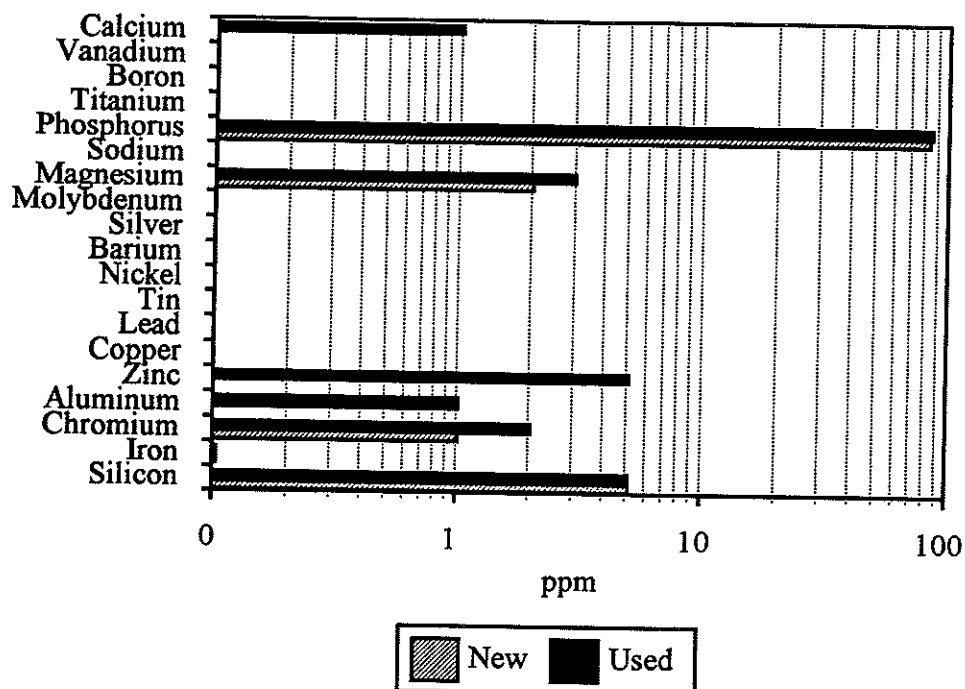


Figure 6-13. Spectrographic Analysis of Mobil EAL 224H

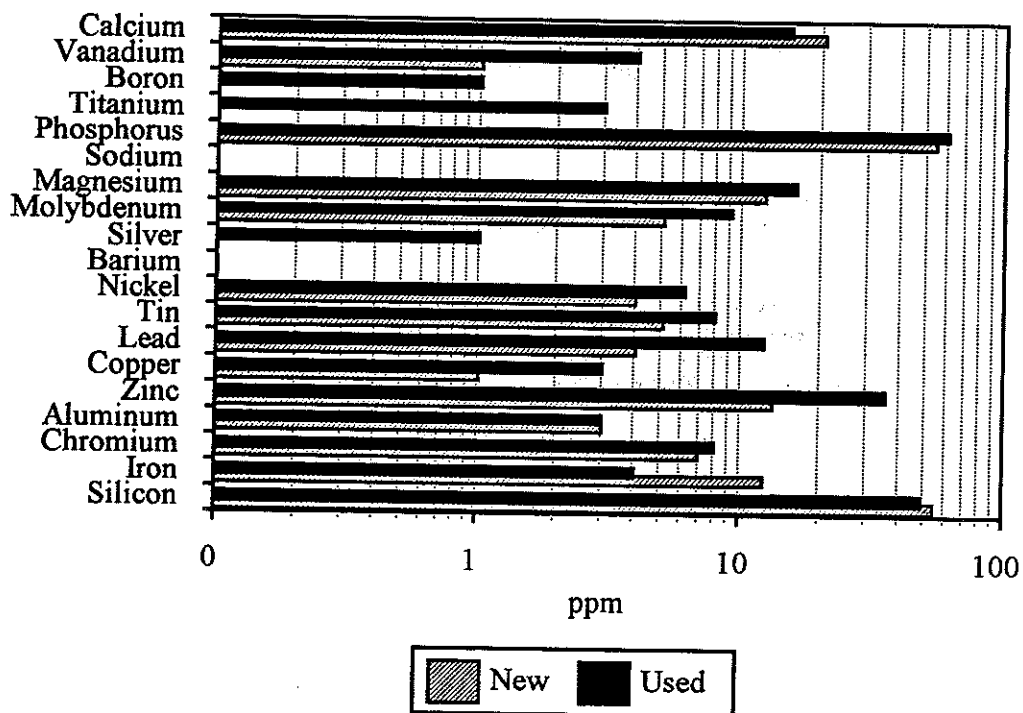


Figure 6-14. Spectrographic Analysis of Rapeseed Oil

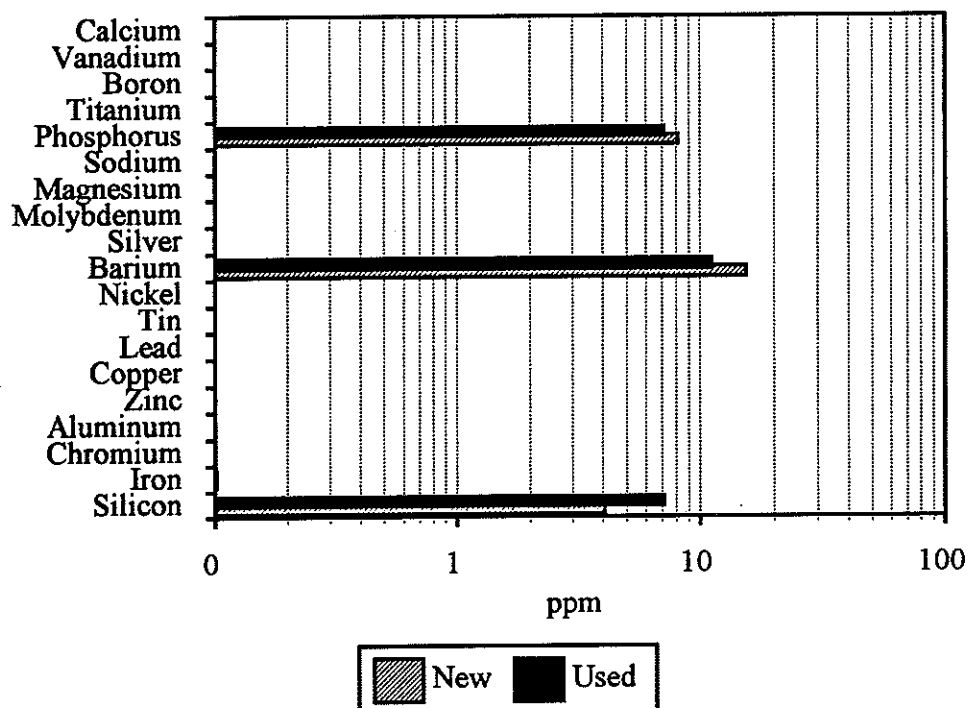


Figure 6-15. Spectrographic Analysis of PlantoHyd

CONCLUSIONS

The test results documented in this report suggest that the potential of rapeseed oil as a hydraulic oil is very good, however it is obvious that commercial fluids based on rapeseed oil have additional additives. The following conclusions are based on the data collected and presented in this paper.

1. Rapeseed oil displays a slight increase in its viscosity after the wear test, where as the viscosity of Mobil EAL, PlantoHyd 40N and Hy-TransPlus decreased.
2. Rapeseed oil displays a very high viscosity index. It is almost equal to Mobil EAL and PlantoHyd 40N, and much higher than Hy-TransPlus.
3. Rapeseed oil has a relatively high pour point when compared with Mobil EAL, PlantoHyd 40N and Hy-TransPlus. Mobil EAL and PlantoHyd 40N evidently have an additive or some processing to reduce the pour point.

4. Rapeseed oil responds favorably for both flash point and mist spray flammability characteristics. It is better than Hy-TransPlus, Mobil EAL and PlantoHyd 40N hydraulic oils.
5. Rapeseed oil displays high wear when compared with Mobil EAL, PlantoHyd 40N and Hy-TransPlus. Considering that rapeseed oil does not contain any additives and its silicon content is approximately eight times more than its counterparts, the wear characteristics of rapeseed oil is good.
6. Rapeseed oil has a higher acid number than its counterparts. The acid number is approximately twice of Mobil EAL, three times that of Hy-TransPlus and almost six times that of PlantoHyd 40N.
7. Rapeseed oil was similar to Mobil EAL in the test for volume change of elastomeric material. The specimen used in this test was an O-ring, made of Buna N from the Vickers 20VQ5 vane pump.
8. Rapeseed oil displays elements like, Vanadium, Boron, Titanium, Molybdenum, Silver, Nickel, Lead, and Iron, which are not present in Mobil EAL, PlantoHyd 40N or Hy-TransPlus, as measured by spectrographic analysis.

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BIODEGRADABILITY OF BIODIESEL IN THE AQUATIC ENVIRONMENT

This report tested the biodegradability of various biodiesel fuels and diesel fuel; examined the biodegradation pattern in the REE/diesel blend; investigated the biodegradation rates for REE and compared them with those for the diesel in the aquatic environment by the CO₂ evolution method (EPA, 1982) and calibrated the results by GC analysis.

MATERIALS AND METHODS

Shake flask system

A 2-liter Erlenmeyer flask (Fig. 7-1) contained 900 ml deionized distilled water (DIW), 100 ml of inoculum (acclimation medium), 1 ml of each stock solution (Table 7-1), and 10 mg/L carbon from the test compound. A reservoir holding 10 ml of barium hydroxide solution was suspended in the flask to trap the CO₂. After inoculation, the test flasks were sparged with CO₂ free air (by passage of compressed air through a series of three 2-liter bottles each containing 1000 ml of 5N NaOH) to ensure that the trapped CO₂ came only from the microorganisms metabolizing the test substrate. The flasks were sealed and incubated with shaking in a dark room.

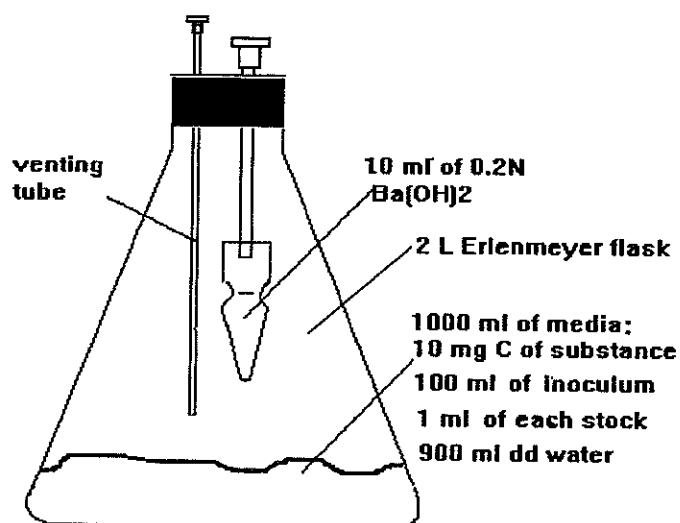


Figure 7-1. Shaker Flask System

Table 7-1. Medium employed for assay of CO₂ evolution.

| Stock Solution | Compound | Conc. (g/L ⁻¹) |
|----------------|--|----------------------------|
| I | NH ₄ Cl | 35 |
| | KNO ₃ | 15 |
| | K ₂ HPO ₄ ·3H ₂ O | 75 |
| | NaH ₂ PO ₄ ·H ₂ O | 25 |
| II* | KCl | 10 |
| | MgSO ₄ | 20 |
| | FeSO ₄ ·7H ₂ O | 1 |
| III | CaCl ₂ | 5 |
| | ZnCl ₂ | 0.05 |
| | MnCl ₂ ·4H ₂ O | 0.5 |
| | CuCl ₂ | 0.05 |
| | CoCl ₂ | 0.001 |
| | H ₃ BO ₃ | 0.001 |
| | MoO ₃ | 0.0004 |

*=Final pH is adjusted to 3.0 with HCL

Inoculum

1000 ml DIW dissolved in one gram of organic matter rich soil, 2 ml of activated (aerated) sewage mixed liquor, 50 ml of raw domestic sewage water, 25 mg/L of Difco vitamin-free casamino acids, 25 mg/L of yeast extract, and 1 ml of each stock solution I, II, III (Table 7-1). For test system I and II (Table 7-2), test compounds were added at concentrations equivalent to 4, 8, and 8 mg carbon/L by calculation on days 0, 7, 11, respectively. At day 14, refilter the inoculum through glass wool. The inoculum is ready for use. For test system III, the acclimation period is 2 to 3 days to simulate a real oil spill situation.

Table 7-2. Test system design

| System | Substrates | Concentration mg carbon L ⁻¹ | Methods |
|--------|---|---|-----------------|
| IA | REE, RME, SME SEE, NR, NS, 2-D | 10 | CO ₂ |
| IB | REE | 10 | GC |
| IIA | REE/diesel blend v/v = 80/20, 50/50, 20/80 | 10 | CO ₂ |
| IIB | REE, REE50/d50, 2-D | 10 | GC |
| IIIA | REE and D-2 | 4, 8, 16, 32, 40, 50, 60, 80, 100, 120, 150, 180, 200, 300, 500, 1000 | CO ₂ |
| IIIB | REE | 50, 100, 200, 500, 1000 | GC |

Measurement of CO₂ evolution

The quantity of CO₂ evolved is measured by titration of the entire Ba(OH)₂ sample (10 ml of Ba(OH)₂ plus 10 ml of rinse water) with 0.1 N HCl to the phenolphthalein end point. After sampling, the reservoir was refilled with fresh Ba(OH)₂. All the samples were analyzed at least five times in a 28 day period to allow for a smooth biodegradation plot. Three milliliters of 20% H₂SO₄ were added on the day prior to terminating the test. The percent theoretical CO₂ evolved from the test compound was calculated at any sampling time from the formula:

$$\% \text{ CO}_2 \text{ evolution} = \frac{TF - CF}{C} \times 100\% \quad (1)$$

where,

- TF = ml of 0.1 N HCl required to neutralize the Ba(OH)₂ from the flask with the test substance;
- CF = ml of 0.1 N HCl required to neutralize the Ba(OH)₂ from the control flask;
- C = Theoretical volume of the HCl required to neutralize the CO₂ converted from all the 10 mg carbon.

GC analysis

The GC method involved extraction of the samples with hexane and injection of a portion of the extract into a gas chromatograph. Quantitation was accomplished by using internal and external standards. In the extraction, the sample was first acidified to a pH of 2.0 or lower by adding 5 ml hydrochloric acid (1:1). One ml of internal standard was then added to the sample and shaken to mix well. Finally, 30 ml of hexane was added and the mixture was vigorously shaken for one minute. The layers are allowed to separate. The solvent layer was passed through a funnel containing sodium sulfate. The extract was transferred to a vial, sealed, and kept in a refrigerator (4°C) prior to the GC analysis.

The parameters of the GC analysis for biodiesel were: methyl ester of heptadecanoic acid C17:0 (methyl 17:0) was the internal standard with the concentration at 0.003 g/ml and hexane was the solvent. The instrument used was an HP 5890 series II GC equipped with a flame ionization detector (FID), J&W DB-23 (30m x 0.25 mm I.D, 0.25 μm film thickness) column. The temperatures were: injection port 250°C, detector 300°C, oven initial 215°C for 3 minutes, and final 230°C by a rate of 3°C per minute. Five μl of extract were injected at a 50:1 split ratio.

The parameters of the GC analysis of 2-D were: 2-fluorobiphenyl was the internal standard and methylene chloride was the extraction solvent. The instrument used was an HP series II 5890 gas chromatograph equipped with a capillary fused silica DB-5MS column (25 m by 0.21 mm by 0.33 μm; J&W Scientific, Folsom, Calif.) and MS interface. The interface temperature was set at 280°C. The MS detector was set initially at 250°C. A linear gradient of the oven temperature from 100°C to 320°C at 20°C per minute was used.

The percentage of primary degradation was determined by subtracting the substrate concentration at sampling time from the initial substrate concentration, and the difference was divided by the initial concentration.

Test system design

A total of three test systems were conducted (Table 7-2). System I was to compare the biodegradability of different biodiesel fuels and diesel. System II was to test the biodegradability of mixtures of REE/diesel at different ratios (v/v). In system III varying concentrations of REE and diesel from low to high were tested to obtain the biodegradation rates. All results from the CO₂ evolution were compared to those from the GC analysis. Dextrose was the reference compound and the three flasks which contained Hg/Cl₂ were for inhibition control of microbial activity.

Determination of biodegradation rates

Determination of biodegradation rates from CO₂ evolution (mineralization rates) employed the Warburg method used by Novak and Kraus (1973), but the method was modified. Varying substrate concentrations of REE were added into the test flasks and the rates of CO₂ evolution were measured. Initial slopes of all CO₂ evolution curves were taken to represent the rates of CO₂ evolution for the initial substrate concentration. These rates were multiplied by the initial concentrations of the test substrate to convert CO₂ evolution rates to mineralization rates, q_m s (mg L⁻¹ day⁻¹). The rate for each concentration obtained was previously described and was plotted against the initial substrate concentration in each flask to determine the maximum mineralization rate q_{Mmax} .

PART I

Biodegradability of REE, RME, SEE, SEE, NR, NS, 2-D

The composition of test substrates

The test substrates included: Rape Ethyl Ester (REE), Rape Methyl Ester (RME), Neat Rapeseed Oil (NR), Soyate Ethyl Ester (SEE), Soyate Methyl Ester (SME), Neat Soybean Oil (NS), and Phillips 2-D diesel. The composition and specific properties of biodiesel fuels are listed in Table 7-3 and of Phillips 2-D diesel in Table 7-4. REE and RME were made by the Department of Agricultural Engineering (Peterson et al., 1991) from neat Rapeseed oil and SEE and SME from neat soybean oil using a transesterification process. A more complete description of the process and a complete set of fuel characterization data is given in Peterson et al. (1994).

Table 7-3. Composition and main specific properties of Biodiesel.

| | NR | RME | REE | NS | SME | SEE |
|----------------------------------|--------------------------|-------|-------|-------|-------|-------|
| Fatty acid components | Concentration (%) | | | | | |
| Palmitic (16:0) | 2.6 | 2.2 | 2.6 | 10.0 | 9.9 | 10.0 |
| Stearic (18:0) | 1.0 | 0.9 | 0.9 | 3.8 | 3.8 | 3.8 |
| Oleic (18:1) | 13.5 | 12.6 | 12.8 | 19.0 | 19.1 | 18.9 |
| Linoleic (18:2) | 11.7 | 12.1 | 11.9 | 55.7 | 55.6 | 55.7 |
| Linolenic (18:3) | 7.4 | 8.0 | 7.7 | 10.2 | 10.2 | 10.2 |
| Eicosenoic (20:1) | 8.5 | 7.4 | 7.3 | 0.2 | 0.2 | 0.2 |
| Erucic (22:1) | 48.9 | 49.8 | 49.5 | 0.0 | 0.0 | 0.0 |
| Major Specific Properties | | | | | | |
| Specific gravity, 60/60 | 0.91 | 0.88 | 0.88 | 0.92 | 0.89 | 0.88 |
| Viscosity cSt @ 40°C | 46.7 | 5.65 | 6.17 | 32.5 | 3.89 | 4.49 |
| Net heat combustion, | 40.40 | 37.77 | 38.00 | 39.02 | 37.04 | 37.44 |
| Flash point °C | 274 | 179 | 124 | 257 | 188 | 171 |
| Carbon, wt% | 79.4 | 78.7 | 76.8 | 82.1 | 82.4 | 83.4 |
| Hydrogen, wt% | 11.8 | 12.66 | 11.80 | N/A | 12.9 | 11.8 |
| Percent esterified | | 98.02 | 94.75 | | 98.1 | 94.5 |

Table 7-4. Composition and major physical properties of Phillips 2-D reference fuel¹

| <u>Components (hydrocarbon type)</u> | <u>volume (%)</u> |
|--------------------------------------|-------------------|
| Saturates | 66.2 |
| Aromatics | 29.9 |
| Olefins | 3.9 |
| <u>Physical properties</u> | |
| Specific gravity, 60/60 | 0.8466 |
| Flash point °F, PM | 152 |
| Viscosity, cSt @ 40°C | 2.7 |
| Net heat combustion, | 42.9 |
| Carbon, wt% | 86.8 |
| Hydrogen, wt% | 13.2 |

¹The analysis was performed by Specialty Chemicals, Phillips 66 Company, A division of Phillips Petroleum Company.

RESULTS

Biodegradability of different biodiesel fuels (System I)

The percent accumulated CO₂ evolution of six biodiesel fuels REE, RME, SEE, SME, NR, and NS and 2-D in 28 days is summarized in Table 5 (all triplicates are averaged and an arithmetic mean, standard deviation, and RSD% is calculated). The maximum percent CO₂ evolution from the flasks of REE, RME, SEE, SME were between 85.54-88.49% in 28 days, the same as that of dextrose. It indicates there is no difference in their biodegradability. The maximum percent CO₂ evolution from neat rapeseed oil and neat soybean oil were 78.45 and 75.95% separately, which are slightly lower than their modified products. Yet, the CO₂ evolution for 2-D was only 26.24 % (average). The increase of the percent accumulated CO₂ evolution with time is graphically shown in Fig. 7-2. The data fits the exponential model well (Equation 2).

$$y = a(1 - e^{-bx}) \quad \text{for } x > c \quad (2)$$

where y = the accumulated percent CO₂ evolved at day x; x = time in days; a = asymptote of CO₂ evolution curve (percent total CO₂); b = rate constant of CO₂ evolution, day⁻¹; c = lag time before CO₂ evolution begins, days.

Table 7-5. CO₂ evolution from different substrates (conc. = 10 mg/L)

| Days | CO ₂ evolution (%) | | | | | | | |
|------|-------------------------------|--------|--------|--------|--------|--------|--------|----------|
| | REE | RME | SEE | SME | NR | NS | 2-D | dextrose |
| 7 | 69.01% | 66.32% | 67.68% | 68.4% | 58.39% | 60.57% | 13.20% | 59.84% |
| 14 | 79.15% | 80.72% | 78.40% | 77.83% | 70.47% | 70.12% | 21.04% | 80.19% |
| 28 | 86.92% | 88.49% | 86.40% | 85.54% | 78.45% | 75.95% | 26.24% | 87.79% |

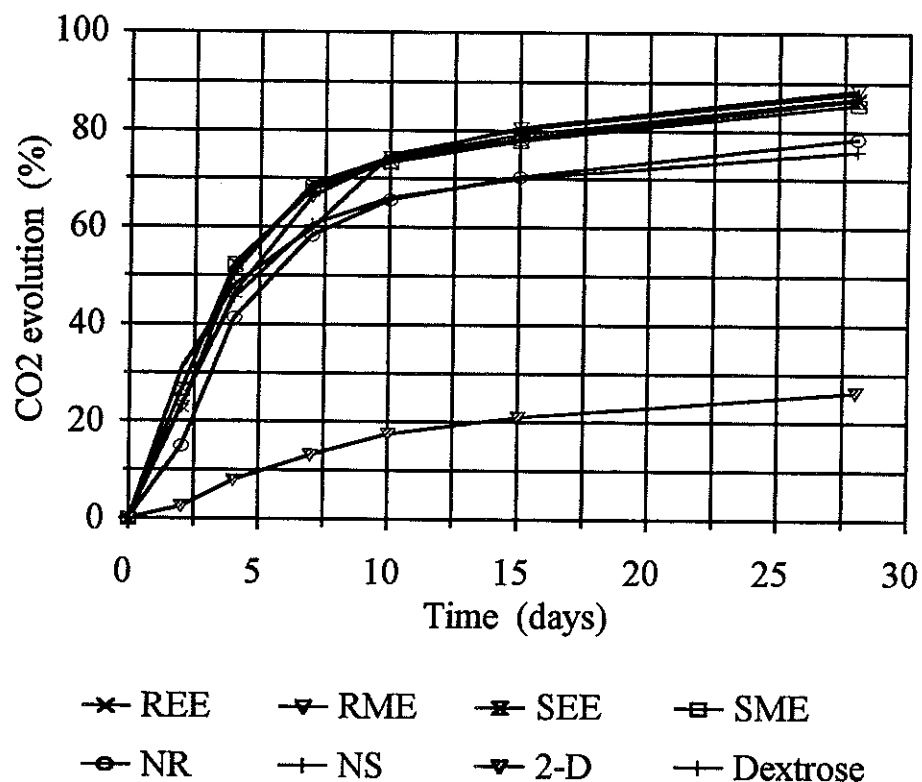


Figure 7-2. CO₂ evolution from seven biodiesel fuels and 2-D in 28 days when conc. = 10 mg/L.

The substrate (REE and diesel) disappearance versus time and percent degradation by the GC analysis are given in Table 7-6 and plotted in Fig. 7-3. As they illustrate, within one day, 63.82% of fatty acids in REE disappeared while diesel was 26.99%. All the fatty acids in REE were not detectable after day 2. It is obvious that the primary biodegradation rates of REE and the diesel are much faster than the rates of mineralization (by CO₂ evolution method).

Table 7-6. Substance disappearance and percent degradation vs. time by GC analysis

| days | REE | | 2-D | |
|------|--------------|----------|--------------|----------|
| | conc. (mg/L) | deg. (%) | conc. (mg/L) | deg. (%) |
| 0 | 10.00 | 0.00 | 10.00 | 0.00 |
| 1 | 3.82 | 61.80 | 8.37 | 16.27 |
| 2 | 0 | 100.00 | 6.41 | 35.90 |
| 4 | 0 | | 4.65 | 53.54 |

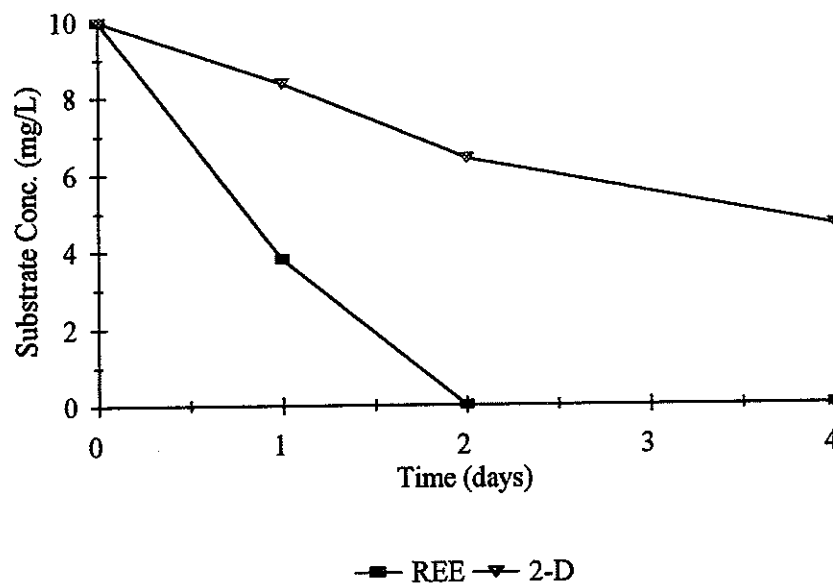


Figure 7-3. The disappearance of REE and diesel in 2 days by GC analysis (conc. = 10 mg/L)

Biodegradation of biodiesel/diesel mixture (System II)

The percent CO₂ evolution from REE/diesel mixtures increased with the increase of REE concentration in the mixture proportionally (Table 7-7 and Fig. 7-4). Higher REE concentrations in the mixture produced higher percentage of CO₂ evolution, and therefore, better biodegradability. This relation can be described by a linear equation $Y = 0.596 X + 0.207$ with an R² of 0.970, where X = the concentration of REE in a biodiesel mixture and Y = the maximum of CO₂ evolution after 28 days). The CO₂ evolution data fit the exponential model (Equation 2) very well by SAS non-linear regression (Fig. 7-4). The constants a and b for different mixtures are given in Table 7-8.

Table 7-7. CO₂ evolution from REE/diesel mixtures

| days | CO ₂ evolution (%) | | | | |
|------|-------------------------------|---------|---------|---------|--------|
| | REE100 | R80/D20 | R50/D50 | R20/D80 | 2-D |
| 0 | 0% | 0% | 0% | 0% | 0% |
| 7 | 64.09% | 52.33% | 37.85% | 25.24% | 12.08% |
| 14 | 77.51% | 61.26% | 45.74% | 31.59% | 14.96% |
| 28 | 84.37% | 67.82% | 51.90% | 35.67% | 18.18% |

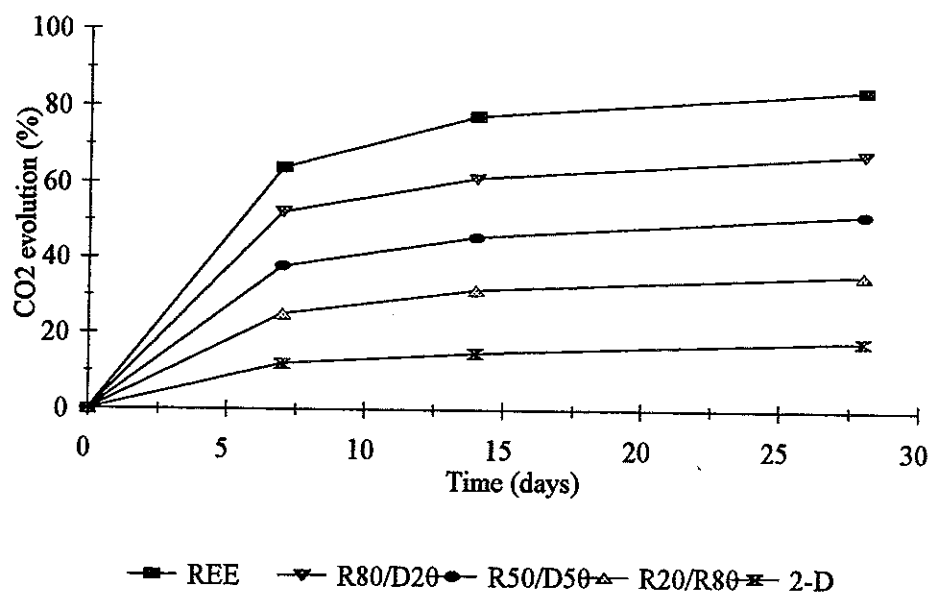


Figure 7-4. CO₂ evolution from REE/diesel mixtures after non-linear regression when conc.= 10 mg/L

Table 7-8. The dynamics constants of CO₂ evolution for different REE/diesel mixtures

| | REE100 | R80/D20 | R50/d50 | R20/D80 | Diesel100 |
|---|--------|---------|---------|---------|-----------|
| a | 0.8163 | 0.6419 | 0.4878 | 0.3227 | 0.2214 |
| b | 0.2336 | 0.2259 | 0.1745 | 0.1709 | 0.1169 |

Again, the GC analysis shows a much faster degradation rate in the mixture. At day 1, 63.62% of the REE/diesel mixture was degraded and about 96% disappeared after day 2. An interesting result is that the diesel in the mixture was degraded twice as fast as diesel alone, 62.8% versus 26.99% at day 1 (Table 7-9 and Fig. 7-5). It suggests that in the presence of REE, microorganisms use the fatty acids as an energy source to promote the degradation of diesel. A comparison of the GC identification in these two cases is shown in Fig. 7-6. From the GC peak identification of diesel (top part), there is no significant change in the peak counts between time 0 and day 1 when diesel alone was the sole carbon source. However, the diesel peaks in the REE/diesel mixture (bottom part of Fig. 7-6, the peaks for fatty acids of REE are at the right and so do not show) decreased significantly within one day (only the internal standard peak, retention time = 7.072 min., remains the same which indicates the same extraction efficiency).

The biodegradation pattern of the mixture can be seen by comparing the percent degradation of the blend and the diesel in the blend (Table 7-9) at day 1, 63.62.81% versus 62.80%. It is clear that the microorganisms attacked the fatty acids in REE and alkane chains in the diesel at the same time and at almost same rates instead of favoring the fatty acids only.

Table 7-9. The disappearance of diesel in different media

| days | REE/2-D 50/50 | 2-D in blend | 2-D alone |
|------|------------------|--------------|-----------|
| 1 | 63.62 | 62.80 | 26.99 |
| 2 | 95.55 | 95.55 | 46.87 |

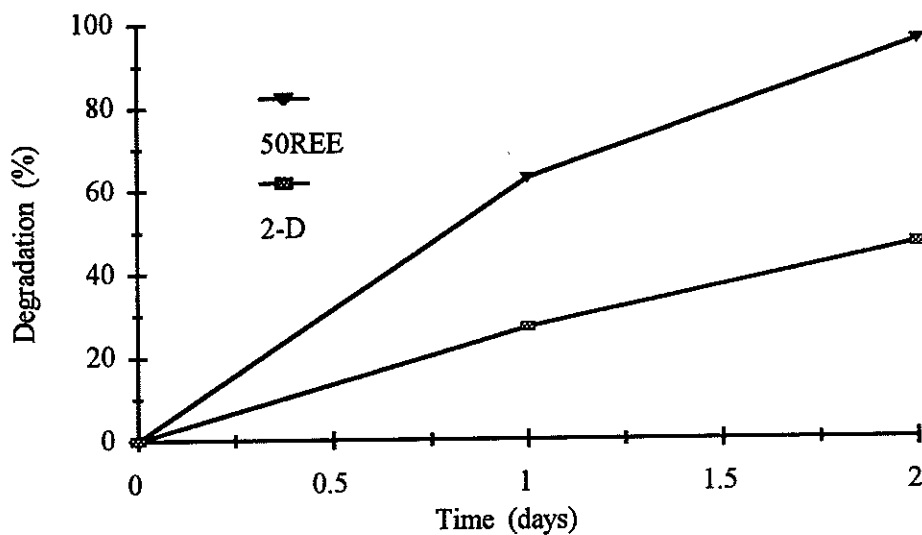


Figure 7-5. Degradation of 2-D in the 50%REE/50%2-D and 100% 2-D in 2 days with GC analysis.

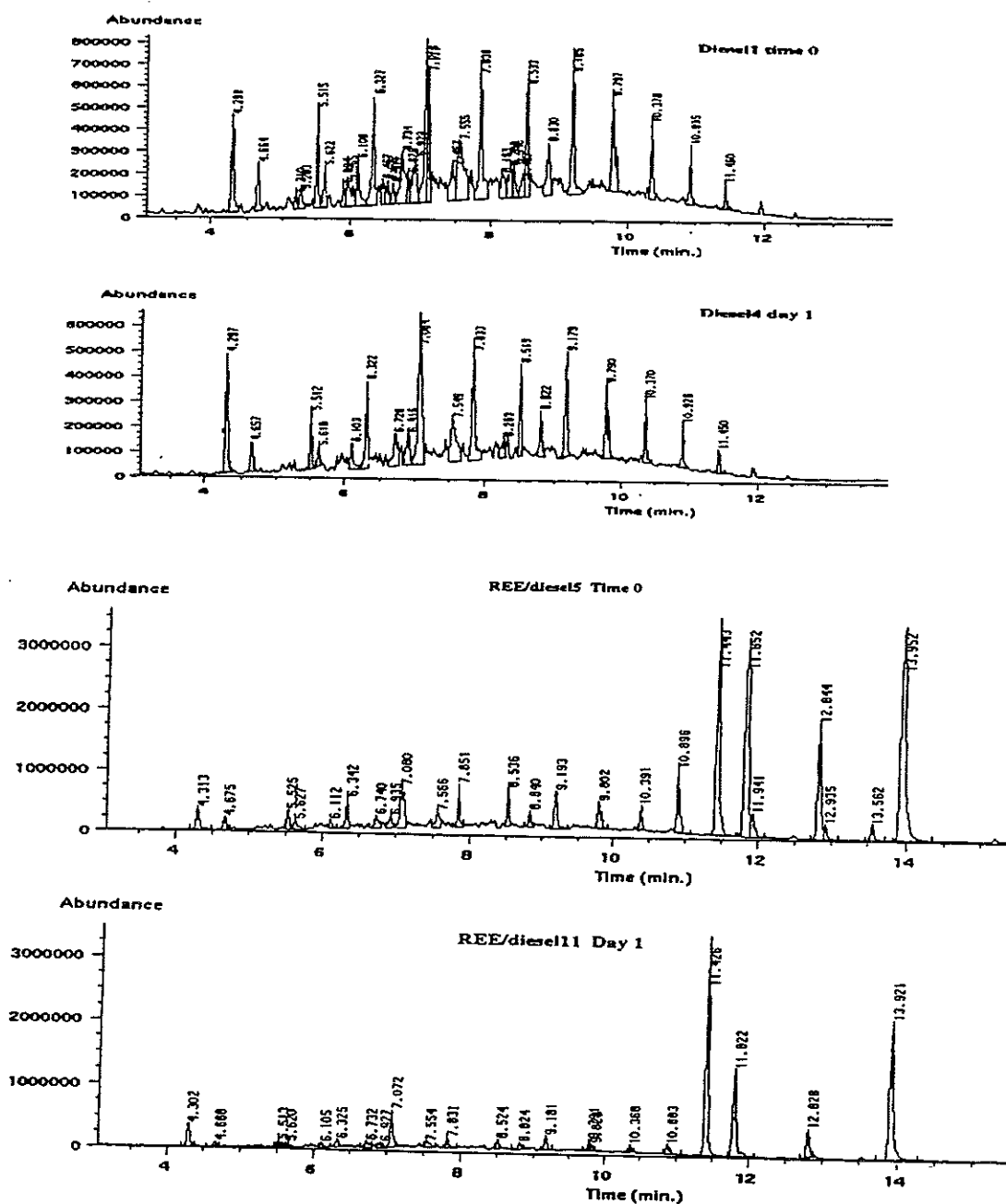


Figure 7-6. GC analysis of the disappearance of the diesel in two different media at time 0 and day 1. The top part is the case of diesel alone as the sole carbon source and shows almost no difference in the area counts between time 0 and day 1. The bottom part demonstrates the significant change of the area counts of the REE/diesel blend (50/50) between time 0 and day 1. The larger peaks on the right are REE's. In both cases, the concentration of the diesel is 10 mg/L or 10 ppm.

Biodegradation rates of biodiesel (System III)

The mineralization rates (q_M) for REE determined by the CO_2 evolution versus REE concentrations is shown in Fig. 7-7. When the REE concentration is below 180 mg L^{-1} , the rates increase with an increase in REE concentrations linearly ($R^2 = 0.95$). However, when REE concentration is greater than 200 mg L^{-1} , the q_M s stay almost constant. The maximum mineralization rate for REE was approximately $25 \text{ mg L}^{-1} \text{ day}^{-1}$. The pattern of the CO_2 evolution rates of the diesel changing with the concentration was almost the same as that of REE (Fig. 7-8), but the maximum mineralization rate for the diesel was about $12.5 \text{ mg L}^{-1} \text{ day}^{-1}$, half that of REE.

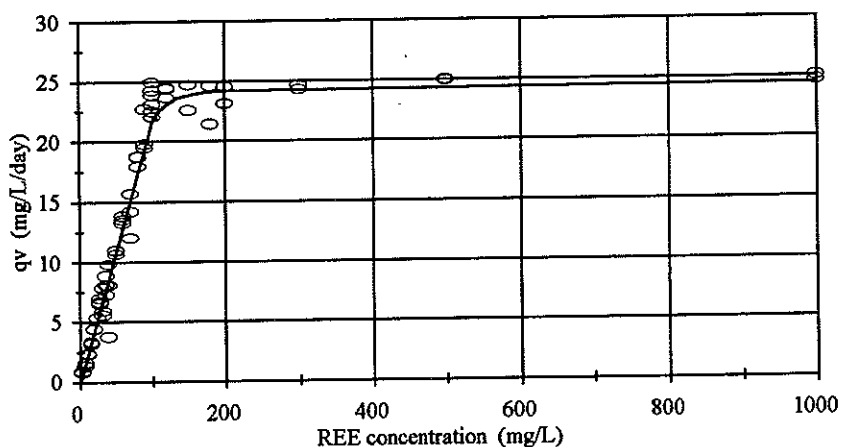


Figure 7-7. The dynamic response of mineralization rates of REE determined by CO_2 evolution to the increase of REE concentration (0-1000 mg/L).

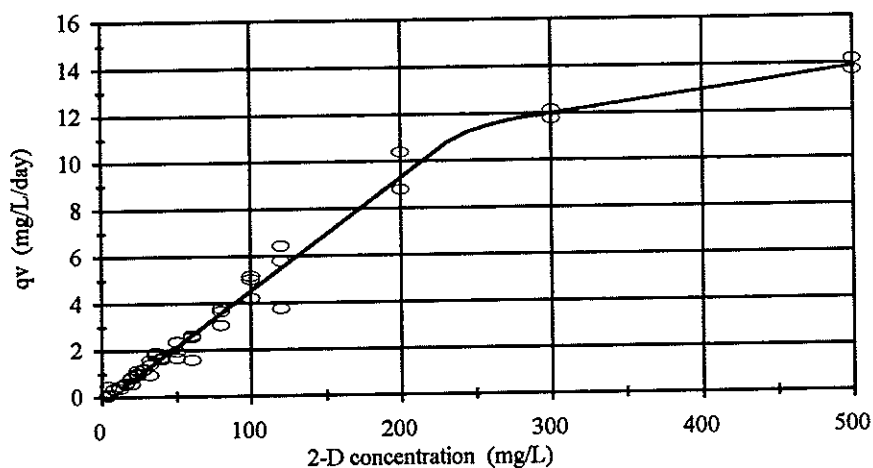


Figure 7-8. The dynamic response of mineralization rates of 2-D diesel determined by CO_2 evolution to the increase of diesel concentration (0-500 mg/L).

REE disappearance with time and volumetric substrate removal rate, q_v , for each REE concentration are summarized in Table 7-10. The maximum degradation rate, q_{vmax} , for REE is about $160 \text{ mg L}^{-1} \text{ day}^{-1}$, which is 6.4 times higher than the maximum mineralization rate, q_{Mmax} ($= 25 \text{ mg L}^{-1} \text{ day}^{-1}$), obtained by CO_2 evolution. The q_v s plotted against REE concentrations is illustrated in Fig. 7-9.

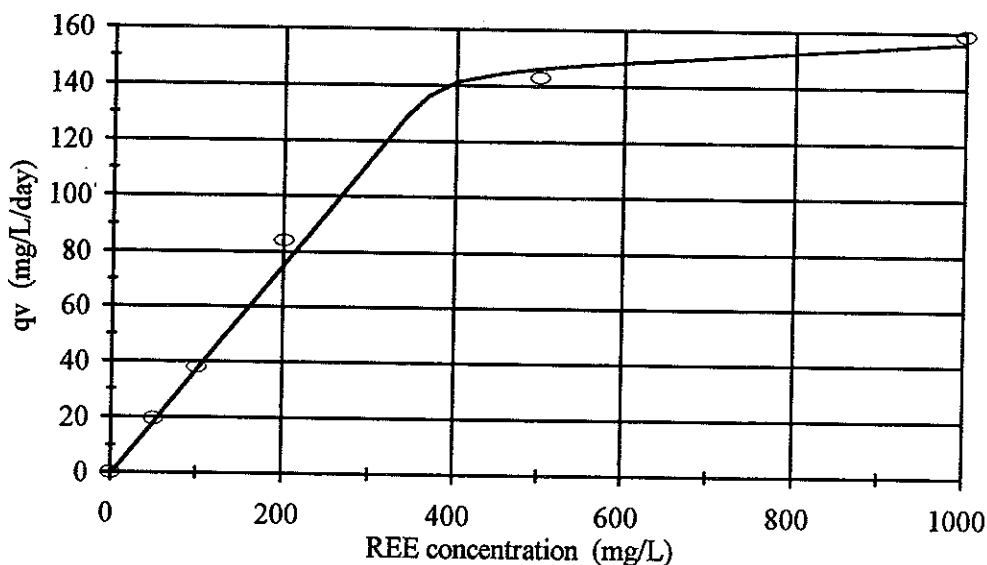


Figure 7-9. The dynamic response of biodegradation rates of REE determined by GC analysis to the increase of REE concentration (0-1000 mg/L)

Table 7-10. REE disappearance with time by GC analysis

| days | REE concentration (mg/L) | | | | |
|--------|--------------------------|-------|-------|--------|--------|
| | 50 | 100 | 200 | 500 | 1000 |
| 0 | | | | | |
| 2 | 10.58 | 23.45 | 31.54 | 213.78 | 682.02 |
| 5 | 0.09 | 2.62 | 13.55 | 153.36 | 598.80 |
| 14 | 0.00 | 0.87 | 3.23 | 18.76 | 400.00 |
| % deg. | 100.0 | 99.1 | 98.4 | 96.3 | 60.0 |
| q_v | 19.71 | 38.25 | 84.23 | 143.11 | 158.99 |

By comparing Fig. 7-6 and Fig. 7-9, one can see that both follow the same pattern.

Calibration

A comparison of percent REE degradation in 14 days by CO₂ evolution and in 5 days by the GC method (because both have different rates) is summarized in Table 7-11 and graphically shown in Figure 7-10. Apparently, they have the same trend. Their relation could be described by linear equation with a slope=1, %degradation = %CO₂ evolution + 11.0% (Fig 7-11). From a comparison calibration curve (Fig. 7-12), one can see that both maximum CO₂ evolution rate and substrate depletion rate happen within 5 days.

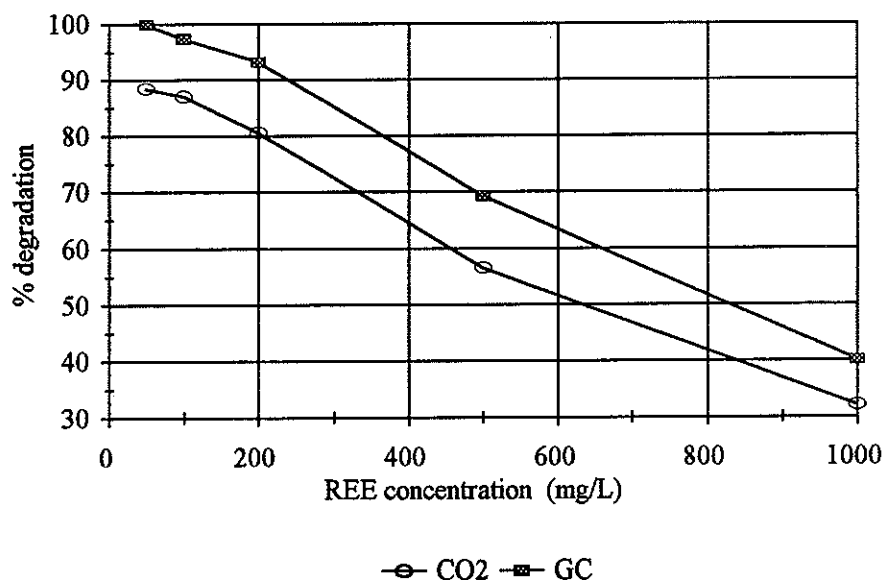


Figure 7-10. A comparison of percent degradation from CO₂ evolution in 14 days and GC analysis in 5 days when REE concentration = 100 mg/L⁻¹.

Table 7-11. A comparison of degradation

| Concentration (mg/L) | % Degradation | |
|-------------------------|------------------------------|----------------|
| | CO ₂ (in 14 days) | GC (in 5 days) |
| 50 | 88.54 | 99.83 |
| 100 | 87.11 | 97.38 |
| 200 | 80.59 | 93.22 |
| 500 | 56.66 | 69.33 |
| 1000 | 32.20 | 40.12 |

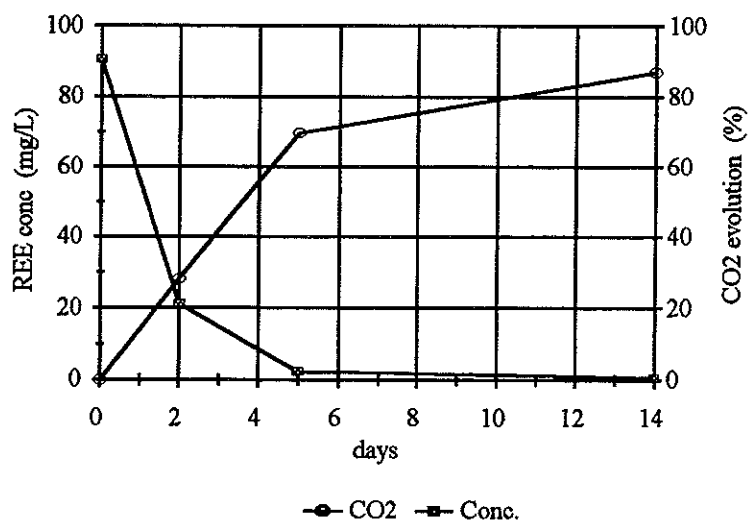


Figure 7-11. A comparison calibration (REE concentration = 100 mg/L⁻¹).

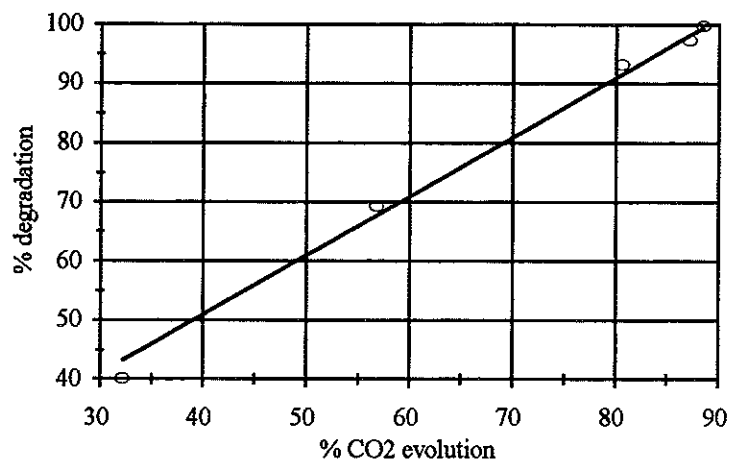


Figure 7-12. Calibration curve (REE concentration = 100 mg/L⁻¹).

DISCUSSION

The experiment shows that biodiesel degrades much faster degraded than diesel. There are several reasons explaining this. First, the rate of a catalyzed reaction is regulated by the amount of catalyzing enzymes that are present in the cell. In other words, for a biochemical process to occur rapidly, appropriate enzymes must be available. Biodiesel is a natural product consisting of pure fatty acids, the enzymes responsible for their breakdown also naturally exist. All the fatty acids are even hydrocarbon chains in ester form with two oxygen atoms attached which makes them very biologically active. The enzymes such as Acetyl-CoA dehydrogenase can recognize and attack them immediately. In the process of degradation, fatty acids are oxidized at the carbon (hence oxidation) and degraded to acetic acid and a fatty acid with two fewer carbons (Zubay, 1993). On the other hand, diesel consists of a large amount of alkane and alkene (hydrocarbon chains from C:10-C:20) without oxygen attached, therefore, they are not biologically active. The natural enzymes may not recognize them. However, bacteria have very strong adaptability. They can either produce new enzymes or mutate the original genes of enzymes to adapt new products, especially during times of starvation. According to Pavel Pitter (Pitter and Chudoba, 1990), initial-oxidation of the terminal CH_3 group to the carboxylic group is the main metabolic pathway during the biochemical oxidation of alkanes (monoterminal oxidation). This is followed by-oxidation of the aliphatic chain. Finally, the composition of diesel is much more chemically complicated than biodiesel. Except for alkanes and alkenes, it also contains aliphatic cyclic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and alkylbenzenes, as well as their derivatives such as toluene, xylenes, PCBs (phenyl and biphenyls), and so on. Alkylbenzenes are toxic to microorganisms. Benzene itself is very stable, and therefore, needs more energy for microorganisms to open the ring (Cole, 1993).

Another theoretical question to address is why mineralization rates determined by CO_2 evolution method is much slower and lower than the degradation determined by the GC analysis. There are at least three reasons that account for this. First of all, microbial breakdown of fatty acids to CO_2 and H_2O is a complex process and consists of a series of reactions. It begins in the cytosol and completes in the mitochondrion and involves totally different enzymes located in different places within the cell. At the first stage of metabolism, substrates are transported across the plasma membrane of a cell by specific enzymes. At the second stage, they are transported again into the mitochondrion where degradation of fatty acids occurs by oxidation with two carbon atoms less in each degradation cycle. Apparently, it takes some time for cells to digest 16-22 carbon chains. The GC method detects only the results of the first stage (substrate disappearance) while the CO_2 method examines the latter one (digestion). Secondly, a portion of the carbons from the substrates will be assembled into cell structure instead of being converted to CO_2 . Higher substrate concentrations, more significant cell growth, more carbon incorporated into cells, and therefore, less CO_2 detected. Thirdly, it is possible that some fatty acids are broken down to intermediates accumulated in the media so that there are no fatty acids detected by GC but degradation of these intermediates continues by the microorganisms. Hejalar and Chudoba (1986) found that

organic substances excreted by activated sludge microorganisms into the cultivation medium can be both end products and intermediates. Whereas intermediates are readily re-assimilated during the growth of a mixed culture. Why are intermediates accumulated? According to Dawes (Hejzlar and Chudoba, 1986), some bacteria, e.g. *Pseudomonas aeruginosa*, can metabolize glucose in two ways. At low concentrations glucose is completely oxidized inside the cells whereas at high concentrations it blocks itself from this method and it is instead oxidized via the extracellular pathway (by periplasmatic enzymes) to gluconic acid which released from the cells.

It was noticed from the results of System I that neat rapeseed oil and soybean oil have slightly lower percent degradation. Their higher viscosity may limit their solubility, therefore, limit their biodegradability.

PART II

Biodegradability with HySEE

HySEE, one of the prospective biodiesel fuels, is made from waste hydrogenated soybean oil recovered from a potato processing plant. This report tested the biodegradability of HySEE and HySEE/diesel blends in the aquatic environment and compared them with that of REE and diesel by the CO₂ evolution method (EPA, 1982).

Test substrates

The test substrates included: HySEE, HySEE/diesel blends (v/v) 80/20 and 20/80, Rapeseed Ethyl Ester (REE), 2-D, and dextrose as a reference. The composition and specific properties of HySEE, REE, and 2-D are listed in Table 7-12.

Table 7-12. Fuel Properties and fatty acid composition.

| | REE | HySEE | 2-D |
|----------------------------------|------------|--------------|------------|
| Fuel Properties | | | |
| Specific gravity, 60/60 | 0.876 | 0.872 | 0.8495 |
| Viscosity, cSt @ 40°C | 6.1 | 5.78 | 2.98 |
| Heat of Combustion, net, MJ/kg | 38.0 | 37.19 | 42.90 |
| Carbon, wt% | 76.83 | 77.72 | 86.67 |
| Hydrogen, wt% | 11.8 | 12.34 | 12.98 |
| Oxygen, wt% | 11.36 | 9.92 | 0.0 |
| Flash Point, °C | 338 | 345 | 165 |
| Fatty Acid Composition, % | | | |
| Palmitic (16:0) | 2.6 | 10.3 | |
| Stearic (18:0) | 0.9 | 15.0 | |
| Oleic (18:1) | 12.8 | 24.6 | |
| Linoleic (18:2) | 11.9 | 48.6 | |
| Linolenic (18:3) | 7.7 | 0.0 | |
| Eicosenoic (20:1) | 7.3 | 0.3 | |
| Erucic (22:1) | 49.5 | 0.0 | |

Quality control

Duplicate experiments were conducted and in each experiment triplicate flasks were set up for each substrate.

RESULTS AND CONCLUSION

The percent accumulated CO₂ evolution from all the substrates in 28 days is summarized in Table 7-13 and graphically shown in Figure 7-13 (the six samples for each substrate in two experiments were averaged and an arithmetic mean, standard deviation, and RSD% was calculated). The maximum percentage of CO₂ evolution from HySEE was 89.5%, almost the same as REE and dextrose, 91.9% and 89.81%, respectively. Whereas the CO₂ evolution from diesel was only 28.7%. Therefore, by EPA definition, HySEE is a “readily biodegradable” compound in the aquatic environment.

The percent CO₂ evolution from HySEE/diesel mixtures increased with the increase of HySEE concentration in the blend, 77.62% vs. 42.5% for HySEE80/diesel20 and HySEE20/diesel80, respectively.

Table 7-13. Percentage of CO₂ evolution from the substrates in 28 days

| Day | Average CO ₂ evolution | | | | | |
|-----|-----------------------------------|--------|---------|---------|--------|--------|
| | REE | HySEE | H80/D20 | H20/D80 | Diesel | Dex. |
| 0 | 0% | 0% | 0.00% | 0% | 0% | 0% |
| 2 | 33.64% | 31.71% | 27.12% | 10.00% | 4.08% | 30.30% |
| 4 | 59.94% | 56.97% | 49.13% | 20.13% | 10.53% | 57.05% |
| 7 | 76.56% | 73.43% | 63.93% | 29.09% | 17.70% | 78.27% |
| 10 | 82.18% | 80.13% | 69.07% | 32.99% | 21.17% | 84.60% |
| 14 | 86.62% | 84.48% | 71.91% | 36.12% | 23.64% | 87.89% |
| 28 | 91.90% | 89.47% | 77.62% | 42.47% | 28.68% | 89.81% |

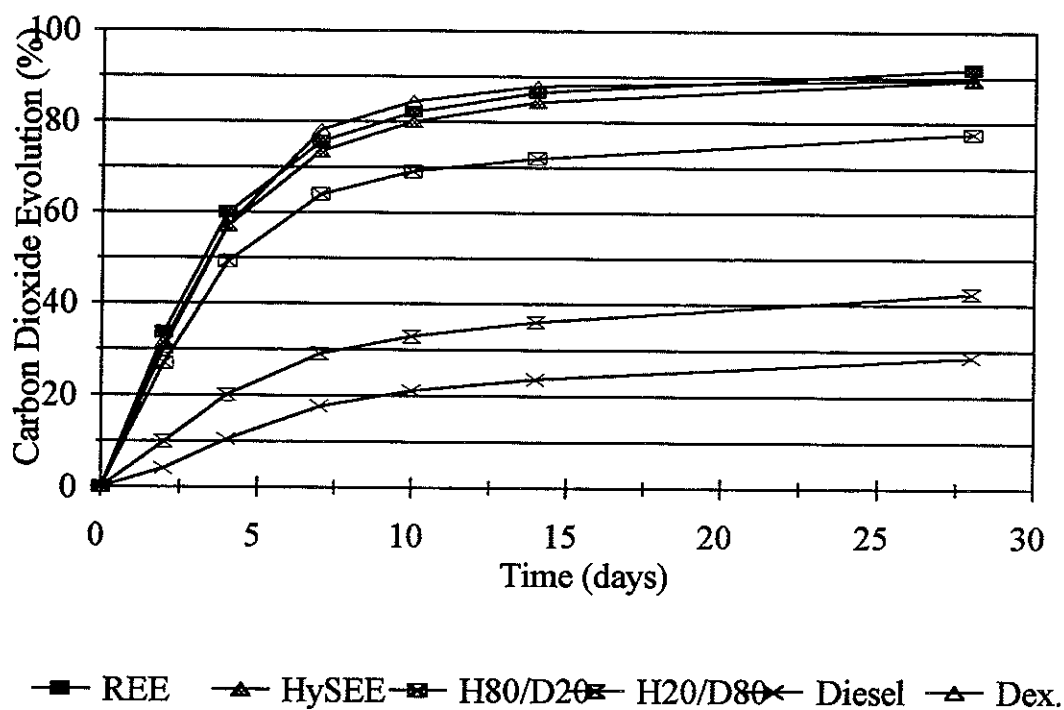


Figure 7-13. 28 day percent accumulated carbon dioxide evolution,

CONCLUSIONS

1. All the biodiesel fuels are "readily biodegradable" compounds according to EPA standard (EPA, 1982) and have a relatively high biodegradation rate in the aquatic environment. The maximum mineralization rate for REE determined by CO₂ evolution is 25 mg L⁻¹ day⁻¹, while the diesel is 12.5 mg L⁻¹ day⁻¹, only half of REE's. The maximum volumetric substrate removal rate for REE obtained from GC analysis is about 160 mg L⁻¹ day⁻¹.
2. Biodiesel can promote and speed up the biodegradation of diesel. The more biodiesel present in a biodiesel/diesel mixture, the faster the degradation rate. The biodegradation pattern in a biodiesel/diesel mixture is that microorganism metabolize both biodiesel and diesel at the same time and at almost the same rates.
3. The mineralization rate for a compound determined from CO₂ evolution is much slower than its primary degradation rate from GC. However, the results from CO₂ evolution method have good correlation with that from GC analysis. It is therefore possible to use the CO₂ evolution method to estimate the biodegradation rate for an organic compound and it is economical and environmentally safe.

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ACUTE TOXICITY OF BIODIESEL TO FRESHWATER AND MARINE ORGANISMS

This report is on static tests with rapeseed methyl ester (RME), rapeseed ethyl ester (REE), and used hydrogenated soybean cooking oil (HySEE) performed according to EPA/600/4-90/027. The acute aquatic toxicity tests with RME and REE were conducted with both rainbow trout and daphnia magna by CH2M Hill in Corvallis, Oregon under contract to the University of Idaho. HySEE tests were conducted by the University of Idaho Analytical Sciences Laboratory with rainbow trout.

LITERATURE REVIEW

Cheng et al. (1991) compared hydraulic oils of mineral oil, vegetable oil, polyglycol, and a synthetic ester for biodegradability, toxicity, and fluid performance parameters. They used an oil-water dispersion procedure by the Ministry of Agriculture, Fisheries and Food, England, and provided mechanical agitation to continually disperse the test materials as small droplets in the water column. This procedure simulates physical dispersion by wave and current action. Rainbow trout were exposed to five concentrations of each test material and a control. Toxicity was expressed as the concentration of material in ppm to kill 50% of the fish after 96 hours of exposure (LC50). They reported that the base stocks for the vegetable oil formulations were nontoxic (> 1000 ppm) but the formulated products did not meet this criteria because of one or more of the additives. The LC50 with rainbow trout for mineral oil was 389 ppm; vegetable oil, 633 ppm; polyglycol, 80 ppm; and synthetic ester, > 5000 ppm.

Lockhart et al. (1984) studied rainbow trout in forty-eight hour-LC50 (acute lethal toxicity) tests exposed to water-soluble fractions (WSF) for a range of crude and refined oils. The results were compared to the concentrations of volatile very low-boiling ($<115^{\circ}\text{C}$) and low-boiling ($115\text{-}270^{\circ}\text{C}$) hydrocarbons determined by a two-stage analytical method. The results suggest that toxicity of the water-soluble fractions is associated largely with the substituted benzenes and naphthalenes, with boiling points between 115 and 270°C .

Lockhart et al. (1984) found that the LC50 values were highly dependent on the particular exposure conditions. Thus, survival of rainbow trout and their LC50 values were consistently higher in test containers that were open to the atmosphere than in sealed closed containers. Aeration of test containers, by bubbling air through the WSF, virtually eliminated toxicity to the trout in even the most toxic test preparations. The results were discussed in terms of the design of bioassays relevant to ice-covered environments and to other situations where volatilization may be low or reduced.

Weber, C.I. (1993) documents the EPA methods for acute toxicity of effluents and receiving waters to freshwater and marine organisms for the use in the National Pollutant Discharge Elimination System Permits Program. Summaries of the test conditions for the daphnids, daphnia magna, fathead minnows, rainbow trout, brook trout, the mysid,

sheepshead minnows, and silversides are given. Three test types are given: static non-renewal, static renewal, and flow-through. Test duration may vary from 24 to 96 hours depending on the objective of the test. The tests are designed to provide dose-response information, expressed as the percent effluent concentration that is lethal to 50 percent of the test organisms (LC50) within the prescribed period of time (24-96 hours), or the highest effluent concentration in which survival is not statistically different from the control.

Nearly identical procedures are outlined in 40 CFR part 797.1300 (Daphnid acute toxicity test) and part 797.1400 (fish acute toxicity test), and ASTM E 729-88. These procedures include, with the LC50 (median lethal concentration), an EC50 (median effective concentration), and an IC50 (inhibition concentration).

PART I - REE AND RME MATERIALS AND METHODS

Toxicity Tests

The University of Idaho Department of Agricultural Engineering contracted with CH2M Hill in Corvallis, Oregon to conduct two static definitive bioassays. The first bioassay was a 48-hour bioassay using the water flea, daphnia magna. A 96-hour bioassay using rainbow trout was conducted for the second study. Two rounds of tests were conducted for this study. All tests were performed according to: Methods for Measuring the Acute Aquatic Toxicity of Effluents to Freshwater and Marine Organisms EPA600/4-90/027F.

Fuels

Fuel nomenclature is as follows: (1) Phillips 2-D low-sulfur diesel control fuel (2-D); (2) 100 percent rapeseed methyl ester (RME); (3) 100 percent rapeseed ethyl ester (REE); (4) 50 percent RME - 50 percent 2-D (50RME); (5) 50 percent REE - 50 percent 2-D (50REE); (6) 20 percent RME - 80 percent 2-D (20RME); 20 percent REE - 80 percent 2-D (20REE); and 100 percent soybean methyl ester (SME).

Test quantities of each Biodiesel fuel tested were supplied by the University of Idaho. The rapeseed oil was expelled at the University of Idaho's Agricultural Engineering farm scale process facility. The RME, REE, and SME fuels were produced using the process developed by University of Idaho researchers. Phillips 66 Company 0.05 low sulfur diesel fuel was used as the baseline for the Biodiesel fuels.

Test Methods

All static tests were performed according to: Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms, Weber C., et al. (1991); EPA/600/4-90/027.

Test Organisms

Daphnia Magna

The daphnia magna were obtained from CH2M Hill's in house cultures and were less than 24 hours old prior to initiation of the test. All organisms tested were fed and maintained during culturing, acclimation, and testing as prescribed by EPA (1989). The test organisms appeared vigorous and in good condition prior to testing. The daphnia magna were placed below the test surface at test initiation due to the non-soluble nature of the sample.

Rainbow Trout

The rainbow trout used in the first round of tests were obtained from Thomas Fish Company, Anderson, California, and were 22 days old and 32 ± 2 mm in length. The rainbow trout were acclimated to test conditions (dilution water and temperature) for 10 days prior to test initiation. The rainbow trout used in the second round of tests were obtained from Spring Creek Trout Hatchery, Lewiston, Montana, and were 24 days old and 28 ± 1 mm in length. The rainbow trout were acclimated to test conditions (dilution water and temperature) for 12 days prior to test initiation. All the test organisms appeared vigorous and in good condition prior to testing.

Dilution Water

Daphnia Magna

The water used for acclimation and dilution during the static testing was reconstituted moderately hard water with a total hardness of 98 as CaCO_3 , alkalinity of 64 mg/l as CaCO_3 , and a pH of 8.0 to 8.2.

Rainbow Trout

The water used for acclimation and dilution during the rainbow trout static testing was reconstituted moderately hard water with a total hardness of 92-98 as CaCO_3 , alkalinity of 70-74 mg/l as CaCO_3 , and a pH of 7.9 to 8.0.

Test Concentrations

Daphnia Magna

The concentrations tested in definitive test on REE were 33, 167, 833, 4170, and 20800 ppm of sample and dilution water for the control. The concentrations tested in the definitive test on RME were 67, 333, 1330, 6670, and 26700 ppm of sample and dilution water for the control. The concentrations tested in the definitive test on 2-D were 6.67, 13.3, 33.3, 66.7, and 1333 ppm of sample and dilution water for control. The concentrations tested in the definitive test on Methyl Soyate were 13.3, 33.3, 66.7, and 6667 ppm of sample and dilution water for control. The fuel mixture concentrations were run in quadruplicate with five organisms per replicate. Additional concentrations of 1.43 and 3.33 ppm were set up for 2-D with 10 organisms in on chamber. The fuel was stirred into the water before the daphnia magna were introduced into the chamber. There was a sheen of fuel on the top of each chamber.

Rainbow Trout

The concentrations tested for round 1 in the definitive test on 2-D, 20RME, and REE were 100, 300, 600, 1200, and 2400 ppm with dilution water for control. The concentrations tested for round 2 in the definitive test on RME and 50REE were 100, 500, 750, 1000, and 7500 ppm and the 50RME sample was tested at 100, 500, 600, and 7500 ppm due to a shortage of the sample.

The rainbow trout bioassays were run in 5-gallon glass aquaria, with a volume of 5 liters. The samples were run in duplicate with 10 organisms per replicate. The photo period was 16 hours light 8 hours dark. The temperature range was $12 \pm 1^\circ\text{C}$. Loading of test organisms was 0.53g wet fish weight per liter in round one, and 0.26g wet fish per liter in round two. Mortality was measured by lack of response to tactile stimulation and lack of respiratory movement. The fuel was stirred into the water before the *Daphnia Magna* were introduced into the chamber. There was a sheen of fuel on the top of each chamber.

Monitoring of Bioassays

The static tests were monitored at test initiation for pH, hardness, alkalinity, conductivity, and dissolved oxygen, and every 24 hours thereafter for mortality and at test termination for pH, conductivity, and dissolved oxygen. Temperature was monitored continuously throughout the test periods. The response measured for the *Daphnia Magna* was mortality over the 48-hour exposure period. The median lethal response (LC50) was calculate using Toxis version 2.2.

RESULTS

Daphnia Magna

The raw data is summarized in Table 8-1 below for 100 percent REE. Some of the mortality seen in the tests may have been caused by the physical nature of the test substances. The raw data sheets noted when the *Daphnia Magna* were trapped on the oil sheen at the surface of the test containers. The LC50 for the REE sample was 99 ppm. Table 8-2 summarizes the results of the RME sample with a reported LD50 of 23 ppm.

Table 8-1. REE daphnia magna results.

| Concentration (ppm) | 24 hr | 48 hr |
|---------------------|-------|-------|
| Control | 100 | 100 |
| 33 | 80 | 65 |
| 167 | 70 | 40 |
| 833 | 65 | 30 |
| 4170 | 65 | 25 |
| 20880 | 50 | 20 |

Table 8-2. RME daphnia magna results.

| Concentration (ppm) | 24 hr | 48 hr |
|---------------------|-------|-------|
| Control | 100 | 100 |
| 67 | 90 | 40 |
| 333 | 95 | 40 |
| 1330 | 60 | 20 |
| 6670 | 35 | 5 |
| 26700 | 30 | 30 |

Table 8-3 summarizes the results of the 2-D sample tested with a reported LC50 of less than 1.43 ppm. Table 8-4 summarizes the results of the Methyl Soyate with a reported LC50 of 332 ppm.

Table 8-3. 2-D daphnia magna results.

| Concentration (ppm) | 24 hr | 48 hr |
|---------------------|-------|-------|
| Control | 100 | 100 |
| 1.43 | 30 | 0 |
| 3.33 | 0 | 0 |
| 6.67 | 10 | 0 |
| 13.3 | 10 | 0 |
| 33.3 | 0 | 0 |
| 66.7 | 0 | 0 |
| 1333 | 0 | 0 |

Table 8-4. Daphnia magna results with Methyl Soyate.

| Concentration (ppm) | 24 hr | 48 hr |
|---------------------|-------|-------|
| Control | 100 | 100 |
| 13.3 | 90 | 85 |
| 33.3 | 95 | 80 |
| 66.7 | 85 | 75 |
| 667 | 80 | 45 |
| 6667 | 45 | 10 |

The methyl and ethyl esters are not water soluble and form a sheen on the water surface. This sheen could be easily skimmed off, but the Daphnia Magna got captured in this sheen. Fifty percent of the Daphnia Magna in common table salt had died at a concentration of 3.7 parts per million (ppm). With diesel, 50 percent of them had died at less than 1.43 ppm and CH2M Hill reported all were dead at this concentration. When this test was first completed, CH2M Hill reported that the LC50 for diesel fuel was less than 6 ppm because all the Daphnia Magna had died. They were asked to test lower concentrations. They tested four more concentrations less than 6 ppm and the diesel fuel still killed all the Daphnia Magna. For the RME the LC50 was 23 ppm, and at 26,700 ppm 30 percent of them were still alive. With REE the LC50 was 99 ppm and 20 percent were still alive at 20,800 ppm. With methyl soyate the LC50 was 332 ppm; however, only 45 percent were alive at 667 ppm. This difference between rapeseed esters and SME may be due to the high Erucic acid content of the rapeseed. If one takes the worst case, the 23 ppm for REE, and compare it of the 1.4 ppm for diesel fuel, the acute aquatic toxicity is 15 times less. What is even more significant is the 20 percent and 30 percent that are still alive at very high concentrations of Biodiesel.

Rainbow Trout

The raw data is summarized in Tables 8-5 to 8-10 below for 100 percent 2-D. The LC50 for 2-D was not determined. This data compares cadmium chloride (CdCl), diesel fuel, and methyl and ethyl esters of rapeseed.

Table 8-5. Rainbow trout results with 2-D.

| Concentration (ppm) | 0 hr | 24 hr | 48 hr | 72 hr | 96 hr |
|---------------------|------|-------|-------|-------|-------|
| Control | 100 | 100 | 100 | 100 | 100 |
| 100 | 100 | 100 | 95 | 95 | 90 |
| 300 | 100 | 100 | 100 | 100 | 100 |
| 600 | 100 | 100 | 100 | 100 | 100 |
| 1200 | 100 | 100 | 100 | 95 | 85 |
| 2400 | 100 | 100 | 100 | 95 | 80 |

Table 8-6. Rainbow trout results with 20%RME - 80%2-D.

| Concentration (ppm) | 0 hr | 24 hr | 48 hr | 72 hr | 96 hr |
|---------------------|------|-------|-------|-------|-------|
| Control | 100 | 100 | 100 | 100 | 100 |
| 100 | 100 | 100 | 100 | 100 | 100 |
| 300 | 100 | 100 | 100 | 100 | 100 |
| 600 | 100 | 95 | 95 | 95 | 95 |
| 1200 | 100 | 100 | 100 | 100 | 85 |
| 2400 | 100 | 100 | 100 | 100 | 95 |

Table 8-7. Rainbow trout results with 20%REE - 80%2-D.

| Concentration (ppm) | 0 hr | 24 hr | 48 hr | 72 hr | 96 hr |
|---------------------|------|-------|-------|-------|-------|
| Control | 100 | 100 | 100 | 100 | 100 |
| 100 | 100 | 100 | 100 | 95 | 95 |
| 300 | 100 | 100 | 100 | 100 | 100 |
| 600 | 100 | 100 | 100 | 100 | 100 |
| 1200 | 100 | 100 | 95 | 95 | 95 |
| 2400 | 100 | 100 | 95 | 95 | 90 |

Table 8-8. Rainbow trout results with 100% REE.

| Concentration (ppm) | 0 hr | 24 hr | 48 hr | 72 hr | 96 hr |
|---------------------|------|-------|-------|-------|-------|
| Control | 100 | 100 | 100 | 100 | 100 |
| 100 | 100 | 100 | 100 | 95 | 95 |
| 300 | 100 | 100 | 100 | 100 | 100 |
| 600 | 100 | 100 | 100 | 100 | 100 |
| 1200 | 100 | 100 | 100 | 100 | 100 |
| 2400 | 100 | 100 | 100 | 100 | 95 |

Table 8-9. Rainbow trout results with 100% RME.

| Concentration (ppm) | 0 hr | 24 hr | 48 hr | 72 hr | 96 hr |
|---------------------|------|-------|-------|-------|-------|
| Control | 100 | 100 | 100 | 100 | 100 |
| 100 | 100 | 100 | 100 | 100 | 100 |
| 500 | 100 | 100 | 100 | 100 | 100 |
| 600 | 100 | 100 | 100 | 100 | 100 |
| 1000 | 100 | 100 | 100 | 100 | 100 |
| 7500 | 100 | 100 | 100 | 100 | 100 |

The 50RME percent survival summary results were identical to the 100% RME results.

Table 8-10. Rainbow trout results with 50%REE - 50%2-D.

| Concentration (ppm) | 0 hr | 24 hr | 48 hr | 72 hr | 96 hr |
|---------------------|------|-------|-------|-------|-------|
| Control | 100 | 100 | 100 | 100 | 100 |
| 100 | 100 | 100 | 100 | 100 | 100 |
| 500 | 100 | 100 | 100 | 100 | 100 |
| 600 | 100 | 100 | 100 | 100 | 100 |
| 1000 | 100 | 100 | 100 | 100 | 100 |
| 7500 | 100 | 100 | 100 | 100 | 95 |

The 48-hour LC50 value and Control Chart limits for the reference toxicant (cadmium chloride) was at a concentration of $2.8\mu\text{g/l}$ for the round one rainbow trout and $4.6\mu\text{g/l}$ for the round two trout. The results indicate that the test organisms were within their expected sensitivity range. Comments included in round one test data at 24-hours was a general behavior of twitching and they were swimming on their sides and skittering; at 48-hours their condition was the same as at 24-hours. The trout in the 20REE containers at 100 and 300 ppm were swimming vertically, at 600 ppm the trout were on their sides at the bottom, and at 2400 ppm they were barely moving at the bottom of the tank. The trout in the REE containers were not as active as in the other three test substances. The end condition of survivors was reported as being poor. The only comment in round two was at 48-hours that the fish were dark and swimming vertical at concentrations as low as 500 ppm in the 50RME and 50REE with the end condition of survivors as being poor.

PART II - HySEE

The University of Idaho Analytical Sciences Laboratory in cooperation with the University of Idaho Jim Martin Biological and agricultural Engineering Laboratory studied the Acute Aquatic Toxicity of hydrogenated soybean oil ethyl ester (HySEE); biodiesel mixtures of 80% 2-D / 20% HySEE and 20% 1-D / 80% HySEE; and a reference substance of Phillips 2-D Reference Diesel. The study was performed following the EPA Good Laboratory Practice Standards as outlined in 40 CFR § 792. The test protocol merged the most

applicable portions of the Fish Acute Toxicity Test outlined in 40 CFR § 797.1400 of the TSCA regulations or the Rainbow Trout testing procedures outlined in Methods for Measuring the acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, EPA-600/4-90-027. Rainbow trout fry were exposed to the test substance in a static non-renewal environmental chamber subject to constant mixing, and duplicate test chambers.

MATERIAL AND METHODS

Test System:

Juvenile Rainbow Trout (15-40 day fry) used in the test system were certified disease free and obtained from Aquatic Research Organisms, Hampton, New Hampshire, and Spring Creek Trout Farm, Lewistown, Montana. The fry were exposed to the test and reference substances in a non-renewal static system utilizing duplicate test chambers for serial concentrations. A total of 480 fry were used in the project [4 substances x 6 concentrations (including 0 concentration control) x 20 fry per test substance concentration]. Fry were of normal size and appearance for their age. The longest was not more than twice the length of the shortest.

Individual impellers in each test chamber maintained the distribution of test/reference substance throughout the test chamber (Figure 8-1). The stirring action continued throughout the duration of the test. *Note: the insoluble nature of the test substances requires this extra mixing procedure to ensure a homogenous mixture of test substance and dilution water and allowed for testing at higher concentrations.* Test/reference substances were added to the environmental chambers at the appropriate concentrations and allowed to mix for 6 hours before addition of the fish. This allowed for a homogeneous solution of the test substance mixture.

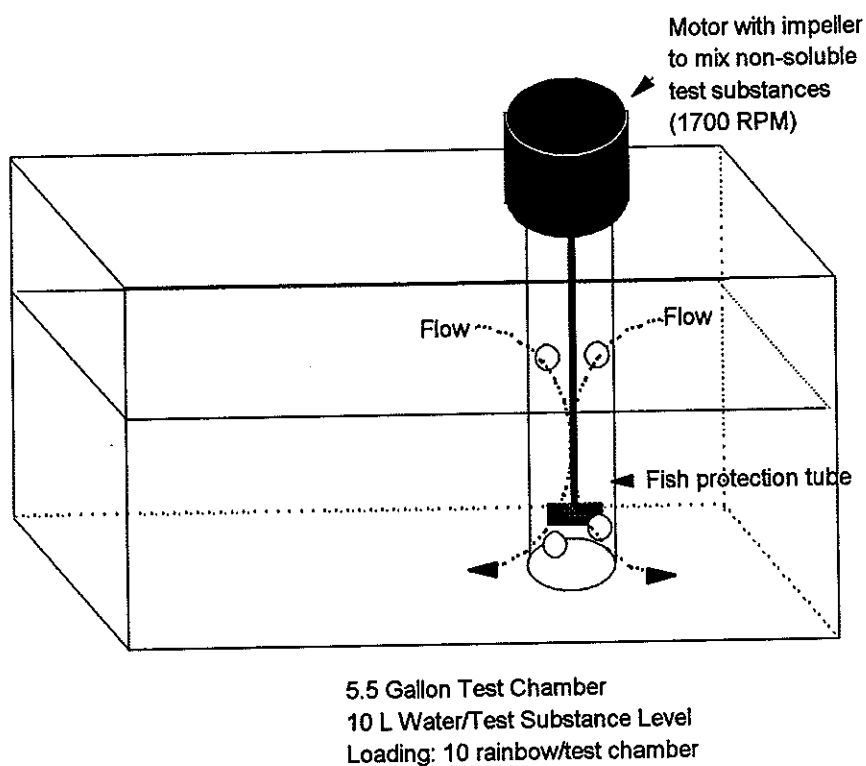


Figure 8-1. Static Environmental Test Chamber for Non-Soluble test Substances

Fry were not be fed during testing and were acclimated for a period of 48 hours in the same water used in the test.

Static Non-renewal Test

Test and reference substances were prepared at target concentrations as specified in Table 8-11. The test duration was 96 hours. Twenty fry per concentration, ten per test chamber in duplicate, were exposed to each concentration of each test substance. A random distribution of fry was made to ensure impartiality and eliminate test bias through distribution. Five concentrations of each test substance were used in a 50% proportional dilution series.

Duplicate control chambers, containing fry of the same population and the same dilution water used in the test without chemical, provided control. Petroleum industry standard practice and the stable nature of the test/reference substance eliminated the need for measurement of test chamber concentration.

The dissolved oxygen concentration, temperature, and pH were measured at the beginning (0h), 24h, 48h, 72h, and 96h. Temperature of the mixture in the system was maintained @ $12^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Dissolved oxygen concentrations remained above 6.0 mg/L, and no aeration was necessary. Photo periods of 16 hr. light and 8 hr. dark were controlled.

Death was the primary criterion used in this test. Each test and control chamber were checked for dead fish and observations recorded at 24h, 48h, 72h, and 96h. The tests

were unacceptable and repeated if more than 10 percent of the control organisms are immobilized during the 96 hour test.

Table 8-11. Dosage Level

| Test / Reference Substance | Conc. 1 (mg/L) | Conc. 2 (mg/L) | Conc. 3 (mg/L) | Conc. 4 (mg/L) | Conc. 5 (mg/L) |
|----------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| HySEE | 2000 | 1000 | 500 | 250 | 125 |
| 80% HySEE / 20% 1-D | 2000 | 1000 | 500 | 250 | 125 |
| 20% HySEE / 80% 2-D | 800 | 400 | 200 | 100 | 50 |
| 2-D | 800 | 400 | 200 | 100 | 50 |

The intent of the study reported herein was to produce data of the highest quality that meets or exceeds possible future requirements of the US Environmental Protection Agency under Section 4 of the Toxic Substances Control Act. Therefore, EPA TSCA GLP Standards as amended in 40 CFR § 792 were followed. The Quality Assurance Unit of the University of Idaho Analytical Sciences Laboratory inspected and reported findings of the following phases of US DOE/BPA Aquatic Toxicity of Biodiesel Fuels: Studies of the Acute Toxicity of HySEE Biodiesel Fuel Using *Oncorhynchus mykiss* (Rainbow Trout) in a Static Non-Renewal System on the corresponding dates: This report is an accurate reflection of the study completed.

Test Procedure

The definitive tests were performed to determine the concentration-response curves and the 24, 48, 72, and 96-hour LC₅₀ values whenever sufficient data exists. The fry were exposed to the test and reference substances in a non-renewal static system utilizing duplicate test chambers. A total of 480 fry were used in the project (4 substances x 6 concentrations x 20 fry per test substance concentration). All the fry originated from the same culture source. The fry were of normal size and appearance for their age and the longest was not more than twice the length of the shortest. The fry were held at the test temperature at least 2 days prior to test initiation.

Twenty rainbow trout 15-40 days old (after yolk sac absorption to 40 days) were exposed to each of five concentrations of test/reference substance and a control for 96 hours. A random distribution of fry were made to ensure impartiality and eliminate test bias through distribution. The dissolved oxygen concentration, temperature, and pH was measured at the beginning (0h), 24h, 48h, 72h, and 96h. Temperature of the mixture in the system was maintained at 12°C ± 2°C. Dissolved oxygen concentrations were above 6.0 mg/L. Photo periods were controlled to 16 hours light and 8 hours dark.

Death was the primary criterion used in the tests. Each test and control chamber was checked for dead fish and observations recorded at 24h, 48h, 72h, and 96h. In addition to death, any abnormal behavior or appearance was reported. The test was unacceptable if more than 10 percent of the control organisms were immobilized during the 96 hour test. The fry were not fed during the 96 hour exposure period of the test.

Mortality data collected during the test were used to calculate a 96-hour LC_{50} . The 24-hour interval values were calculated when there was sufficient mortality data to determine such values. Concentration response curves and 24-hour interval and 96 hour LC_{50} values for immobility were determined with their 95 percent confidence limits. A goodness-of-fit measure was determined for the concentration-response curves.

RESULTS AND DISCUSSION

Twenty rainbow trout fry were exposed to each of five concentrations of test/reference substance and a control for 96 hour periods in a static non-renewal environments as outlined in EPA TSCA Environmental Effects Test Guidelines @ 40 CFR §797.1400 and the Rainbow Trout testing procedures and additional guidelines in EPA Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms Fourth Edition, (EPA/600 4-90-027). Mortality data was collected at 24, 48, 72, and 96 hours and LC_{50} results were calculated using EPA Probit Analysis Program.

The following pages present acute aquatic toxicity mortality data and LC_{50} values for the test and reference substances studied. Results for 100% HySEE and control group are presented in Table 8-12. Tables 8-13 and 8-14 summarize data for biodiesel mixtures of 80% HySEE / 20% 1-D and 20% HySEE / 80% 1-D, respectively. The summary for the 2-D reference substance static testing is presented in Table 8-15. Concentrations reported for static tests were as formulated. Test and reference substances are very stable compounds under test conditions, lacking volatility or degradative tendencies.

Test substances 100% HySEE and 80% HySEE / 20% 1-D were tested at concentrations as high as 2,000 mg/L. This is seen as the upper level of concentration that may be used in the test system, while maintaining the test substance in the aqueous phase by the constant mixing of the impeller. 24-hour LC_{50} values could not be computed for either of these two test substances due to lack of sufficient mortality at any concentration. 96-hour LC_{50} values are reported as >2,000 mg/L for 100% HySEE and 80% HySEE / 20% 1-D, though no fiducial limits could be calculated.

The biodiesel mixture 20% HySEE / 80% 2-D was tested at concentrations from 50 to 800 mg/L. An LC_{50} value of 281.9 mg/L is reported for 72 and 96 hours, with lack of heterogeneity. 100% 2-D reference fuel was tested at concentrations from 50 to 800 mg/L. An LC_{50} value of 242.7 mg/L is reported for 96 hours.

Table 8-12. Static acute aquatic toxicity summary for 100% HySEE.

| Concentration (mg/L) | Number Exposed | Percent Mortality (24 hr.) | Percent Mortality (48 hr.) | Percent Mortality (72 hr.) | Percent Mortality (96 hr.) |
|-------------------------|--------------------------|---|----------------------------------|---|----------------------------------|
| Control | 20 | 0 % | 0 % | 0 % | 0 % |
| 125 | 20 | 0 % | 5 % | 5 % | 10 % |
| 250 | 20 | 0 % | 0 % | 0 % | 0 % |
| 500 | 20 | 0 % | 0 % | 0 % | 5 % |
| 1000 | 20 | 5 % | 5 % | 10 % | 15 % |
| 2000 | 20 | 0 % | 10 % | 15 % | 20 % |
| Exposure Period | LC ₅₀ mg/L | Lower 95% Confidence Limit (mg/L) | | Upper 95% Confidence Limit (mg/L) | |
| 24-hour | - | - | - | - | - |
| 48-hour | >2,000 | - | - | - | - |
| 72-hour | >2,000 | - | - | - | - |
| 96-hour | >2,000 | - | - | - | - |

- Insufficient mortality to compute.

- Slope not significantly different from zero. Fiducial limits cannot be computed.

Table 8-13. Static acute aquatic toxicity summary for 80%HySEE/20%1-D.

| Concentration (mg/L) | Number Exposed | Percent Mortality (24 hr.) | Percent Mortality (48 hr.) | Percent Mortality (72 hr.) | Percent Mortality (96 hr.) |
|-------------------------|--------------------------|--------------------------------------|----------------------------------|--------------------------------------|----------------------------------|
| Control | 20 | 0 % | 0 % | 0 % | 0 % |
| 125 | 20 | 0 % | 0 % | 0 % | 5 % |
| 250 | 20 | 0 % | 0 % | 0 % | 5 % |
| 500 | 20 | 0 % | 0 % | 5 % | 5 % |
| 1000 | 20 | 0 % | 0 % | 0 % | 0 % |
| 2000 | 20 | 10 % | 10 % | 10 % | 15 % |
| Exposure Period | LC ₅₀ mg/L | Lower 95% Confidence Limit (mg/L) | | Upper 95% Confidence Limit (mg/L) | |
| 24-hour | - | - | - | - | - |
| 48-hour | - | - | - | - | - |
| 72-hour | - | - | - | - | - |
| 96-hour | >2,000 | - | - | - | - |

- Insufficient mortality to compute.

- Slope not significantly different from zero. Fiducial limits cannot be computed.

Table 8-14. Static acute aquatic toxicity summary for 20%HySEE/80%2-D.

| Concentration (mg/L) | Number Exposed | Percent Mortality (24 hr.) | Percent Mortality (48 hr.) | Percent Mortality (72 hr.) | Percent Mortality (96 hr.) |
|-------------------------|--------------------------|---|----------------------------------|---|----------------------------------|
| Control | 20 | 5 % | 5 % | 5 % | 5 % |
| 50 | 20 | 0 % | 0 % | 0 % | 0 % |
| 100 | 20 | 0 % | 0 % | 0 % | 0 % |
| 200 | 20 | 5 % | 10 % | 15 % | 15 % |
| 400 | 20 | 25 % | 70 % | 95 % | 95 % |
| 800 | 20 | 70 % | 90 % | 95 % | 95 % |
| Exposure Period | LC ₅₀ mg/L | Lower 95% Confidence Limit (mg/L) | | Upper 95% Confidence Limit (mg/L) | |
| 24-hour | 598.5 | 463.2 | | 838.3 | |
| 48-hour | 359.4 | 281.9 | | 446.3 | |
| 72-hour | 281.9 | — | | — | |
| 96-hour | 281.9 | — | | — | |

— Slope not significantly different from zero. Fiducial limits cannot be computed.

— Tabular Chi-square exceeds calculated Chi-square value for heterogeneity.

Table 8-15. Static Acute Aquatic Toxicity Summary for 100% 2-D Reference Fuel

| Concentration (mg/L) | Number Exposed | Percent Mortality (24 hr.) | Percent Mortality (48 hr.) | Percent Mortality (72 hr.) | Percent Mortality (96 hr.) |
|-------------------------|--------------------------|---|----------------------------------|---|----------------------------------|
| Control | 20 | 0 % | 0 % | 0 % | 0 % |
| 50 | 20 | 0 % | 0 % | 0 % | 0 % |
| 100 | 20 | 5 % | 5 % | 15 % | 15 % |
| 200 | 20 | 25 % | 25 % | 25 % | 30 % |
| 400 | 20 | 70 % | 75 % | 75 % | 75 % |
| 800 | 20 | 90 % | 95 % | 95 % | 100 % |
| Exposure Period | LC ₅₀ mg/L | Lower 95% Confidence Limit (mg/L) | | Upper 95% Confidence Limit (mg/L) | |
| 24-hour | 306.5 | 242.4 | | 392.8 | |
| 48-hour | 283.5 | 227.2 | | 355.6 | |
| 72-hour | 262.8 | 206.6 | | 337.4 | |
| 96-hour | 242.7 | 192.9 | | 306.5 | |

CONCLUSIONS

Part I

Biodiesel is not as toxic to *Daphnia Magna* as NaCl. When compared to the reference toxicant (sodium chloride) diesel fuel was 2.6 times more toxic, RME was 6.2 times less toxic, REE was 26 times less, and SME 89 times less toxic. When compared to number two diesel fuel RME is 16 times less toxic, REE is 69 times less toxic, and SME was 237 times less toxic. CH2M Hill has been asked to repeat the toxicity study with rainbow trout at the water accommodated fraction (WAF) and below to produce a LC50.

Part II

The insoluble and sticky nature of the test substances required modification of the conventional test apparatus to alleviate mortality occurring by accumulation of the substance at the surface. Tests were performed at relatively high concentrations (2,000 mg/L for 100% HySEE and 80% HySEE / 20% 1-D; and 800 mg/L for 20% HySEE / 80% 2-D and 100% 2-D) as compared to petroleum industry standards of testing at the water accommodated fraction. Even at these exaggerated concentrations, an LC₅₀ could not be computed for 100% HySEE or 80% HySEE / 20% 1-D due to insufficient mortality in the test organisms. The 96-hour LC₅₀ for these test substances is reported as >2,000 mg/L, with 2,000 mg/L concentrations effecting only 20% mortality. The addition of 20% 1-D in a biodiesel mixture appears to have had no effect of toxicity to the rainbow trout over the 100% HySEE. The authors feel a static non-renewal test at concentrations higher than 2,000 mg/L would exceed the limits of the test system.

The 100% 2-D reference substance yielded a 96-hour LC₅₀ that was slightly lower than the value for the 20% HySEE / 80% 2-D mixture, 242.7 and 281.9 mg/L, respectively. This slight difference may be explained as a lower concentration of diesel in the 20% HySEE / 80% 2-D mixture resulting in a less toxic test system than the 100% 2-D test system. Also, the solubility of the diesel may have been modified by the presence of HySEE. Diesel is aliphatic and aromatic, whereas HySEE is very non-polar. Therefore, the HySEE may exhibit low level micellar activity, possibly encasing some diesel molecules.

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TWO YEAR STORAGE STUDY WITH RME AND REE

This project was designed to determine the extent of deterioration of Rapeseed Methyl Ester (RME) and Rapeseed Ethyl Ester (REE) in storage. The study involved triplicate samples of RME and REE stored in both glass and steel containers at room temperature (inside) and at the local ambient outdoor temperatures (outside). The study was conducted for 24 months. At the beginning of the study and at 3 month intervals, samples were taken for measurement of peroxide value, acid value, density, viscosity, and heat of combustion. At the conclusion of the study, engine performance tests were conducted with the two year stored REE and RME, new REE and RME, and low sulfur diesel reference fuel.

LITERATURE REVIEW

Previous work on the storage stability of vegetable oil fuels includes a three year study reported by Klopfenstein and Walker (1984), Klopfenstein and Walker (1985), Klopfenstein and Walker (1986). In that study, samples of soybean methyl esters were stored in three different environments (indoor, outside and underground), two container types (steel and plastic) and two formulations (with and without antioxidants). Samples were analyzed initially and at four month intervals for: fatty acid composition, peroxide value, density and viscosity. Results favored underground storage, plastic-lined containers and the use of 0.5% butylated hydroxy toluene as an antioxidant.

A study performed at the University of Idaho by Korus (1983) and continued by Jo (1984) involved neat vegetable oils as fuels. Oil deterioration was measured as a function of storage conditions (aerobic and anaerobic at room temperatures) and vegetable oil composition (fatty acid saturation vs. unsaturation). Parameters measured at six month intervals over a two year period were peroxide values and fatty acid profiles. Engine testing was also performed using the stored oils to test injector coking as a function of fuel deterioration. Fuels tested were 50/50 blends of winter rapeseed, linoleic safflower and oleic safflower with diesel fuel and 100% 2-D as a reference. All vegetable oil fuel blends gave a statistically significant ($\alpha < 0.05$) increase in carbon deposits relative to diesel fuel with linoleic safflower having an injector coking area of 7.57 cm² relative to diesel fuel, 50% oleic safflower 5.01 cm² and 50% winter rapeseed 3.93 cm². Results indicated that deterioration was reduced by anaerobic storage and by high levels of saturated fatty acids in the oil.

OBJECTIVES

1. Produce batches of RME and REE and characterize their properties according to ASAE EP552.
2. Store triplicate sets of vented glass and steel containers of RME and REE in flammable solvent storage cabinets at both inside and outside ambient temperatures.

3. Analyze fuel properties (peroxide value, acid value, density, viscosity, and heat of combustion) from each storage container every 3 months for a 24 month period and compare with the initial values.
4. Compare two year stored RME and REE in short term engine performance tests with new RME and REE.

MATERIALS AND METHODS

Fuel Preparation

Thirty five gallons of each fuel (RME and REE) were made at the beginning of the study. Samples of each fuel were taken for triplicate determinations in all of the 5 test procedures at the beginning of this test and at each 3 month interval thereafter.

The Biodiesel fuels were processed in a batch type reactor. The methyl ester process utilized 100 percent molar excess alcohol (preferably absolute or 100 percent pure), or a molar ratio of 6:1 alcohol to oil ratio. Based on the amount of input oil by weight, 1.1 percent potassium hydroxide (KOH) was used. Table 9-1 shows the equations used for the quantities of methyl ester processed.

The ethyl ester process utilizes 70 percent stoichiometric excess ethanol (absolute, 100 percent pure), or a molar ratio of 5.1:1 ethanol to oil ratio. Based on the amount of input oil by weight, 1.3 percent of KOH was used. Table I also shows the equations used for quantities of ethyl esters processed.

Table 9-1. Equations for Processing Methyl and Ethyl Ester Fuels.

| Table 9-1. Equations for Processing Methyl and Ethyl Ester Fuels. | | |
|---|--|---------------------------------|
| Methyl Ester Process | | |
| | $\text{MeOH} = 0.225 \times \text{Oil}$ | $\text{KOH} = \text{Oil} / 100$ |
| where; | Oil = desired amount of oil in liters (L) MeOH = amount of methanol needed in L KOH = amount of potassium hydroxide (kg) | |
| Ethyl Ester Process | | |
| | $\text{EtOH} = 0.2738 \times \text{Oil}$ | $\text{KOH} = \text{Oil} / 85$ |
| where; | Oil = desired amount of oil in liters (L) EtOH = amount of ethanol needed in L KOH = amount of potassium hydroxide (kg) | |

The transesterification procedure used has been reported in several other University of Idaho reports (Peterson et al., 1990; Peterson et al., 1995).

Storage Containers

Fuel containers for the study were: 4-liter brown glass reagent bottles and 8-liter steel pails with crimp on lids. All containers were filled 3/4 full and vented to the atmosphere to simulate actual fuel storage. The study used triplicate samples of two esters, RME and REE. Each fuel was arranged in four different configurations: glass and steel containers stored at room temperature (inside) and at the local outside ambient temperature (outside) for a total of 24 samples.

Fuel Analysis

After each three month storage period samples were analyzed according to the following procedures (AOCS, 1987; ASTM, 1991): Peroxide Value, AOCS Cd 8b-90; Acid Value, ASTM Test D974; Density, ASTM Test D1298; Viscosity, ASTM Test D445; and Heat of Combustion, ASTM Test D240.

The fuels were characterized initially and after the two year storage study by evaluating the parameters in ASAE EP552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, peroxide value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Biological and Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed by Phoenix Chemical Labs, Chicago, Illinois.

Short Term Engine Tests

Each of the 24, one gallon samples from the storage study were combined into two large REE and RME samples, respectively, for use in the short term engine testing. New batches of REE and RME were produced for comparative purposes. Phillips 66 low sulfur number two diesel fuel (2-D) was used in this study as a reference. The test engine was a John Deere (4239T) direct-injection, turbocharged diesel. This is a four cylinder engine with a bore of 106 mm, a stroke of 110 mm, a displacement of 3.917 L and a compression ratio 16.2:1. It has a high RPM of 2650, with 61 kW (82 HP) at 2500 RPM and 290 N•m (214 lbf•ft) of torque at 1500 RPM. Attached to the engine was a General Electric 119 KW (159 HP) cradle type dynamometer.

Two short term engine performance test procedures were performed. The first was a rapid engine test to measure injector fouling in diesel engines using vegetable oil fuels (Korus, 1985). For this test the engine was operated at maximum power and 2500, 2300, 2100, 1900, 1700, and 1500 revolutions per minute (RPM) for 10 minutes at each RPM. Readings of ambient air, opacity, exhaust, fuel, lube oil and intake air temperatures and opacity were acquired every 30 seconds. After each fuel test the injectors were removed and the carbonaceous tips were measured using machine vision. There was only enough fuel for one replication of this test.

The second test was a SAE torque test (SAE J1349, 1990). This test was performed under full throttle and full load conditions at 100 RPM intervals from 2600 to 1300 RPM. This test was replicated once also. Both test procedures were set up in random order. For more information on engine test procedures and equipment refer to (Hammond, 1996; Perkins et al., 1991).

Statistical Analysis

The storage study was set up as a randomized complete block with replication. Blocks were inside and outside storage locations. Treatments were fuels (RME and REE) and containers (glass and steel). Each fuel and container type were replicated 3 times for a total of 12 containers inside and 12 containers outside. Statistical analyses were performed with SAS (SAS Institute, Cary, NC). This consisted of a statistical analysis (ANOVA) followed by a Tukey multiple range procedure to separate the means for each of the parameters, peroxide value, acid value, density, viscosity, and heat of combustion.

In addition a regression model was formulated for each parameter by using SAS. Initially a multiple regression was run on each parameter against the variables container, location, time, location and time, time squared and fuel. The variables in the models were coded as shown in Table 9-2.

Table 9-2. Storage Variables

| |
|---|
| Container - Listed from 1 to 2, glass = 1, metal = 2 |
| Location - Listed from 1 to 2, inside = 1, outside = 2 (inside temp = 70°F, outside temp varied from 34°F to 72°F) |
| Time - Listed from 1 to 9 |
| Fuel Type - Listed from 1 to 2, RME = 1, REE = 2 |

RESULTS AND DISCUSSION

In the following discussion the nomenclature used is as follows: G=Glass, M=Metal, ME=Methyl Ester, EE=Ethyl Ester, I=Inside and O=Outside. The storage study was started in November, 1993 with analysis occurring in February, May, August, November, May, August, and November. Many of the trends observed in the results may be attributed to the time of year the samples were analyzed.

Peroxide Value

Peroxide values, measured in milliequivalents of peroxide per kilogram of sample for each

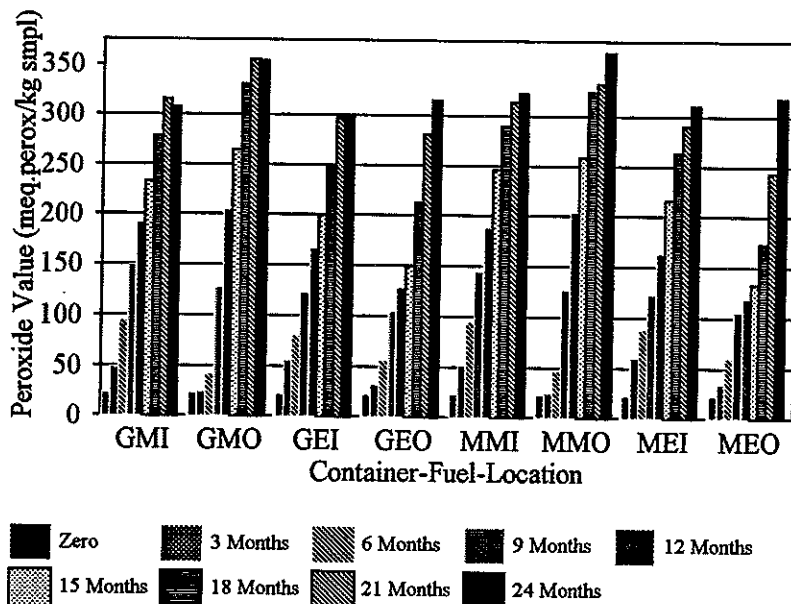


Figure 9-1. Peroxide value versus container type-fuel type-location for two years.

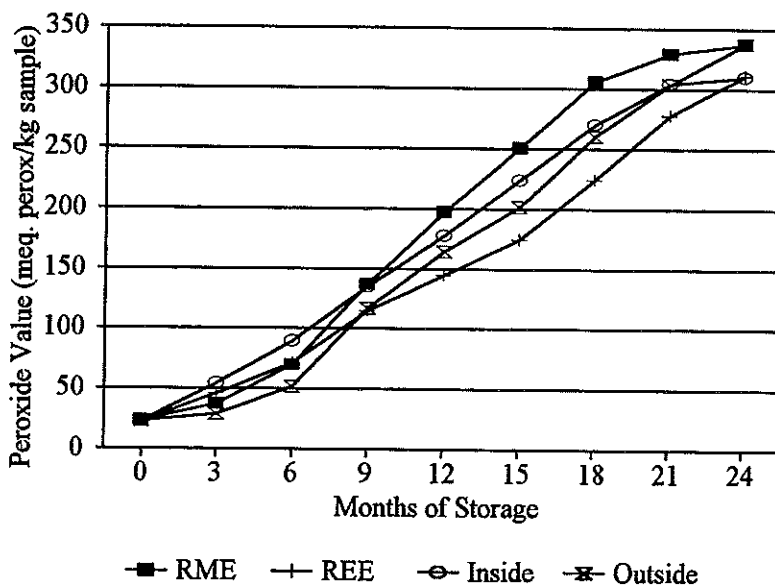


Figure 9-2. Peroxide value versus two year storage study for RME and REE.

sampling period, are shown in Figure 9-1. There was a consistent increase in peroxides over time with an acceleration of that increase from the 6th through the 18th month.

Peroxide values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location, based on the overall means, indicated REE was significantly higher between inside and outside storage for peroxide values. RME showed no significant difference for interactions between fuel and location for peroxide values. There was a significant increase for peroxide from initial readings with RME after six months. REE showed a significant increase after three months.

Figure 9-2 shows that after 6 months the peroxides in the RME increased at a faster rate than in the REE. Peroxide values at the

outside location had a slower rate of increase than did the values at the inside location for the first six months. This was most likely due to an overall lower sample temperature during that time. Peroxide values at the outside location had a slower rate of increase than did the values at the inside location for the first six months. A steady increase of peroxide value over time was observed for REE. Peroxide value for the RME leveled off after eighteen months. At 24 months the peroxide value was 14.5 times higher for RME and 13.7 times higher for REE compared to the beginning value. Fuel stored outside had a peroxide value 14.7 times higher while fuel stored inside was 13.5 times higher compared to the beginning value.

The best fit regression model for the change in Peroxide value were as follows:

$$P_{\text{perox}} = -30.906 \cdot \text{loc} - 33.41 \cdot \text{fuel} + 35.19 \cdot \text{time} + 3.95 \cdot \text{loc} \cdot \text{time} + 61.624$$

The R^2 value for this equation is 0.94 using the values in Table 9-2.

This equation, over the 24 months, shows that fuel type affected Peroxide by a change of 33.41, each quarter of time increased peroxide by 35.19, outside location decreased peroxide value by 30.906, and there was a small location by time interaction.

Table 9-3 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means.

Table 9-3. Results of ANOVA analysis for peroxide values on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

| Peroxide Value (meq. peroxide/kg of sample) | | | | |
|---|-----------|-----------|--------------|---------------|
| Sampling Period | RME Means | REE Means | Inside Means | Outside Means |
| Beginning | 23.26 a | 22.68 a | 22.97 a | 22.97 a |
| 3 Months | 37.27 ab | 45.67 ab | 54.15 b | 28.80 ab |
| 6 Months | 69.63 c | 71.25 bc | 89.45 c | 51.43 abc |
| 9 Months | 136.83 d | 114.19 d | 134.73 d | 116.29 d |
| 12 Months | 197.13 e | 144.33 de | 177.33 e | 164.13 de |
| 15 Months | 250.70 f | 174.39 ef | 223.75 f | 201.34 ef |
| 18 Months | 305.59 g | 224.42 g | 270.06 g | 259.95 g |
| 21 Months | 329.30 h | 278.19 h | 304.18 h | 303.31 gh |
| 24 Months | 336.93 hi | 310.88 i | 309.97 hi | 337.85 hi |

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p < 0.05$).

Acid Value

The acid values (Figure 9-3), measured in milligrams of KOH per gram of sample, increased with time as did the peroxide values. Since both of these values are related to autoxidation,

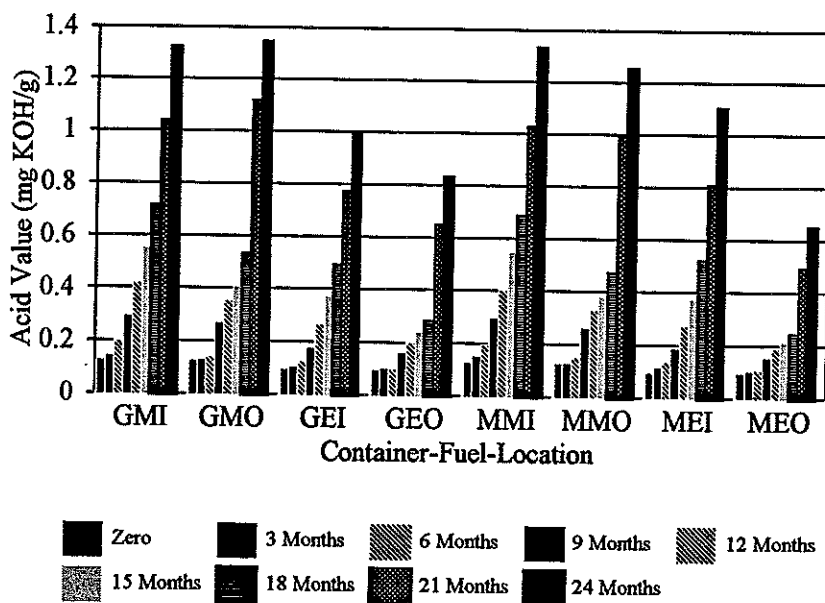


Figure 9-3. Acid value versus container type, fuel type, and location for two years.

Statistical analysis of the interactions between fuel and location indicated REE and RME had a significant difference between inside and outside storage for acid values. The effects of time on REE and RME show that after nine months, there was a significant increase in acid values

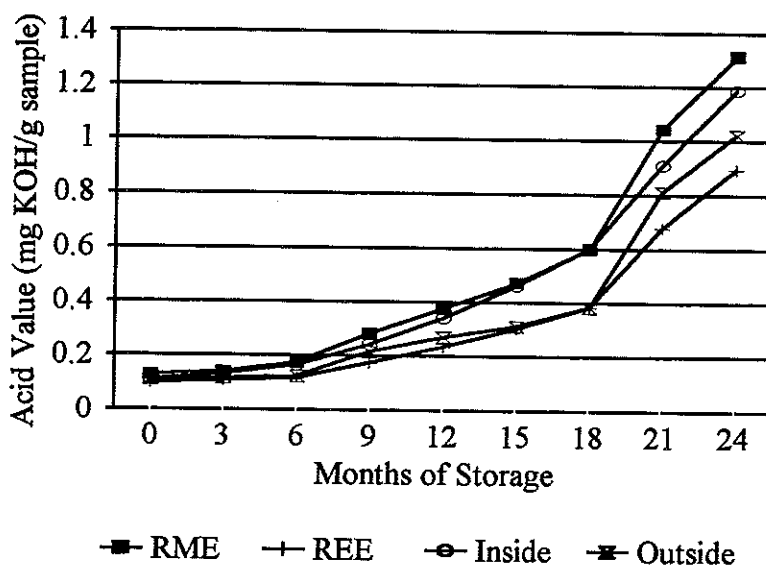


Figure 9-4. Acid value versus container type, fuel type, and location for two years.

the acid values naturally increase with an increase in peroxides because the esters first oxidize to form peroxides which then undergo complex reactions including a split into more reactive aldehydes which further oxidize into acids. Acids can also be formed when traces of water cause hydrolysis of the esters into alcohol and acids (Formo, 1979).

Acid values for either fuel were not significantly affected by the type of container.

from initial readings and the increase accelerated toward the end of the 24 month period.

Figure 9-4 shows acid value versus time for both RME and REE, and inside and outside locations. The acid values were fairly constant for the first 6 months then took a significant upward trend. The RME acid values increased at a faster rate than the REE values after 6 months as was the case with peroxides. The acid value of the

outside samples lagged behind the inside samples. At 24 months the acid value was 10.3 times higher for RME and 9.2 times higher for REE compared to the beginning values. Fuel stored outside had acid values 9.0 times higher while fuels stored inside had acid values 10.5 times higher compared to the beginning value. The best fit regression model for the change in acid levels was as follows:

$$P_{\text{acid}} = -0.064 \cdot \text{time} - 0.172 \cdot \text{fuel} - 0.0187 \cdot \text{loc} \cdot \text{time} + 0.0209 \cdot \text{time}^2 + 0.473$$

The R^2 value for this equation is 0.93 using the values in Table 9-2.

This model shows a significant time to location interaction and a quadratic relationship for time. The acid value was -0.172 higher for fuel type (the negative sign indicates that REE was lower than the RME) and the outside samples had a 0.06 lower acid value than the inside samples.

Table 9-4 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means. A steady increase in acid values over the 24 month storage time is noted.

Table 9-4. Results of ANOVA analysis for acid values on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

| Acid Value (mg KOH/g of sample) | | | | |
|---------------------------------|-----------|------------|--------------|---------------|
| Sampling Period | RME Means | REE Means | Inside Means | Outside Means |
| Beginning | 0.128 a | 0.097 a | 0.113 a | 0.113 a |
| 3 Months | 0.140 ab | 0.108 ab | 0.131 ab | 0.116 ab |
| 6 Months | 0.173 abc | 0.118 abc | 0.165 abc | 0.125 abc |
| 9 Months | 0.282 d | 0.173 abcd | 0.241 bcd | 0.214 abcd |
| 12 Months | 0.377 e | 0.233 cde | 0.340 de | 0.270 abcde |
| 15 Months | 0.472 f | 0.301 ef | 0.462 f | 0.312 cdef |
| 18 Months | 0.601 g | 0.385 fg | 0.603 g | 0.383 defg |
| 21 Months | 1.043 h | 0.678 h | 0.909 h | 0.812 h |
| 24 Months | 1.315 i | 0.894 i | 1.183 i | 1.021 i |

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p < 0.05$).

Density

It was found that the density of the esters increased over time; however, outside samples tended downward during the first half of the study before increasing (Fig 9-5). Density values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated REE had a significant increase between inside and outside storage for density values. RME showed no significant difference for

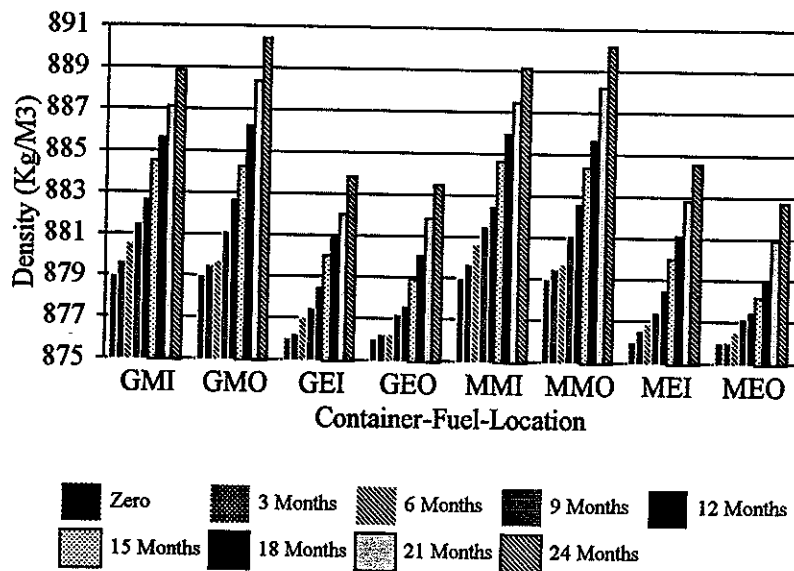


Figure 9-5. Density versus container type, fuel type, and location for two years.

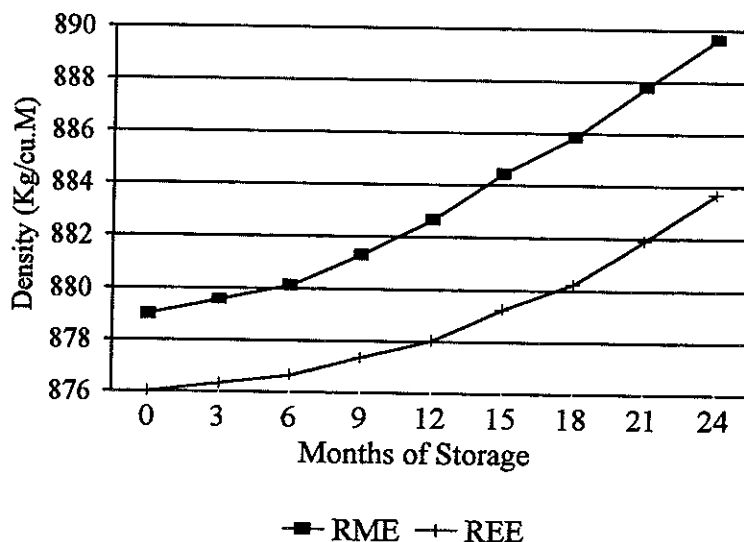


Figure 9-6. Density versus two year storage study for RME and REE.

0.88%. Fuel stored outside increased 1.048% and fuel stored inside 1.037%.

interactions between fuel and location for density values. The effects of time on RME show that after three months, there was a significant difference for density from initial readings. REE showed a significant difference after six months.

Figure 9-6 shows density versus time for both RME and REE. The density of the RME at the beginning of the study was higher than that of REE and increased at a faster rate after 6 months. Significant differences were found among means from each sampling period with the exception of the density values of REE between 0 and 3 months. Location was not a major influence in changing density values over time, however, the inside samples had higher density values the outside samples. A 1.046% increase of density with time was measured. RME density increased 1.22% and REE density increased

The best fit regression model for the change in density values was as follows:

$$P_{den} = -0.4815*loc - 4.61*fuel + 0.114*time^2 + 885.28$$

The R^2 value for this equation is 0.966 using the values in Table 9-2.

The model shows a quadratic relationship for time. The density increment for fuel type was -4.61 (the negative sign indicates a lower density for REE than RME) and a -0.48 reduction in density for the outside stored samples.

Table 9-5 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means.

Table 9-5. Results of ANOVA analysis for density on test data with groupings according to sampling period.

| Sampling Period | Density (Kg/M ³) | | | |
|-----------------|------------------------------|-----------|--------------|---------------|
| | RME Means | REE Means | Inside Means | Outside Means |
| Beginning | 879.0 a | 876.0 a | 877.5 a | 877.5 a |
| 3 Months | 879.5 b | 876.3 ab | 878.0 ab | 877.9 ab |
| 6 Months | 880.1 c | 876.7 abc | 878.8 abc | 878.0 abc |
| 9 Months | 881.3 d | 877.3 cd | 879.5 abcd | 879.2 abcd |
| 12 Months | 882.7 e | 878.0 de | 880.6 bcde | 880.1 abcde |
| 15 Months | 884.4 f | 879.3 f | 882.3 def | 881.4 cdef |
| 18 Months | 885.9 g | 880.2 g | 883.4 fg | 882.7 defg |
| 21 Months | 887.8 h | 881.9 h | 884.9 fgh | 884.8 fgh |
| 24 Months | 889.7 i | 883.7 i | 886.6 hi | 886.7 hi |

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p < 0.05$) according to the Tukey Multiple Range Procedure.

Viscosity

Viscosity tended to increase over time (Fig 9-7); however, the outside samples tended

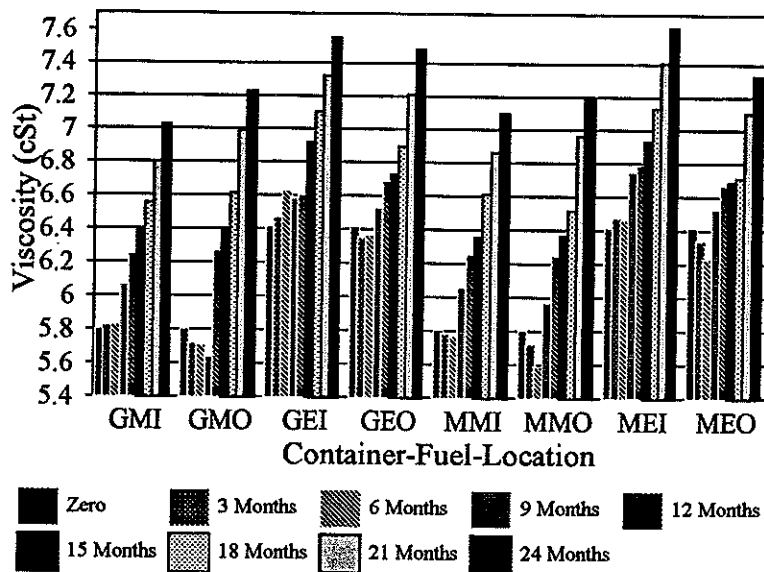


Figure 9-7. Viscosity at 40°C versus container type, fuel type, and location for two years.

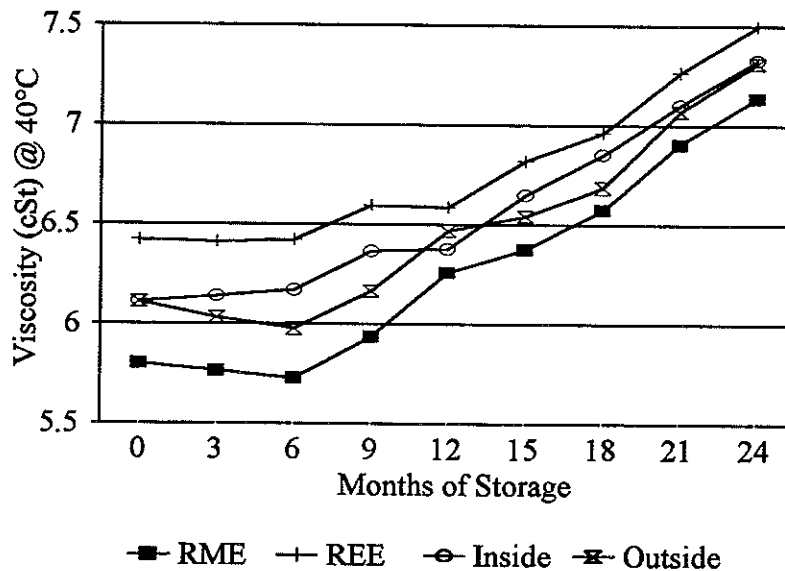


Figure 9-8. Viscosity at 40°C for the two year period for RME, REE, and inside and outside locations.

downward during the first half of the study before going up. This could be due in part to the lower average temperatures of the outside samples during the early period.

Viscosity values for either fuel were not significantly affected by the type of container.

The viscosity of REE (Fig 9-8) started out about 10% higher than that of RME but after year of storage was only 5% higher.

RME experienced a significant rise in viscosity after 6 months of storage and continued to rise significantly over the 9 to 24 month periods. REE stayed fairly constant for the first 12 months and then increased at about the same rate as RME for the final 12 months. The viscosity of RME increased 23.1% and viscosity of REE 16.8% over the 24 months. Inside and outside samples had nearly identical 19+% increases.

The best fit regression model for the change in viscosity was as follows:

$$P_{\text{visc}} = -0.0807 \cdot \text{loc} + 0.0394 \cdot \text{time} + 0.5006 \cdot \text{fuel} + 0.0198 \cdot \text{time}^2 + 5.46$$

The R^2 value for this equation is 0.91 using the values in Table 9-2.

The model shows viscosity was 0.08 cSt lower for outside stored samples, the effect of fuel type changed viscosity by 0.5 cSt (REE higher than RME) and a quadratic effect of time.

Table 9-6 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means.

Table 9-6. Results of ANOVA analysis for density on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

| Sampling Period | Viscosity (cSt) | | | |
|-----------------|-----------------|------------|--------------|---------------|
| | RME Means | REE Means | Inside Means | Outside Means |
| Beginning | 5.80 a | 6.42 a | 6.11 a | 6.11 a |
| 3 Months | 5.76 ab | 6.41 ab | 6.14 ab | 6.03 ab |
| 6 Months | 5.73 abc | 6.42 abc | 6.17 abc | 5.98 abc |
| 9 Months | 5.93 ad | 6.60 abcd | 6.37 abcd | 6.17 abcd |
| 12 Months | 6.26 e | 6.59 abcde | 6.38 abcde | 6.47 de |
| 15 Months | 6.37 ef | 6.82 df | 6.65 def | 6.54 ef |
| 18 Months | 6.57 g | 6.96 fg | 6.86 fg | 6.69 efg |
| 21 Months | 6.91 h | 7.26 h | 7.10 gh | 7.07 h |
| 24 Months | 7.14 i | 7.50 i | 7.33 hi | 7.31 hi |

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p < 0.05$).

Heat of Combustion

The values for heat of combustion (Fig 9-9) tended to decrease over time. This was most likely due to the breakdown of the fuel by oxidation which was verified by the increase in the

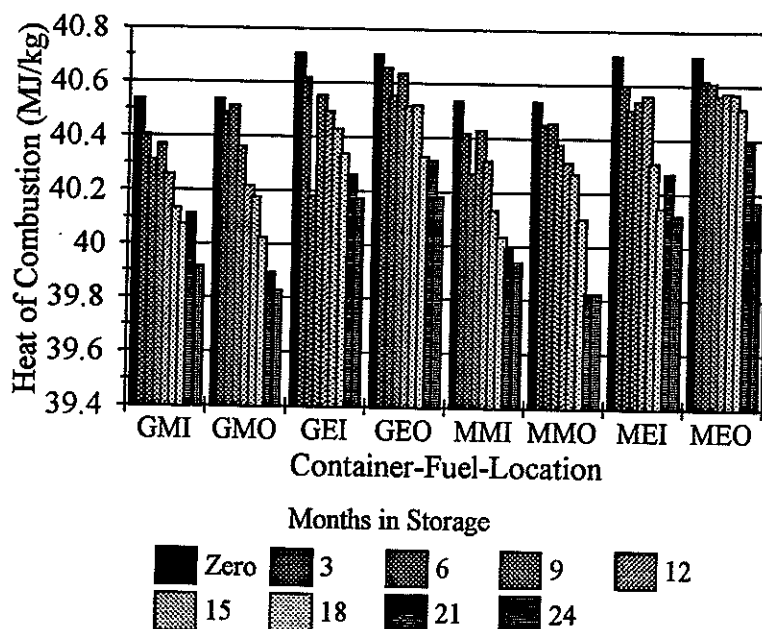


Figure 9-9. Gross heat of combustion versus container type, fuel type, and location for two years.

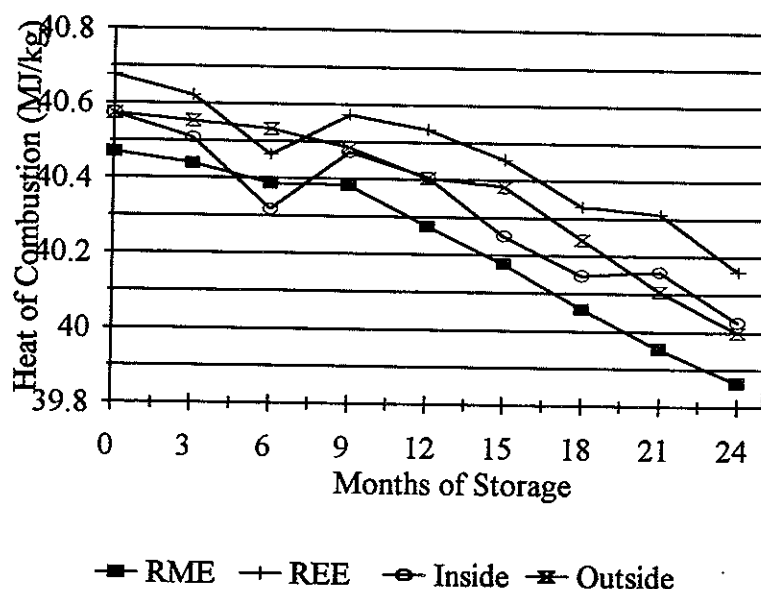


Figure 9-10. Gross heat of combustion for the two year storage period for RME and REE, and inside and outside locations.

peroxide and acid values.

Heat of combustion values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated REE had a significant difference and RME no significant difference between inside and outside storage for heat of combustion values. Figure 9-10 shows a decline in the heat of combustion of the two fuels with the exception of REE between month 6 and 9. The heat values for RME 12 months were significantly lower than values at both 0 and 3 months. The REE heat of combustion values on the other hand showed a significant drop at 6 months which corresponds with a rise in the other four parameters at 6 months, however it then increased at 9 months, although not significantly. The final reading at 24 months was significantly lower than the beginning value for heat of combustion.

Heat of combustion declined about 1.4% over the 24 months of storage. RME declined 1.50% and REE 1.27%. Inside and outside samples declined at about the same 1.4% rate.

The best fit regression model for the change in heat of combustion was as follows:

$$P_{HOC} = 19.94*loc + 101.231*fuel - 2.89* time^2 + 17254$$

The R^2 value for this equation is 0.747 using the values in Table 9-2.

The model shows a quadratic change in heat of combustion with time, 101.2 Btu/lb less energy for RME than for REE and 19.94 Btu/lb more energy for samples stored outside compared the inside stored samples.

Table 9-7 represents the results of ANOVA analysis on heat of combustion test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means.

Table 9-7. Results of ANOVA analysis for density on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

| Heat of Combustion (BTU/lb) | | | | |
|-----------------------------|------------|--------------|--------------|---------------|
| Sampling Period | RME Means | REE Means | Inside Means | Outside Means |
| Beginning | 17399 fghi | 17488 efi | 17444 efhi | 17444 defghi |
| 3 Months | 17386 fgh | 17465 efh | 17416 efh | 17435 defgh |
| 6 Months | 17363 efgh | 17396 bcdefg | 17333 bcdefg | 17426 defg |
| 9 Months | 17362 efg | 17444 def | 17401 ef | 17405 cdef |
| 12 Months | 17315 de | 17427 de | 17372 de | 17371 cde |
| 15 Months | 17273 cd | 17393 bcd | 17305 bcd | 17362 cd |
| 18 Months | 17222 bc | 17339 bc | 17260 abc | 17301 abc |
| 21 Months | 17178 ab | 17331 ab | 17266 ab | 17243 ab |
| 24 Months | 17139 a | 17266 a | 17208 a | 17197 a |

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p < 0.05$).

Fuel Characterization

Table 9-8 is the fuel characteristics for the initial and two year stored fuel. The SREE and SRME are the REE and RME fuels, respectively, stored for two years. The cetane number increased more than 12%, viscosity increased more than 16%, and particulate matter all increased during storage as did the peroxide value.

Table 9-8. Fuel Characterization Data

| | REE | SREE | RME | SRME |
|----------------------------------|--------|--------|--------|--------|
| Fuel Specific Properties | | | | |
| Specific Gravity, 60/60 | 0.8760 | 0.8837 | 0.8790 | 0.8897 |
| Viscosity, cSt @ 40°C | 6.42 | 7.50 | 5.80 | 7.14 |
| Cloud Point, °C | -2 | 0 | 0 | 1 |
| Pour Point, °C | -10 | -9 | -15 | -15 |
| Flash Point, °C | 170 | 148 | 179 | 148 |
| Boiling Point, °C | 273 | 254 | 347 | 271 |
| Water and Sediment, % Vol. | <0.005 | <0.005 | <0.005 | <0.005 |
| Carbon Residue, % mass | 0.06 | 0.12 | 0.08 | 0.07 |
| Ash, % mass | 0.002 | 0.011 | 0.002 | 0.003 |
| Sulfur, wt% | 0.014 | 0.008 | 0.012 | 0.009 |
| Cetane Number | 64.9 | >72.7 | 61.8 | >72.7 |
| Heat of Combustion, Gross, MJ/kg | 40.51 | 40.16 | 40.54 | 39.86 |
| Copper Corrosion | 1A | 1A | 1A | 1A |
| Karl Fischer Water, ppm | 761 | 949 | 757 | 1077 |
| Particulate Matter, mg/L | | | | |
| Total | 1.9 | 48.45 | 1.1 | 57.00 |
| Non-Combustible | 0.9 | 8.10 | <0.1 | 2.05 |
| Elemental Analysis | | | | |
| Carbon, % | 76.83 | 78.85 | 78.7 | 77.76 |
| Hydrogen, % | 11.8 | 12.49 | 12.66 | 12.49 |
| Oxygen, % (by difference) | 11.36 | 8.64 | 9.22 | 9.74 |
| Iodine Number | 96.7 | 90.1 | 91.9 | 93.9 |
| Peroxide Value | 22.68 | 310.88 | 23.26 | 336.93 |
| Acid Value | 0.097 | 0.894 | 0.128 | 1.315 |

Short Term Engine Tests

At maximum power output, the fuel stored for two years increased 1.9% for REE and 1.5% for RME compared to newly produced fuel

(Fig.9-11). The stored fuels also increased maximum torque by 0.9%. The new fuels had 3.4% less power than 2-D at maximum power and 1.4% less torque than 2-D at peak torque RPM.

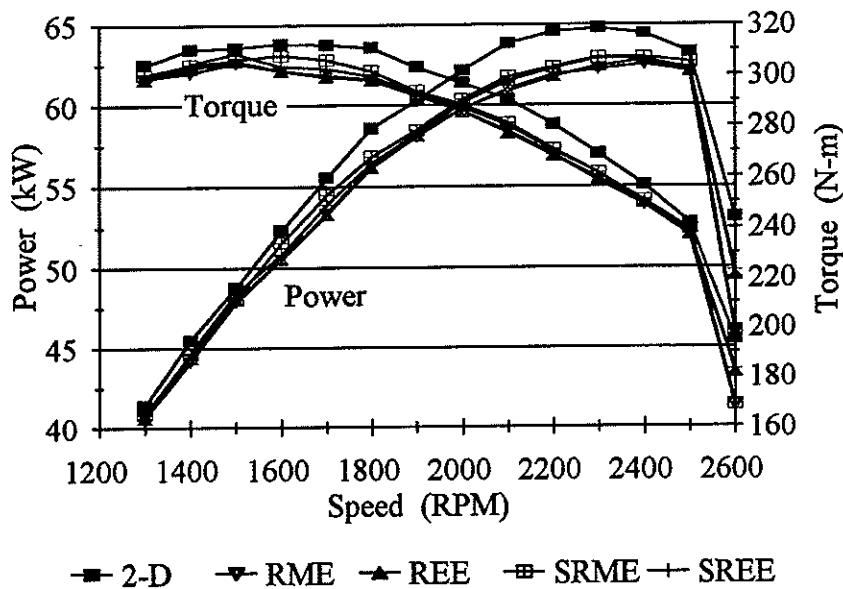


Figure 9-11. Power and torque plotted against engine speed for five fuels.

Smoke density for the Biodiesel fuels were 18% to 52% that of 2-D. The smoke density for the stored REE was 1.175 times more than that of the new REE and the stored RME produced 3% less smoke than the new RME (Fig. 9-12).

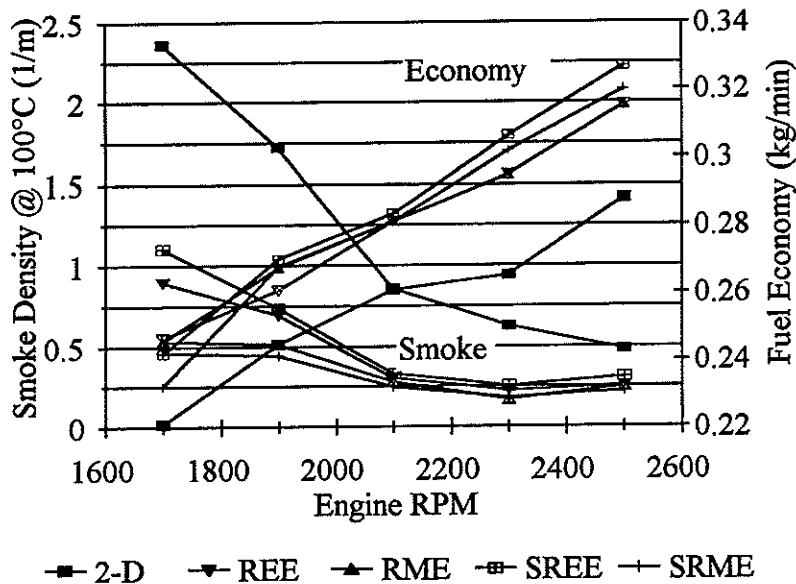


Figure 9-12. Smoke density and fuel economy for five fuels at five different engine RPM's.

Fuel economy was compared at each RPM level (Fig.9-12). For example, at 1500 RPM, the stored RME used 1.13 percent more fuel than did the new RME and the stored REE used 1.2 percent more fuel than the new REE.

The injector tip coking index for the 2-D, new RME and REE, and stored RME and REE fuels were found by dividing each of the

fuel's coking area by the diesel coking area. The coking on the injector tips for the stored

fuels was 7.8% more for RME and 2.8% more for REE. The coking observed for RME in this test was extremely low (1.016, for SRME (1.102), for REE (1.474), and 1.517 for SREE. This data was at or below other tests for Biodiesel reported by the authors recently. The effect due to storage was extremely small in both cases.

CONCLUSIONS

According to test results from this 24 month study of rapeseed methyl and ethyl esters, there was a slight deterioration of the fuel over time. The following trends emerged: In general no effect was found for container type; test values compare very closely for both metal and glass containers. Significant differences were, however, found in the values for each of the five measured parameters for both fuel type and storage location with passage of time. For both fuels the peroxide and acid values, density, and viscosity tended to increase over time. The heat of combustion, on the other hand, tended to decrease slightly over time. Fuels tended to degrade at a slightly faster rate, particularly as indicated by the peroxide and acid values, at the indoor location. This was evidently due to the higher average temperature at the indoor location. Initially, and over the 24 month storage period, properties of the two esters displayed slightly different values. The ethyl esters were higher in viscosity and heat of combustion, but lower in density, peroxide and acid values than the methyl esters. Over time, degradation occurred at a different rate for the two fuels. The RME increased in peroxide value, acid value, and density at a faster rate than did the REE. Specific observations are noted below.

1. Peroxide values were increased 14.5 times for RME and 13.7 times for REE after 24 months.
2. Acid values were increased 10.3 times for the RME and 9.2 times for REE after 24 months.
3. Density increased 1.22% for RME and 0.88% for REE after 24 months.
4. Viscosity increased 23.1% for RME and 16.87% for REE after 24 months.
5. Heat of Combustion declined 1.50% for RME and 1.27% for REE after 24 months.
6. The cetane number increased more than 12% and particulate matter increased during storage.
7. Regression models showed second order time effects for acid value, density, and viscosity.
8. In general outside samples stored slightly better than indoor samples. It was noted that during the fall and winter the change in samples stored outdoors was less than those inside. In the summer when outside temperatures were higher the changes were similar.
9. The short term engine tests, including torque, power, and fuel economy, and coking tests showed very small amounts of change between the stored fuels and the new fuels. The high peroxide and acid values of the stored fuels had little effect on the performance of the engine in short term tests. Long term durability tests would be the next step needed to determine if these changes affect engine life. The small amount of fuel stored in this study precluded such testing.

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EMISSIONS CHARACTERISTICS OF ETHYL AND METHYL ESTER OF RAPESEED OIL COMPARED WITH LOW SULFUR DIESEL CONTROL FUEL IN A CHASSIS DYNAMOMETER TEST OF A PICKUP TRUCK.

Comprehensive tests were performed on an on-road vehicle in cooperation with the Los Angeles County Metropolitan Transit Authority emissions test facility. All tests were with a transient chassis dynamometer. Tests included both a double arterial cycle of 768 s duration and an EPA heavy duty vehicle cycle of 1,060 s duration. The test vehicle was a 1994 pickup truck with a 5.9 L turbocharged and intercooled, direct injection diesel engine. Rapeseed methyl (RME) and ethyl esters (REE) and blends were compared with low sulfur diesel control fuel. Emissions data includes all regulated emissions: hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), oxides of nitrogen (NO_x) and particulate matter (PM).

OBJECTIVES

The objectives of this experiment were:

- 1) to compare regulated emissions data including total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x), and particulate matter (PM), for ethyl ester of rapeseed oil, methyl ester of rapeseed oil, and diesel control fuel;
- 2) to obtain emissions data for blends of REE and RME with diesel control fuel at the 20% and 50% levels.

A REVIEW OF LITERATURE

One of the critical issues to be resolved for vegetable oil fuels as they seek status as replacements for petroleum diesel fuel is how they affect emissions from a standard diesel engine. This literature review examines many of the tests that have been conducted in the past several years related to emissions of vegetable oil fuels. Test procedures, engines, and instrumentation vary widely from one report to another. Standard EPA procedures are rarely followed. Emissions testing on the official level requires more human, capital, and equipment resources than most engine test facilities have available.

The EPA procedures for measuring exhaust emissions from diesel engines require the monitoring of both gaseous and particulate emissions. Exhaust emissions testing for a diesel engine utilizes the constant volume sampling concept of measuring emissions, it requires a positive displacement pump-constant volume sampler (PDP-CVS) or critical flow venturi (CFV) with heat exchanger, and must be connected to a dilution tunnel for sampling particulate emissions. Specific operating requirements are detailed by the EPA for both systems. CI engines require a heated flame ionization detection sampler for hydrocarbon

analysis. The HFID must be taken directly from the diluted exhaust stream through a heated probe in the dilution tunnel. Other analyzers are required for carbon monoxide, carbon dioxide, and oxides of nitrogen. One such facility is described in detail by Dunlap et al. (1993).

Emissions testing is a case where the protocol is so restrictive as to limit testing to only a very few laboratories. To counteract the official level, many scientists use techniques of their own to give "relative" data. As the data is examined, it is easy to see that these many different local procedures shed more dark on the question than light. Acceptable research protocols should be suggested within the reach of the average engine test cell that would bring uniformity to this maze of tests.

The reports reviewed can be broken into a range of sophistication. Many labs have only an opacity or smoke meter available and report this as emissions testing. Some have maintenance shop type instruments for the regulated emissions total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), oxides of nitrogen (NO_x), and particulate matter (PM). These instruments are usually operated with little or no calibration and offer, in many cases, too little precision and/or sensitivity to give real "relative" data. The validity of most of those tests should be suspect. The literature clearly shows that smoke meter or opacity data indicate only visible smoke and are not necessarily related to the regulated emission called "particulate matter" (PM).

Particulates are defined by the EPA as any diesel exhaust effluent collected on a binderless glass fiber filter in a dilution tunnel at temperatures below 125 degrees F. Hence, particulates include not only solid carbon, but sulfate emissions and soluble organic fractions (SOF). The SOF found in diesel particulates are comprised of unburned fuel and lube oil, and partially oxidized fuel and lube oil (Hunter et al., 1989).

Barenescu (1994) and Holmberg and Peebles (1994) report an inverse correlation between emissions of NO_x and PM. If an engine is optimized to reduce NO_x emissions, each unit of NO_x reduction will routinely result in a unit increase of PM. Similarly, a reduction in PM will result in an increase in NO_x. Although the inverse correlation holds true for Biodiesel as well, the severity of the trade-off is not as significant as in petrodiesel.

The next level of sophistication is from tests which have good quality analyzers with heated lines and, hopefully, good calibration procedures for HC, CO, CO₂, and NO_x. In every case, these test cells did not have access to a dilution tunnel for measuring PM. In most cases they still use opacity or smoke for PM. These test cells also do not have capability for transient cycles and report steady state data. In some cases they use the 13 mode test, in most cases they use a protocol of their own. This is most generally a constant speed, variable load test. This data is often referred to as being "relative" to the transient cycle required by EPA.

The third level of sophistication is a testing lab with a transient capable dynamometer, a dilution tunnel, calibration and all the required sophistication to be called "EPA Certified" for

emissions testing. Even in these labs, however, there is not uniformity of data because cycles differ, reference fuels differ, engines differ, methods of changing fuels differ and there is a wide selection of vegetable oil ester fuels from different origins have been used as test fuels. Another problem is the need for "cold start" and "hot start" tests. These requirements are probably reasonable for certifying an engine if the lab is available. However, when one does a comparison of many different fuels, additives, engine adjustments, or blends it becomes an impossible task to create an adequate scientific experiment given a normal budget and time to use a certified emissions testing facility.

The last level of emission testing involves laboratories that also measure the unregulated aldehydes, ketones, and polycyclic aromatic hydrocarbons (PAH) that are possibly potential health problems. Only a few studies report these constituents; however, most show that vegetable oil esters produce PAH's lower than those from diesel fuel.

The overriding conclusion that was reached from this literature review was that ethyl and methyl esters of vegetable oils are essentially similar to diesel fuel in their emissions characteristics. Minor engine adjustments can bring about minor changes in results. Several studies show that NO_x is increased. That may or may not be relevant, 10 or 15 % of the very small amount of NO_x produced was accompanied by an equally important benefit such as reduced HC, CO, or PM. The chemistry of combustion requires emissions. Hydrocarbons are transformed into carbon dioxide and water accompanied by nitrogen in the air passing through the process. Incomplete combustion results in HC and CO. The high temperatures and pressures of combustion form NO_x. Reductions in HC and CO must be accompanied by increases in CO₂. Sales of diesel fuel in the U. S. are nearly 50 billion gallons per year, 53.4 % goes to transportation according to the Energy Information Administration (1989). Diesel engines were designed over many years to operate on petroleum diesel. It is interesting that they perform as well as they do on methyl and ethyl esters of vegetable oils and that the emissions are comparable to that of commercial diesel fuel for which the engines were designed.

In the U.S., the regulations that take effect in 1994 and 1998 will push the design limitations of heavy-duty diesel engines. The Federal heavy-duty diesel engine emission regulations for 1991 and 1994 have prompted a comprehensive re-examination of the diesel combustion process. These regulations require major reductions in the NO_x and particulate emissions of diesel engines used in trucks over 8500 lb gross vehicle weight (GVW). According to EPA 86.094-11 exhaust emissions from new 1994 and later model year diesel heavy-duty engines shall not exceed the following: HC 1.3 gm/bhp-hr; CO 15.5 gm/bhp-hr; NO_x 5.0 gm/bhp-hr; PM for diesel engines to be used in urban buses 0.07 gm/bhp-hr; PM for all other diesel engines 0.10 gm/bhp-hr. The opacity of smoke emissions shall not exceed the following: 20 % during the acceleration mode; 15 % during the lugging mode; 50 % during the peaks in either mode.

Zhang et al. (1988) in two replicates of 200 hour tests reported "based on evaluations of engine performance, wear and combustion chamber component condition as indicators of engine durability, winter rape methyl ester appears to be equivalent to number 2 diesel."

Schumacher et al. (1994) reported on tests with two 5.9 L Cummins engines in on-road vehicles that the black exhaust smoke normally observed when a diesel engine accelerates was reduced as much as 86 % when the diesel engine was fueled with 100 % soydiesel.

Humke and Barsic (1981) in tests with degummed crude soybean oil and crude soybean oil found that nozzle deposit formation after 10 hours caused engine performance to decrease and emissions to increase.

Schumacher et al. (1993) studied engine exhaust from four farm tractors using portable exhaust emission testing equipment. As fuel changed from diesel to methyl soyate, CO dropped from 0.67 to 0.04 %, CO₂ exhibited no clear trends, NOx increased from 843 ppm to 1006 ppm, while opacity decreased from 15.6 to 8.0 %. NOx exhaust emissions tended to be lower when the engines were fueled with 10-40 % soydiesel/diesel blends as compared to 100 % diesel or 100 % soydiesel.

Zubik et al. (1984) used a Case 188D, 4 cylinder, naturally aspirated, 4-stroke diesel engine to study exhaust emissions of diesel fuel, a blend of 25 % sunflower oil in diesel fuel and 100 % sunflower oil methyl ester. Emissions were measured with continuous flow, heated line analyzing instruments. Particulates were measured with a smoke meter. At a constant speed of 1800 rpm, CO and NOx emissions were essentially the same for all three fuels. Smoke was the lowest for the methyl ester and highest for pure diesel fuel. Throughout the operating range the pure diesel fuel gave the lowest HC values, however at the lightest loads HC from diesel was above the methyl ester and blend values.

Ishii and Takeuchi (1987) used a one cylinder, Yanmar indirect injection engine to compare emissions for diesel and transesterified curcas oils. They used steady state measurements at 2400 rpm and different load settings. HC and CO were higher at light loads and lower at full load for the ester compared to diesel fuel. NOx was essentially unchanged. There was a slight reduction in black smoke concentration when operating on the transesterified curcas oils compared to diesel.

Muryama et al. (1985) compared rapeseed and palm oils and their methyl esters with diesel fuel for performance, emissions, and carbon deposits in a one cylinder, DI diesel engine. It was found that shortening the combustion duration was effective in reducing smoke regardless of fuel.

Reece and Peterson (1993) measured smoke opacity using the snap idle test with a 1992 Dodge with a Cummins 5.9 L, DI, turbocharged and intercooled engine comparing methyl

ester of rapeseed oil and diesel fuel. They found a decrease in opacity of 63 %, and 9 % reduction in hp for the RME when compared with diesel.

Geyer et al. (1984) operated a single cylinder, 0.36 L, DI Diesel engine on certified no. 2 diesel, cottonseed oil, sunflower seed oil, methyl ester of cottonseed oil, and methyl ester of sunflower seed oil to compare performance and emission data. A primary objective was to assess aldehyde emissions and the potential health effects of particulate emissions when operating a diesel engine with vegetable oils. The engine was operated at 2400 rpm and load conditions of 1/3, 2/3 and full rack. They collected data for CO, HC, NO_x, and total aldehydes, as well as individual aldehyde concentrations from formaldehyde through heptaldehyde. They found that the gas phase emissions were slightly higher for the vegetable oils. NO_x was significantly higher for the methyl esters at all rack settings. They found that total aldehydes increased dramatically with the vegetable oil when compared to diesel; the averages for the methyl esters were slightly higher than the neat oils. The amount of formaldehyde increased with rack setting and was consistently higher for the methyl esters than for diesel. The diesel had a large increase in aldehydes with rack settings while the vegetable oils did not. Overall the aldehydes averaged 12 % for diesel and 31 % for the vegetable oils. They indicate significant variability in data "this may indicate some problem in the collection or extraction methods".

Goering et al. (1984) tested diesel oil, a blend of 25 % sunflower oil in diesel, and sunflower methyl ester. They reported that "all behaved similarly in terms of brake thermal efficiency, ignition delay, exhaust temperatures and exhaust emissions of carbon monoxide and nitrous oxide." Methyl ester produced lower smoke than the blend and considerably less than diesel.

Wagner et al. (1985) reported that all regulated emission levels for the ester fuels were similar to diesel fuel except for NO_x. They state, "Smoke was definitely less visible under full rack conditions for the methyl and ethyl esters compared to diesel fuel, but the butyl ester was greater" Esters tested were purchased from Emery industries and an additive package purchased from Ethyl Corporation was added. The test engine was a John Deere 4239TF. Emissions measurements were steady state and no PM equipment was available. Carbon dioxide, carbon monoxide, and oxygen emissions were very similar for all four fuels at both the 2200 and 1500 rpm speed settings. The NO_x emissions for the esters measured 2 to 5 times that of the diesel fuel. The methyl ester produced the highest levels, the butyl esters the next highest, with the ethyl ester producing the lowest levels of NO_x emissions at both engine speed settings. Visible smoke was less for the methyl and ethyl esters at full rack compared to diesel fuel.

Clark et al. (1984) used a 3.9 L, John Deere 4239TF, 4-cylinder, direct injected (DI), turbocharged, CI diesel engine on a stationary dynamometer equipped with a constant speed or constant load mode of automatic control to study emissions from both methyl and ethyl esters. Exhaust gas measurements for HC, CO, CO₂, NO_x, and O₂ were made according to SAE J1003. They found that CO was very low, with no differences between fuels;

however, the CO emissions were too low to be reliable on their instrumentation. Soyates had slightly lower HC levels than the reference diesel fuel. Methyl and ethyl soyates had consistently higher levels of NO_x than the reference fuel. Ethyl esters were lower in NO_x than methyl esters.

Alfuso et al. (1993) used a DI, CI diesel engine for emissions tests with the ECE 15, a non-standard STOP and GO test cycle, and the European 13 mode test procedure. Fuel tested was rapeseed methyl ester (RME). Tests indicated that RME promoted a rise in NO_x, decreased HC and CO, and reduced smoke. PM produced by RME in transient cycles was higher than that obtained with diesel fuel. They also measured Polycyclic Aromatic Hydrocarbons (PAH) by taking a sample of diluted exhaust through a glass-fiber filter and then two cold traps in series that were respectively at 0 degrees C and 20 degrees C. The PAH measured with three or four rings, that at ambient temperature are still in the gas phase, were collected into cold traps. PAH with 5 rings or more were mainly collected on the filter. The volume of extract from the filter and the condensed phase were reduced by rotary evaporation and then analyzed by GC-MS equipment. This technique allows for the analysis of more than 20 compounds. They observed that NO_x was increased, smoke was lower for the RME, and in effect increased with load. It is well known that PM emissions may not follow the trend of smoke because of the contribution of SOF. Particulate matter is composed of dry soot and a condensed phase. At low loads the contribution of SOF is higher. At light loads RME produced more SOF and particulate matter than the diesel fuel, while in proximity of full load the trend was the opposite. HC for diesel was higher at light loads and less at high loads. CO was about the same for light and high loads with diesel, but was reduced with RME. NO_x production was generally higher for the biofuel, but this effect was more important for the 13-mode cycle than for the transient one. It can be observed that dangerous PAH's did not show significant differences in ECE 15 tests, while they were lower for biofuel on the STOP and GO tests.

Vander Griend et al. (1988) used a laboratory and modeling study with the KIVA combustion model to study combustion of vegetable oil fuels. They reported "The RME appeared to be an ideal fuel under the conditions tested; it displays short ignition delay, sufficient charge for an extensive premixed burn, and a smooth diffusion burn stage. Therefore, there exists an opportunity for the optimization of parameters such as injector timing and swirl. Advanced timing should result in a slightly earlier and more vigorous premixed burn. Since RME shows signs of a vapor rich core during injection, increased swirl should result in some increase in the amount of premixed burn and in an enhanced rate of diffusion burn."

Sholl and Sorenson (1993), in tests with SME, found that HC emissions were 50 % less than those of the reference diesel fuel; smoke for SME was generally lower than for the diesel reference fuel. They used a 4-cylinder, 4-stroke, normally aspirated, direct injection diesel engine. They only had 3.8 L (1 gallon of each fuel available) and took their data over 100 consecutive engine cycles at 1800 rpms and 50, 150, 300, 450, and 600 kPa BMEP. At all loads the HC emissions from SME were about one-half of those from diesel fuel. CO

emissions were slightly lower than for SME except for the very lightest loads, where they were slightly higher. NO_x was essentially unchanged. Conditions which have the highest peak pressures and rate of pressure rise at a given load and timing tended to have the highest NO_x. Scholl and Sorenson show that the differences in NO_x emissions are attributable to changes in ignition delay and burning rate only. This study showed reduced NO_x at equal BMEP, and more reduction at 5 degrees retarded timing with SME compared to diesel.

Bosch smoke numbers were lower for SME, but when using a small injector nozzle at retarded timing, the two fuels gave equal results. They state that "the correlation between smoke number and particulate emissions is tenuous at best...". Their conclusions were "In terms of combustion behavior and exhaust emission characteristics, soybean oil methyl ester can basically be regarded as interchangeable with diesel fuel." NO_x emissions for the two fuels are comparable (but slightly lower for SME) and are related to the peak rate of pressure rise which occurs during the initial portion of the combustion process. Smoke numbers for the soybean oil methyl esters were lower than those for the diesel fuel.

Xiao (1993) tested emissions in a Detroit Diesel 6V-92 engine rated at 277 BHP at 2100 rpm. Fuels used were house number 1 diesel (DF#1) and number 2 diesel (DF#2), both low sulfur fuels. They found that 100 % SME reduced baseline DF#1 and DF#2 total particulates by 35 %, linear with percentage of SME in the fuel. Volatile particulate portions remained at a constant level so particulate reduction was mainly due to the reduction in soot (up to 65 % with 100 % SME). NO_x was increased by up to 8.5 % for DF#2 blend and 19 % for DF#1 blends. The emission effects of 20 % SME blends were small.

Mittelbach and Tritthart (1988), in tests with methyl esters of used frying oil, reported slightly lower HC and CO emissions, but increased NO_x. Particulate emissions were significantly reduced, especially the insoluble portion. These two researchers say that the reduction of particulate emissions can be explained by the oxygen content of the used frying oil fuel. They reported that PAH emissions are, in general, slightly higher than those from number 2 diesel fuel, but that the differences are within tolerance limits.

Hemmerlein et al. (1991), in tests with neat rapeseed oil, reported increased HC (up to 290 %), increased carbon monoxide (up to 100 %), lower nitrogen oxides (up to 25 %), lower soot emissions (reduced Bosch number of 0.1 to 0.4 depending on engine type), and particulate emissions reduced 30 to 50 % with "divided" chamber and increased 90 to 140 % with a DI engine. The soluble organic fraction of particulate emissions increased by up to 15 % when rapeseed oil was used. They found that total emissions of aldehyde and ketones were 30 to 330 % higher with rapeseed oil; emissions of aromatic hydrocarbons were significantly higher with rapeseed oil. Emission profiles of particulate bound polycyclic aromatic hydrocarbon emissions (PAH) showed anthracene and phenanthrene had the highest concentrations followed by pyrene, chrysene, and fluoranthene. PAH emissions "were reduced to about one-third with big pre-combustion and swirl chamber engines. They

increased with rapeseed oil in DI engines and the small swirl chamber engines by 10 to 140 % compared with diesel fuel.

Marshall (1993) reported on using methyl esters in a stationary Cummins L-10E engine and a Cummins 5.9 L in a Dodge pickup tested on a chassis dynamometer. The L-10E engine was tested using the 13-mode emissions test and the pickup with a transient Federal Test Procedure test. They reported "Emission trends were very similar to those reported for other heavy duty diesel engines. That is, emission levels of HC, CO, and particulates decreased significantly for the SoyDiesel blends compared to the diesel fuel. The decrease from the base fuel for these three components was about 5% per 10% incremental addition of methyl soyate to the fuel. NOx emissions tended to increase linearly with the level of methyl soyate in the fuel-- approximately 1.4% per 10% incremental addition of methyl soyate." They hypothesized that the increase in NOx was associated with cetane number or ignition delay characteristics. They reported that fuels with very high cetane numbers are associated with very high NOx emissions. They further comment that there is much information in the technical literature associating increased NOx emissions with lower cetane fuels. However, they say the low cetane number was created by increasing the aromatics content, which was not done in their study.

Marshall (1993) found the following for the pickup truck. There was no regular, systematic effect of soyate level on HC and NOx, particulates increased with the content of methyl soyate and reached 70% above the low sulfur diesel, and CO decreased with increasing soyate level. They reported quite high NOx -- 6 grams per mile (gpm) whereas the EPA standard for vehicles of this weight class is 1.7 gpm. Emission levels of HC, CO, and particulates were at or below the EPA standards. In this study, 5 % by volume methyl soyate resulted in a 1 % increase in BSFC, 18 % reduction in HC, 8 % reduction in CO, 0.7 % reduction in NOx, and a 4.5 % decrease in PM.

Marshall (1993) reported that there did not appear to be any fuel effect on aldehyde emissions. The levels with the 5.9 L Cummins engine were quite high for all three fuels -- approximately 90 milligrams per mile compared to levels of 3 to 10 mgpm for spark ignition vehicles. One possible reason is the difference in the test procedures for light and heavy duty vehicles.

Mittelbach et al. (1985) used a 2.3 L turbocharged, four cylinder, four stroke, DI prototype diesel engine with exhaust gas recirculation (EGR) under transient operating conditions on a chassis dynamometer for emissions tests with methyl ester of refined (RME) and unrefined (URME) rapeseed oil. Two U.S. diesel fuels and an Austrian diesel fuel were used for controls. They state, "It is common knowledge that by heating fats and oils various volatile compounds like aldehydes and ketones are produced." When using rape oil and RME as diesel fuels, the typical smell of burnt fat can be detected, which could originate from unsaturated aldehyde like acrolein. They determined 10 polycyclic aromatic hydrocarbon compounds. For all fuels, the tests showed high formaldehyde (40 %) and very low acetaldehyde. For the sum of C-3 aldehydes, URME was highest and RME was similar to

US fuel B, whereas US fuel A and Austrian diesel fuel were lowest. The transformation of rapeseed oil into the methyl ester at least reduces the emissions of C-3 aldehydes significantly. In these tests, HC was reduced, CO unchanged, and NOx increased. NOx of the ester fuels was 0.56-0.62 gm/km while NOx of the diesel fuels was 0.47 -0.5 gm/mile. They conclude, "rapeseed oil methyl esters do not lead to irregular PAH-emissions."

Recently completed tests by ORTECH (Goetz, 1993) using a 20 % blend of Biodiesel and 80 % diesel fuel showed that a 3-degree timing change decreased NOx by 4.6 %, HC by 14.5 %, CO by 9.8 %, and PM by 17.2 % compared to diesel with no timing changes. Humphrey and Schumacher (1994) reported on emissions testing conducted by Cummins Engine Company in an EPA certified testing laboratory. Cummins tested a 5.9 liter, turbocharged, intercooled, direct injected diesel engine. The engine was fueled on biodiesel and reference diesel fuel. The tests revealed the following significant results: 1) reduction in smoke up to 83 %; 2) reduction in hydrocarbons by 48 %; 3) a decrease of CO by 1 %; 4) an increase in NOx by 14 %; and 5) a reduction in particulate emissions by 20 %.

Additional emissions testing by the University of Missouri with automobile inspection emissions analysis equipment on a 1991 Dodge pickup equipped with a 5.9 liter turbocharged, intercooled direct injection Cummins diesel engine revealed slightly lower CO, CO₂, and HC emission levels. There are very little sulfur emissions due to the absence of sulfur in plant oils.

Manicom et al. (1993) reports that tests were conducted on a 1991, DDC 6V-92 TA engine using the EPA Heavy-Duty Transient Test Cycle. They tested blends of 10, 20, 30, and 40 % methyl soyate in comparison with a diesel control fuel. FMD subcontracted ORTECH International to carry out the testing. The diesel control fuel used was ESSO Diesel # 1. One cold start transient test and four hot start transient tests were completed on each fuel. The results showed nearly linear changes with percent fuel. The 40 % blend of methyl soyate had the following results: HC down 39.5%; CO down 29.1%; NOx up 15.0%; PM down 17.8 %. Increased blend levels increased NOx while reducing PM. Proportionately, PM reductions were slightly more than the increase in NOx. The reduction in PM was attributed to the oxygen in the fuel. Total particulates for a 20 % blend are reduced by 11.1 %, but the soluble fraction increases from 40 % to 51 %.

Manicom et al. (1993) reported that "the addition of methyl soyate to diesel fuel had the effect of lowering particulates, hydrocarbons, and carbon monoxide emissions while increasing NOx emissions. The optimum blend of methyl soyate and diesel, based on the trade-off of particulates decrease with NOx increase, was 20 % methyl soyate in diesel. Due to the increase in NOx emissions in parallel with decreased exhaust temperatures, it is postulated that the methyl soyate is acting as a fuel cetane improver. This improvement in cetane is resulting in a reduced ignition delay time and thus an effective advance in injector timing."

Mills and Howard (1983) conducted an investigation of polynuclear aromatic hydrocarbon emissions with unmodified sunflower, rapeseed and soybean oils and modified ethyl ester of

sunflower vegetable oils. Three engine load/speed conditions were assessed for each fuel and emission levels were determined for 20 PAH compounds. Samples were generated using a probe in the exhaust pipe. The side stream of exhaust was first filtered to collect particulate bound PAH. Following filtration, the exhaust was transferred to two identical condensation traps for the removal of the vapor phase PAH. PAH profiles were strongly influenced by combustion conditions for all fuels tested. PAH profiles from the ethyl ester of sunflower oil (SEE) exhaust extracts showed similarities with diesel but were lower in total quantity. At 1500 rpm and no load, total PAH emissions ($\mu\text{g}/\text{m}^3$) for SEE were $289 \mu\text{g}/\text{m}^3$ compared to $3344 \mu\text{g}/\text{m}^3$ for "gas oil" and at 2350 rpm and full load $560 \mu\text{g}/\text{m}^3$ for SEE and $2405 \mu\text{g}/\text{m}^3$ for "gas oil". This work was conducted on a Petter BA2, DI diesel engine. Instruments were available for CO, CO₂, and Bosch smoke number. Only 1 gallon of each fuel was available which restricted the number of test conditions. Test conditions used were 1500 rpm, no load; 2350 rpm, half load; and 2350 rpm, full load.

Liotta and Montalvo (1992) used a 1991 prototype Detroit Diesel Series 60 engine installed in a transient capable test cell to study the effect of 8 oxygenates, one of which was methyl soyate. They showed that PM emissions were directly related to the concentration of oxygen in the fuel; higher oxygen results in lower PM. PM reductions were accompanied by small increases in NO_x emissions. Addition of the oxygenate to the fuel reduced CO and HC emissions; non-regulated aldehyde and ketone emissions were also reduced with the addition of an oxygenate. The composition of the PM from the 11 oxygenated fuels was compared with the reference fuel. The composition remained essentially unchanged. Volatile aldehydes and ketones found in the engine exhaust were measured for each of the fuels. The aldehydes that were speciated and measured include formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, hexanaldehyde, isobutyraldehyde, and benzaldehyde. Two ketones, acetone, and methyl ethyl ketone also were measured. All of the oxygenated fuels, except for the fuel containing the aliphatic alcohol, had lower aldehyde and ketone emissions. Typically, total aldehydes and ketones were decreased 10 to 25 %. Unfortunately, in this study no data aldehyde and ketone data were taken for the methyl soyate.

This review of literature on emissions test results with vegetable oil fuels brings one to the conclusion that ethyl and methyl esters of vegetable oils are essentially similar to diesel fuel in their emissions characteristics. In some studies, HC is reduced as much as 50 %; CO is reduced by as much as 10 %; NO_x and PM are related and tend to change inversely with each other, differing from diesel by at most 10-15 %. Generally, NO_x was found to be slightly higher than diesel and PM slightly lower than diesel, although this differs with particular conditions. In this case, NO_x was about $0.56 \text{ gm}/\text{mile}^1$ for Biodiesel and $0.48 \text{ gm}/\text{mile}$ for diesel. The last note on this literature review is that of the approximately 20 papers reviewed, no two used exactly the same protocol so as to be directly comparable.

¹EPA suggests grams per mile abbreviated gpm be used in reporting emissions data. Because of the possible confusion with gallons per mile the abbreviations chosen in this paper are those used by Dunlap et al. (1993) and Dunlap (1994) gm/mile to clearly indicate grams per mile.

MATERIALS AND METHODS

The emissions tests were conducted at the Los Angeles Metropolitan Transit Authority (MTA) Emissions Testing Facility (ETF) located in Los Angeles, California. This facility has instrumentation to measure the regulated emissions (total hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matter (PM)) and carbon dioxide (CO₂). The ETF provides quality assurance test results and calibrations in accordance with California Air Resources Board (CARB) quality assurance recommendations. (Dunlap, 1994).

Chassis Dynamometer

The ETF is equipped with a Schenck Pegasus transient chassis dynamometer driven by a 447 kW (600 hp) DC motor, a computerized control room, sophisticated emissions recovery capability, measurement and recording equipment, and various testing stations. The chassis dynamometer comprised a 1829 mm (72-inch) diameter roller assembly connected to a DC motor and planetary gear box assembly. The complete assembly was suspended on flexible supports, facilitating measurement of the torque on the rollers.

Test Cycles

Two test cycles were utilized for this test program. The first was a modified arterial cycle (arterial). The standard form event cycle was doubled, creating a 758 s, 8 event cycle. The arterial cycle, as used, has eight repetitions of accelerating to 64 km/h (40 mph) and decelerating to 0 km/h (0 mph), Figure 10-1. The second was the EPA Dynamometer Driving Schedule for Heavy-Duty Vehicles (Code of Federal Regulations 40, Part 86, Appendix I, Cycle D), Figure 10-2. The EPA cycle has a total time of 1060 s.

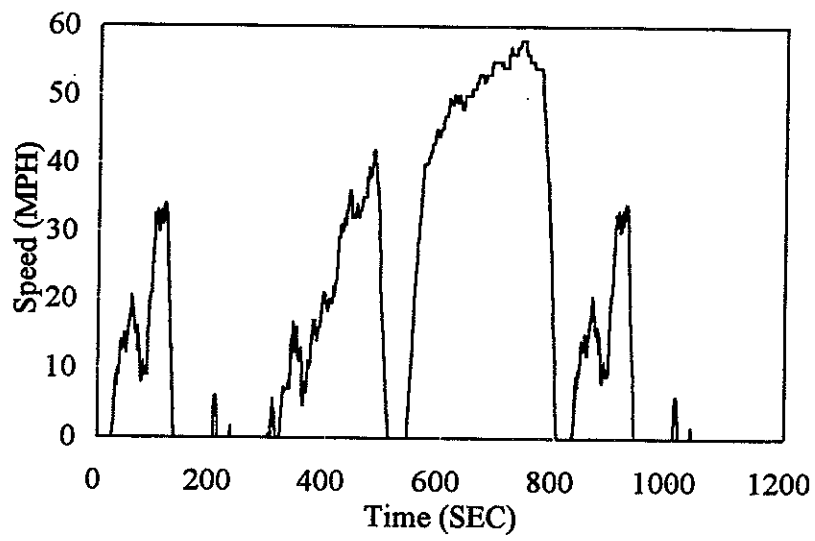
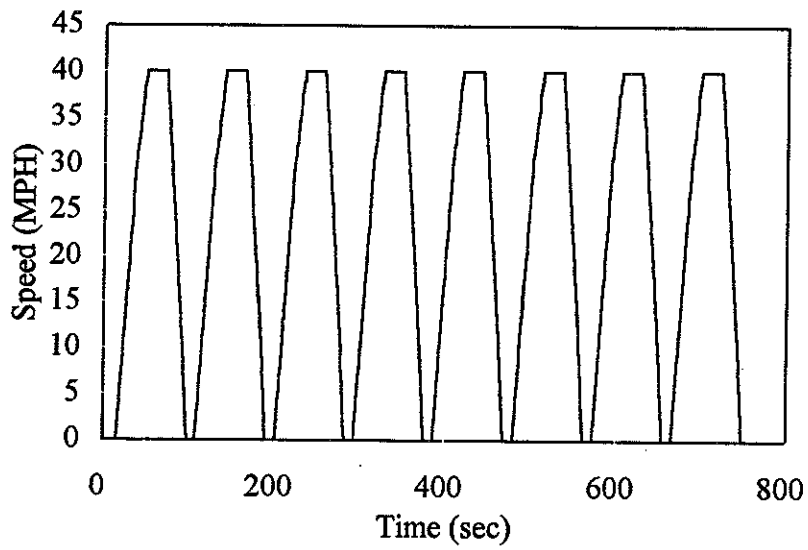


Figure 10-1. Modified Arterial Cycle.

Figure 10-2. EPA Cycle.



Road Load Simulation

In order to measure the emissions of a vehicle during operation, the actual driving conditions

of the vehicle on the road must be simulated on the dynamometer. The dynamometer control system must simulate the force that would act on the vehicle if the vehicle were traveling on the road. This force, or Road Load (RL), is defined by the equation below. (Dunlap, 1994.)

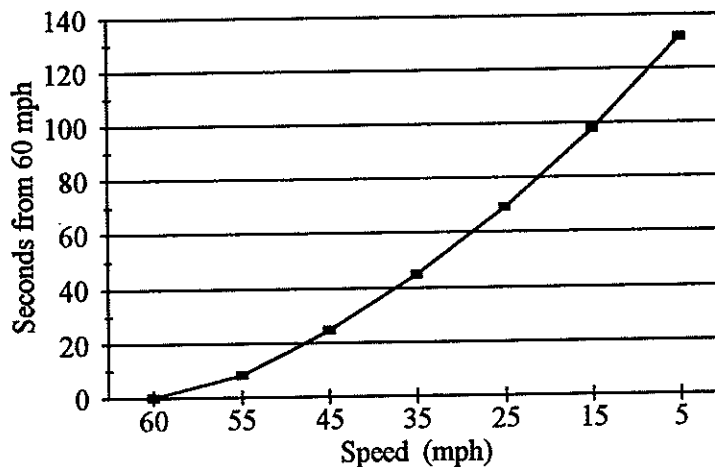


Figure 10-3. Coast-down data for 1994 Dodge pickup, 6,740 lbs Curb weight with driver, 7,900 lbs as tested

$$RL = F_0 + F_1 V + F_2 V^n + I \frac{dv}{dt} + mg \sin(\text{grad})$$

where:

RL = Road Load (force at roller surface)

F_0 = Coefficient of friction force - independent of velocity

F_1 = Coefficient of friction force - dependent on velocity

F_2 = Coefficient of windage force (drag coefficient)

n = Velocity exponent

V = Velocity at the roller surface

I = Vehicle Inertia (Dyno inertia plus appropriate amount of inertia as simulated by the control system)

$\frac{dv}{dt}$ = Acceleration

m = Vehicle Mass

g = Acceleration due to gravity

grad = Gradient in %

The EPA and Arterial test cycles do not include any gradients (uphill or downhill) therefore, the Road Load equation becomes:

$$RL = F_0 + F_1 V + F_2 V^n + I \frac{dv}{dt}$$

To aid in the development of a set of coefficients, University of Idaho personnel conducted a coast down evaluation of the test vehicle in Idaho prior to the scheduled ETF test date, Figure

10-3. The coast down test involves accelerating the vehicle to 96 km/h (60 mph) and then letting it coast (decelerate) while recording the time for each speed until the truck comes to a stop. Based on the coast down data, LA-MTA personnel developed a set of coefficients as a starting point for road load model development. Once the vehicle was installed on the dynamometer, coast downs were conducted and the model was refined to match the average on-road data. This refinement process was necessary to "factor out" the internal dynamometer resistance. The coefficients developed for this program are $F_0 = 22.7$ kg (50 lbs), $F_1 = 0.237$ kg/km (0.84 lbs/mph), $F_2 = 0.000025$ kg/km² (0.00009 lbs/mph²) and $I = 3583$ kg (7,900 lbs).

Fuels Tested

Fuels tested included:

- (1) Phillips 2-D low-sulfur diesel control fuel (2-D)
- (2) 100 % rape methyl ester (100RME)
- (3) 100 % rape ethyl ester (100REE)
- (4) 50 % RME - 50 % diesel (50RME)
- (5) 50% REE - 50% diesel (50REE)
- (6) 20 % RME - 80 % diesel (20RME)
- (7) 20 % REE - 80 % diesel (20REE)
- (8) An ethyl ester of waste hydrogenated soybean oil (HySee)
- (9) A blend of 80 % diesel, 10 % REE and 10 % ethanol (3-CEE);
- (10) A blend of 90 % REE and 10 % ARCO DTBG additive

The RME and REE were produced in the Biological and Agricultural Engineering Laboratory at the University of Idaho. Results for fuels 8, 9, and 10 are beyond the scope of this article and are not reported. A complete set of fuel characterization data for each fuel reported is given in Table 1.

Table 10-1. Fuel characterization data.

| | 2-D | RME | 50RME | 20RME | REE | 50REE | 20REE |
|----------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Fuel Specific Properties | | | | | | | |
| Specific Gravity, 60/60 | 0.8495 | 0.8802 | 0.8632 | 0.854 | 0.876 | 0.862 | 0.8535 |
| Viscosity cSt @ 40°C | 2.98 | 5.65 | 3.9 | 3.1 | 6.11 | 4.06 | 3.2 |
| Cloud Point, °C | -12 | 0 | -7 | -12 | -2 | -9 | -12 |
| Pour Point, °C | -18 | -15 | -15 | -15 | -10 | -13 | -15 |
| Flash Point, PMCC, °C | 74 | 152 | 85 | 82 | 124 | 79 | 76 |
| Boiling Point, °C | 191 | 347 | 209 | 194 | 273 | 204 | 213 |
| Water and Sediment, % vol. | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| Carbon Residue, % wt | 0.16 | 0.08 | 0.07 | 0.08 | 0.1 | 0.07 | 0.12 |
| Ash, % wt | 0.002 | 0.002 | 0.002 | 0.00 | 0.00 | 0.00 | 0.00 |
| Sulfur, % wt | 0.036 | 0.012 | 0.026 | 0.035 | 0.012 | 0.024 | 0.033 |
| Cetane Number | 49.2 | 61.8 | 55 | 51.4 | 59.7 | 54.2 | 50.7 |
| Heat of Combustion, MJ/kg | | | | | | | |
| Gross | 45.42 | 40.54 | 42.88 | 44.54 | 40.51 | 42.94 | 44.64 |
| Net | 42.90 | 37.77 | 40.18 | 41.81 | 37.82 | 40.08 | 41.94 |
| Copper Corrosion | 1A | 1A | 1A | 1A | 1A | 1A | 1A |
| Karl Fischer Water, ppm | 38 | 535 | 288 | 153 | 757 | 308 | 200 |
| Particulate Matter, mg/L | | | | | | | |
| Total | 0.9 | 1.0 | 1.1 | 1.0 | 1.0 | 1.4 | 1.1 |
| Non-Combustible | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Elemental Analysis | | | | | | | |
| Nitrogen, ppm | | 6 | | | 11 | | |
| Carbon, % | 86.67 | 76.3 | 82.75 | 84.76 | 78.11 | 82.07 | 84.73 |
| Hydrogen, % | 12.98 | 11.56 | 12.75 | 12.89 | 12.66 | 13.49 | 12.73 |
| Oxygen, % (by difference) | 0.33 | 12.2 | 4.47 | 2.35 | 9.22 | 4.42 | 2.51 |
| Iodine Number | 8.6 | 95.8 | 54.2 | 24.5 | 91.9 | 52.6 | 24.3 |
| Ester Specific Properties | | | | | | | |
| Percent Esterified | 98.02 | 94.75 | | | | | |
| Acid Value | 0.128 | 0.097 | | | | | |
| Free Glycerine, %wt | 0.4 | 0.72 | | | | | |
| Total Glycerine, % wt | 0.86 | 0.93 | | | | | |
| Free Fatty Acids, %wt | 0.57 | 0.58 | | | | | |
| Monoglycerides, %wt | 0 | 0.58 | | | | | |
| Diglycerides, %wt | 1.35 | 1.33 | | | | | |
| Triglycerides, %wt | 0.45 | 2.17 | | | | | |
| Alcohol Content, %wt | <1 | <1 | | | | | |
| Catalyst, ppm | 11 | 12 | | | | | |
| Fatty Acid Composition | | | | | | | |
| Palmitic (16:0) | 2.8 | 2.6 | | | | | |
| Oleic (18:1) | 12.6 | 12.8 | | | | | |
| Linoleic (18:2) | 12.1 | 11.9 | | | | | |
| Linolenic (18:3) | 8 | 7.7 | | | | | |
| Eicosenoic (20:1) | 7.4 | 7.4 | | | | | |
| Erucic (22:1) | 49.8 | 49.7 | | | | | |

Emissions Analyzers

Dunlap (1993) gave the following description of the test facility. The ETF's analytical system was composed of seven emissions analyzers. The hydrocarbon (HC) analyzer used the principle of hydrogen flame ionization to measure hydrocarbons, and included a complete Heated Flame Ionization Detector (HFID). This analyzer offered proven reliability for diesel testing where high-boiling hydrocarbons were present.

Nitrogen oxides (NO_x) were measured using a chemiluminescent analyzer which monitored the chemiluminescent reaction of ozone (O₃) with nitric oxide (NO). This analyzer measured a wide range of NO and nitrogen dioxide (NO₂) concentrations with negligible interference from other gas components. The analyzer was equipped with an ozone generator, which produced ozone for the reactions (O₃) from oxygen, or air using an ultraviolet ozone generating method.

Carbon monoxide (CO) and Carbon dioxide (CO₂) were measured using non-dispersive infrared (NDIR) detection. The ETF analytical bench was equipped with a total of four NDIR analyzers and was therefore able to measure both low and high concentrations of CO and CO₂. The analyzer that measured low CO concentrations incorporated a unique dual-detector optical bent to obtain high sensitivity and accuracy, even in the presence of water vapor, carbon dioxide, and other interfering gases, eliminating the need for chemical reagents and gas dryers to remove water vapor and CO₂ from the sample for analysis.

Oxygen (O₂) concentrations were measured during raw, or non-dilute, testing using a magnetopneumatic sensing method. The analyzer provided an accurate and continuous determination of O₂ with negligible interference from other gaseous components. Since current CARB testing protocol emphasizes dilute bag results, no raw testing was done on this test vehicle. (Dunlop, 1994)

Test Vehicle

The vehicle tested was a 1994 Dodge pickup with a direct injected, turbocharged and intercooled, 5.9 L Cummins diesel engine. The vehicle had accumulated 2,414 km (1,500 miles) on diesel and 3,860 km (2,400 miles) on rape ethyl ester at the time of this test. The vehicle was driven from Moscow, Idaho to Los Angeles, California on 100 percent REE fuel for testing. Weight used during the test and for coast down was 3,590 kg (7,900 pounds).

The engine was not modified in any way for use with the vegetable oil fuels. The fuel delivery system was modified for convenience of changing fuels between test runs. Fuel delivery and fuel return lines were broken and 3-way, manually operated valves were installed so that stub lines with quick couplers could be installed on one part of the 3-way valves. Individual 19 L (5 gal) fuel tanks were modified with fuel filter and flexible lines which could be connected to the 3-way valves. During normal operation, fuel was delivered and returned to the vehicle tank. During testing the valves were switched to the external lines to which the correct test fuel was connected. For the tests, the fuel filter assembly mounted on the engine was

removed and replaced with an aluminum block with internal connecting ports. This change was necessary to minimize the amount of fuel in the system when a fuel switch was required. Fuel filters were provided on each fuel delivery tank.

Timed practice sessions with fuels of different colors showed that a minimum of 20 s was required for the return lines to be clear of the previous fuel. During actual testing, the return line was directed to a waste fuel tank while the engine was operated for 50 s at which time the return line was directed back into the test fuel tank. The low standard deviations in emissions data between tests of the same fuel were indicative of the success of the procedure for changing fuels.

Vehicle Installation

The test vehicle was installed on the chassis dynamometer in accordance with typical ETF practice. A total of seven sensors were installed but the fuel pressure sensor was not utilized due to a problem that occurred with the fitting. The test sensor locations were at the oil filter adapter housing, boost pressure at manifold, exhaust temperature at tailpipe adapter, fuel pressure at pump inlet, coolant temperature, and inlet air temperature.

Fuel Mass Flow Rate

Fuel use was determined by direct weighing. The fuel containers were placed on an electric scale. Weight of fuel was read at the start and end of each test. In practice, this method had considerable error due to vibrations set up by running the truck because of the direct connection between the fuel tank on the scales, the fuel delivery and return lines, and engine connections.

Test Design

Two problems had to be overcome in developing a test design. The first was that the potential number of test runs was unpredictable. The test facility was scheduled for one week during which time all testing had to be completed. The second problem was a tendency for emissions to vary with ambient conditions. A randomized block design with unequal sample numbers was developed. In this design, the main fuels were randomized and tested first and tests of fuel blends were included in later tests in each block. The fuel test procedure is shown in Table 10-2. As it turned out, sufficient time was available to test each fuel and desired blend.

Table 10-2. Test plan for emissions tests.

| Arterial Cycle | | | |
|-----------------------|-------------|-------------|-------------|
| Block 1: | 100% REE | 100% Diesel | 100% RME |
| Block 2: | 100% Diesel | 100% REE | 100% RME |
| Block 3: | 20% REE | 20% RME | 50% RME |
| | 50% REE | Fuel A | Fuel A |
| | 100% Diesel | | |
| Block 4: | 100% Diesel | 100% RME | 100% RME |
| | 100% REE | 100% REE | |
| Block 5: | 20% REE | 100% Diesel | 20% RME |
| | Fuel B | Fuel B | 50% REE |
| | 50% RME | 100% Diesel | |
| EPA Cycle | | | |
| Block 6: | 100% REE | 100% Diesel | 100% RME |
| | 100% REE | 100% RME | 100% Diesel |
| | 100% RME | | |
| Block 7: | 20% RME | 20% REE | 100% REE |
| | 100% Diesel | Fuel C | 50% REE |

A Fisher's Protected LSD analysis using SAS (Statistical Analysis System) was carried out on the data.

Test Procedure

The test procedure was as follows:

1. The test fuel delivery tube was connected to the input lines and the return line was connected to the waste tank. The engine was started and run for 50 s.
2. The engine was stopped and the return line was connected to the test fuel tank.
3. The engine was restarted and idled for approximately 10 min until the MTA technicians were ready to run the test.
4. The vehicle was operated under load until the operating temperatures stabilized.
5. The test was started and the cycle completed.
6. While the technicians were taking data, weighing particulate filters, and doing span gas tests, the fuel was switched to the next fuel to be tested.

Tests were conducted on March 14-18, 1994. Twenty-six modified arterial cycles and 13 EPA test cycles were completed. On one day, a shortage of gas for the flame ionization detector caused some delay and a need to replicate one run. Otherwise, the tests proceeded very smoothly and with very good repeatability.

PRESENTATION AND DISCUSSION OF RESULTS

Since a large amount of data was collected, only summary data is reported in this paper. It is anticipated that additional papers will be presented as modal summaries or correlations between test variables are completed. Modal data were archived every 1 s during the test. Average and total values were calculated for cycles, phases and overall. Thus the potential exists for additional analysis of test data.

Summaries of these data are shown in three ways. First, averages by arterial and EPA cycle for each fuel and for each of the regulated exhaust emissions were computed using Fisher's Protected LSD. This procedure makes adjustments for the unequal sample numbers. Statistical significance is indicated in each of the summary tables. The statistical analysis for days of test showed that the EPA cycle was significantly different from the arterial cycle for all parameters measured (not shown). All of the measured emissions were higher for the EPA

cycle than for the arterial cycle. This was probably due to the increased idling time and non-repetitive nature of the EPA

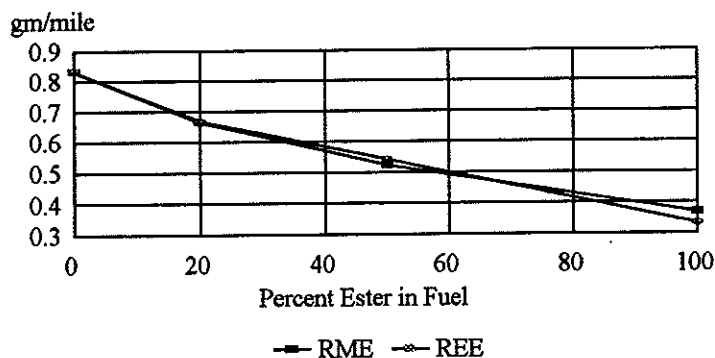


Figure 10-4. Total HCs in gm/mile for the modified arterial cycle.

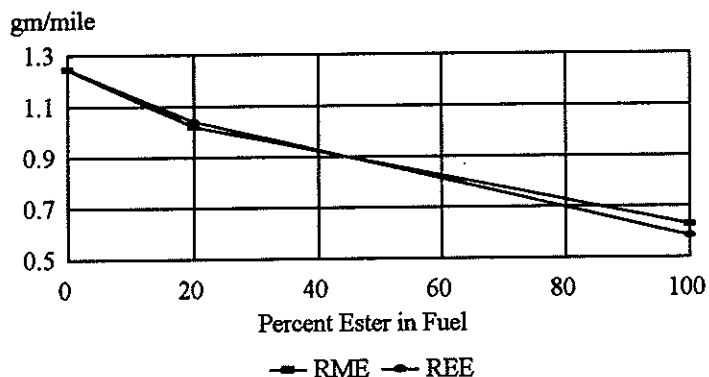


Figure 10-5. Total HCs in gm/mile for the EPA cycle.

and NOx as percent of vegetable oil was increased and a non-significant increase in PM. The PM data had the most variability of the data and an examination of the raw data showed that there was scatter sufficient to neutralize differences.

Figures 10-4 through 10-13 show the data for each test parameter. The graphs show 100% diesel to 100% vegetable oil as the ordinate and the particular emissions parameter reported in gm/mile as the abscissa. Figures 10-14 through 10-16 show a summary of the data, averaged for RME and REE and both cycles, with CO and CO₂ plotted together on one graph, HC and NOx on a second graph, and PM on a third graph.

These data show similar trends for all fuels with a slight reduction in CO and NOx for ethyl ester compared to methyl ester. They also show a significant reduction in HC, CO,

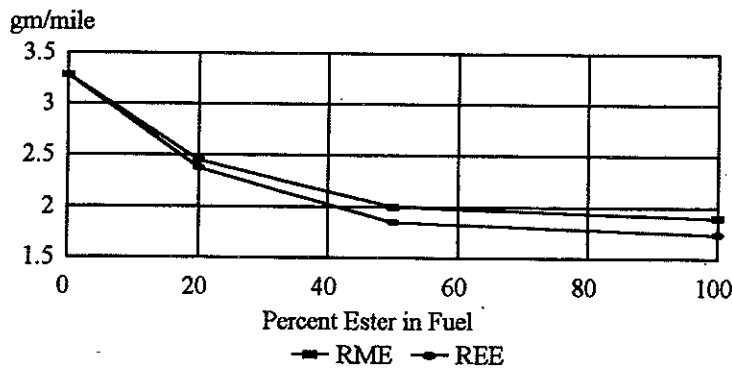


Figure 10-6. Carbon monoxide in gm/mile for the modified arterial cycle.

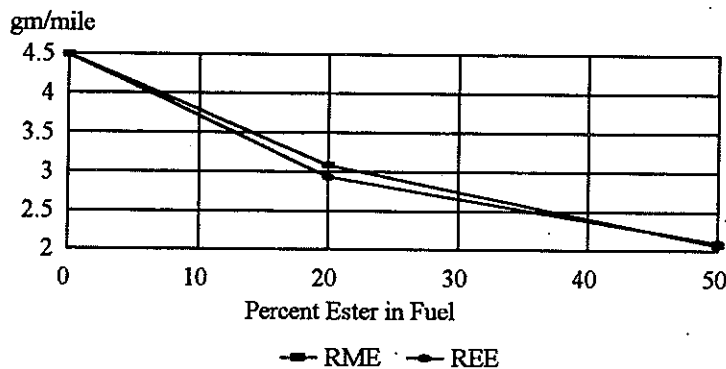


Figure 10-7. Carbon monoxide in gm/mile for the EPA cycle.

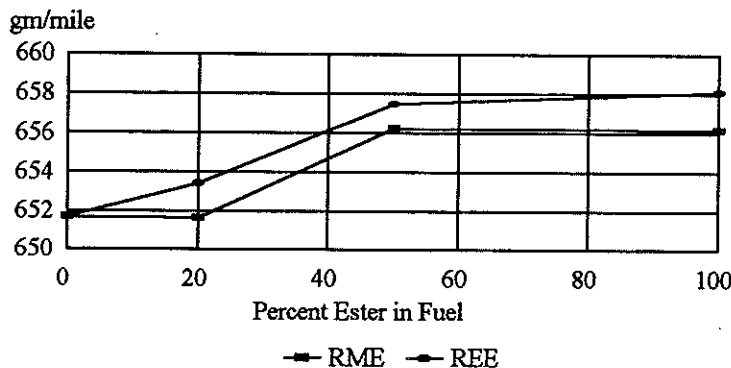


Figure 10-8. Carbon dioxide in gm/mile for the modified arterial cycle.

The third presentation of the data are tables 10-3 through 10-6, showing the percent change in the emissions compared to the diesel control fuel for ethyl and methyl ester of rapeseed oil for arterial and EPA cycles and overall averages. Tables 10-7 and 10-8 compare REE and RME averaged for both cycles. These tables show that HC and CO were reduced approximately 50% by using rapeseed esters. Carbon dioxide increased by an amount indicative of the reduction in CO. No statistically significant change in PM was detected. The trend was for reduced PM for 20% vegetable oil ester and increased PM for the 100% vegetable oil ester fuels.

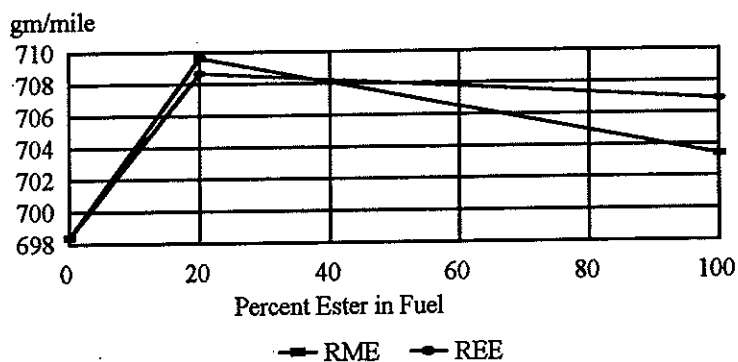


Figure 10-9. Carbon dioxide in gm/mile for the EPA cycle.

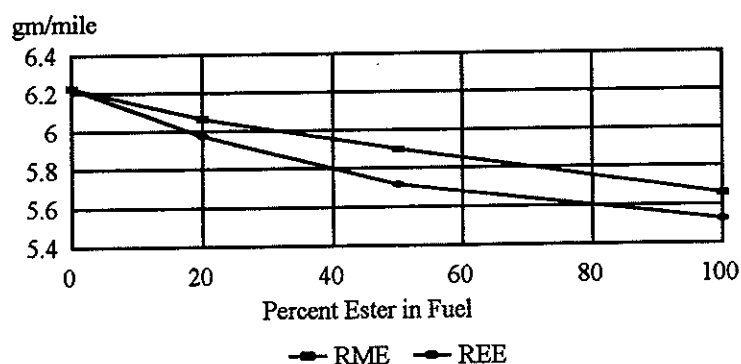


Figure 10-10. Nitrogen oxide in gm/mile for the modified arterial cycle.

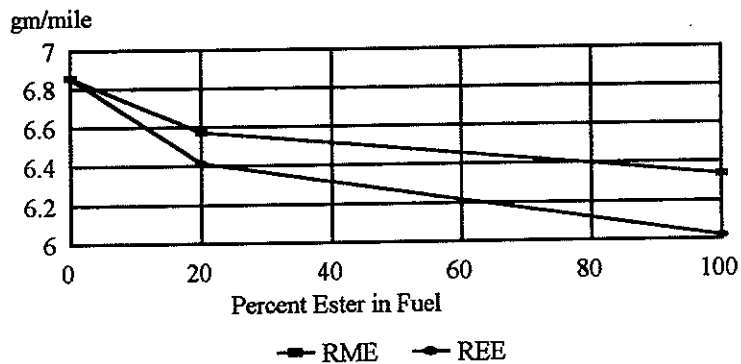


Figure 10-11. Nitrogen oxide in gm/mile for the EPA cycle.

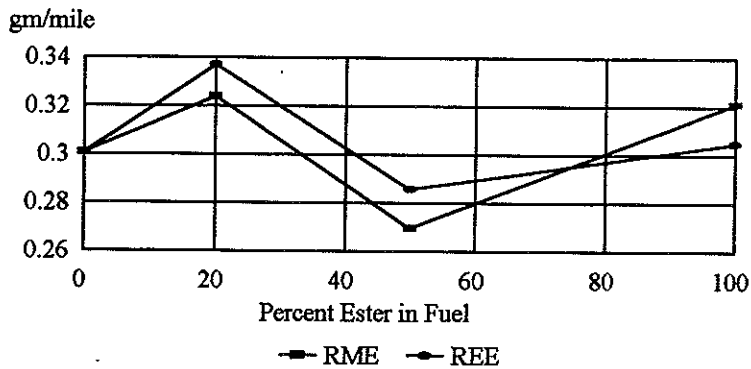


Figure 10-12. Particulate matter in gm/mile for the modified arterial cycle. Differences are nonsignificant according to Fischer's protected LSD comparison.

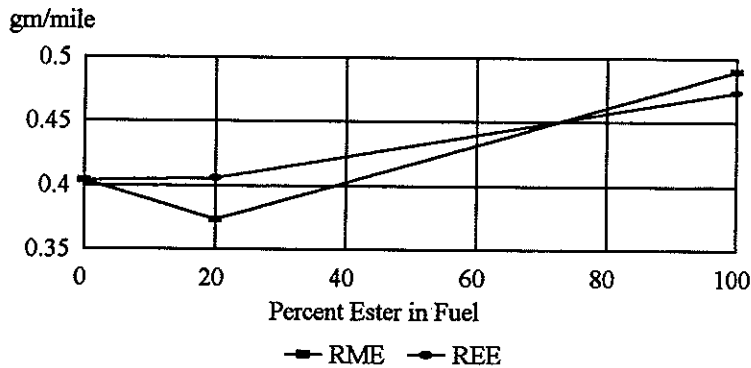


Figure 10-13. Particulate matter in gm/mile for the EPA cycle. Differences are nonsignificant according to Fischer's protected LSD comparison.

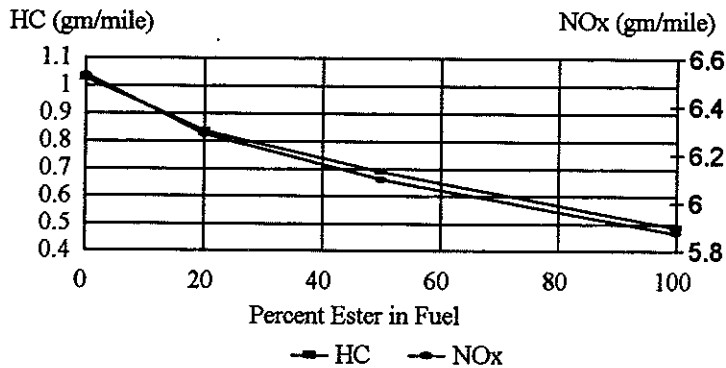


Figure 10-14. Summary of HC and NOx data averaged for both RME and REE and for both the modified arterial and EPA cycles.

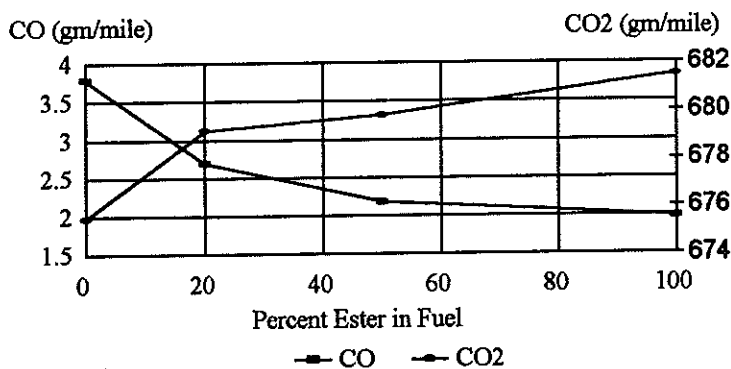


Figure 10-15. Summary of CO and CO₂ data for both REE and RME and for both the Modified arterial and EPA cycles.

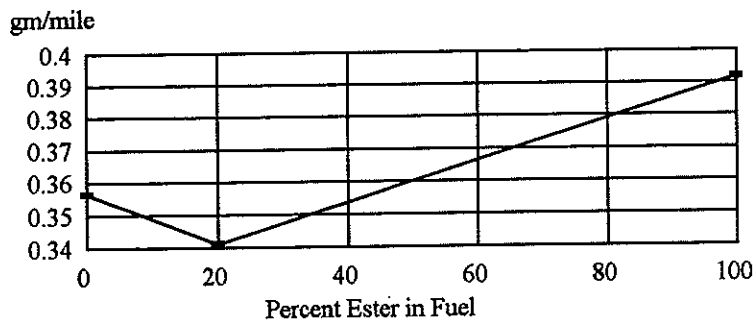


Figure 10-16. Summary of PM data for both REE and RME and for both the modified arterial and EPA cycles.

Table 10-3. Emissions percent increase (+) or decrease (-) for blends of REE compared to diesel control fuel - arterial cycle.

| | Volume Percent of REE in Diesel Control Fuel | | |
|-----------------|--|--------|--------|
| | 20% | 50% | 100% |
| HC | -19.7* | -35.1* | -60.1* |
| CO | -27.6* | -43.7* | -47.1* |
| NO _x | -4.1* | -8.2* | -11.3* |
| CO ₂ | +0.3 | +0.9 | +1.0* |
| PM | -5.0 | +12.1 | +1.3 |

* Significantly different from diesel ($p \leq 0.05$).

Table 10-4. Emissions percent increase (+) or decrease (-) for blends of RME compared to diesel control fuel - arterial cycle.

| | Volume Percent of RME in Diesel Control Fuel | | |
|-----------------|--|--------|--------|
| | 20% | 50% | 100% |
| HC | -20.2* | -37.2* | -55.6* |
| CO | -25.3* | -39.1* | -42.2* |
| NO _x | -2.6* | -5.3* | -9.1* |
| CO ₂ | 0 | +0.7 | +0.7* |
| PM | -10.4 | +7.6 | +6.8 |

* Significantly different from diesel ($p \leq 0.05$).

Table 10-5. Emissions percent increase (+) or decrease (-) for blends of REE compared to diesel control fuel - EPA cycle.

| | Volume Percent of REE in Diesel Control Fuel | | |
|-----------------|--|--------|--------|
| | 20% | 50% | 100% |
| HC | -16.5* | -31.5* | -53.1* |
| CO | -34.6* | -50.0* | -53.2* |
| NO _x | -6.5* | -8.4* | -12.2* |
| CO ₂ | +1.5 | +0.1 | +1.2 |
| PM | -0.4 | +10.8 | +17.2 |

* Significantly different from diesel ($p \leq 0.05$).

Table 10-6. Emissions percent increase (+) or decrease (-) for blends of RME compared to diesel control fuel - EPA cycle.

| | Volume Percent of RME in Diesel Control Fuel | | |
|-----------------|--|-----|--------|
| | 20% | 50% | 100% |
| HC | -18.0* | | -49.5* |
| CO | -31.3* | | -54.0* |
| NO _x | -4.1* | | -7.6* |
| CO ₂ | +1.6 | | +0.7 |
| PM | +7.6 | | +21.2* |

* Significantly different from diesel ($p \leq 0.05$).

Table 10-7. Emissions percent increase (+) or decrease (-) for blends of REE averaged for arterial and EPA cycles compared to diesel control fuel.

| | Volume Percent of REE in Diesel Control Fuel | | |
|-----------------|--|--------|--------|
| | 20% | 50% | 100% |
| HC | -18.0* | -32.3* | -54.6* |
| CO | -30.0* | -45.5* | -48.8* |
| NO _x | -4.6* | -7.9* | -11.6* |
| CO ₂ | +0.5 | +0.6 | +1.1 |
| PM | -1.3 | +1.2 | +8.0 |

* Significantly different from diesel ($p \leq 0.05$).

Table 10-8. Emissions percent increase (+) or decrease (-) for blends of RME averaged for arterial and EPA cycles compared to diesel control fuel.

| | Volume Percent of RME in Diesel Control Fuel | | |
|-----------------|--|--------|--------|
| | 20% | 50% | 100% |
| HC | -18.0* | -32.3* | -54.6* |
| CO | -30.0* | -45.5* | -48.8* |
| NO _x | -4.6* | -7.9* | -11.6* |
| CO ₂ | +0.5 | +0.6 | +1.1 |
| PM | -1.3 | +1.2 | +8.0 |

* Significantly different from diesel ($p \leq 0.05$).

As stated earlier, Barenescu (1995) and Holmberg and Peebles (1994) have indicated that NO_x and PM are inversely related. That may explain the apparent difference in results from these tests. More generally, it has been found that esters increase NO_x and decrease PM. However, in these tests, the reverse was generally true. One might speculate that this trend was due to the fatty acid constituents of rapeseed esters tested or that it was a characteristic of this particular engine. In either case, the result was consistent for both methyl and ethyl ester and for both cycles tested. Ethyl ester at the 100% and 50% level were lower in NO_x than methyl ester.

Repeatability for HC, CO, CO₂ and NO_x was very good. In these experiments, setting up the test procedure was extremely critical because of the limited number of possible runs in the available time. It may have been more desirable to have replicated each fuel two or three times in succession and to have randomly replicated each fuel in time. However, as a compromise, each fuel was tested in random order and then, during one block, fuels were tested in succession. The data show that the test procedure was successful in preventing mixing of fuels and that the choice of previous fuel did not affect the emissions measured for the succeeding fuel.

CONCLUSIONS

Specific conclusions of this study were:

1. HC was reduced by 52.4 % when 100 % vegetable oil fuel was compared to low sulfur diesel control fuel,
2. CO was reduced by 47.6 % when 100 % vegetable oil fuel was compared to low sulfur diesel control fuel,
3. CO₂ increased by 0.9 % when 100 % vegetable oil fuel was compared to low sulfur diesel control fuel,
4. NO_x was reduced by 10.0 % when 100 % vegetable oil fuel was compared to low sulfur diesel control fuel,
5. PM increased by 9.9 % when 100 % vegetable oil fuel was compared to low sulfur diesel control fuel (however, this difference was statistically non-significant. PM was the lone parameter that had variations sufficient to make differences non-significant. The result was in harmony with the literature, which reported a trade-off between PM and NO_x),
6. 100 % REE reduced HC (8.7 %), CO (4.3 %) and NO_x (3.4 %) compared to 100 % RME,
7. Absolute values of emissions data were higher for the EPA Cycle than for the arterial cycle. HC increased from 0.57 to 0.87 gm/mile; CO from 2.34 to 2.865 gm/mile; CO₂ from 657.8 to 703.8 gm/mile; NO_x from 5.88 to 6.41 gm/mile and PM from 0.305 to 0.44 gm/mile.,
8. Acceptable research protocols for exhaust emissions testing should be developed and standards written that are within the reach of the budgets of the average research facility. This would bring more uniformity to test procedures used by the various laboratories and institutions that do not have facilities necessary to meet the criteria for EPA official tests.

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CARBON CYCLE FOR RAPESEED OIL BIODIESEL FUELS

This study provides an outline of the carbon cycle for rapeseed oil derived fuels. Plant processes, fuel chemistry and combustion are examined with respect to the carbon. A diagram is presented to graphically interpret the information presented. A comparison of carbon dioxide emissions from combustion of rapeseed oil Biodiesel and petroleum diesel is made. Complete combustion converts hydrocarbon fuels to carbon dioxide and water. The carbon cycle is fixation of carbon and release of oxygen by plants through the process of photosynthesis, then the recombining of oxygen and carbon to form CO_2 through processes of combustion or respiration. The carbon dioxide released by petroleum diesel was fixed from the atmosphere during the formative years of the earth. Carbon dioxide released by Biodiesel is fixed by the plant in a recent year and is recycled. Many scientists believe that global warming is occurring because of the rapid release of CO_2 in processes such as combustion of petroleum diesel. Using Biodiesel could reduce the CO_2 accumulation in the atmosphere.

INTRODUCTION

According to the Global Change Research Information Office "The Consensus of most scientists worldwide is that increasing concentrations of greenhouse gases [carbon dioxide and methane, for example] will lead to significant climate warming, shifts in precipitation patterns and rising sea levels, although the magnitude, timing, and regional patterns of these changes cannot be accurately predicted at this time" (Gibbons, 1995).

The potential for Biodiesel (replacing petroleum diesel with a diesel engine fuel derived from animal fat or vegetable oil such as rapeseed oil) to reduce the carbon dioxide introduced into the atmosphere as a result of engine combustion has been suggested by several authors Sagar, 1995). Rapeseed oil is a renewable fuel, i.e., the oil is obtained from plant oils and animal fats. All of the carbon released by combustion of the plant oil has been fixed by the plant through the process of photosynthesis. Thus carbon dioxide from the air has been absorbed by the plant, converted to the lipids, processed into a renewable diesel fuel and then when the oil is used in the engine the carbon is again released into the atmosphere as carbon dioxide.

OBJECTIVE

To trace the carbon cycle for rapeseed methyl ester (RME) and rapeseed ethyl ester (REE) Biodiesel fuels and to compare with that of petroleum diesel fuel.

LITERATURE REVIEW

Gust (1995), Encyclopedia Britannica (1993) and Thomas (1984) outline the basic principles of the photosynthesis process. Thomas (1984) presents a brief discussion of the canola plant and the photosynthesis process, discusses different factors that affect photosynthesis and how these factors affect yield. Encyclopedia Britannica (1993) gives a detailed analysis of photosynthesis, offering complex but in-depth explanations which includes an examination of the photosynthetic carbon cycle on a molecular level. General chemical equations are presented, and inputs, such as different nutrients, are correlated to respective products such as fats and other organic compounds. The effect of biomass as both an emitter and a sequesterer of atmospheric carbon is discussed by Emil and Winnett (1997).. They say that domestic policy options can produce substantial carbon benefits although some markets may be disrupted.

Shepherd and Davies (1993) examine the loss of carbon from the rapeseed plant into the soil through the roots. They conclude that 17-19% of the fixed CO₂ is transferred to the roots, with 30-34% of that released into the rhizosphere, 23-24% respired directly as CO₂. Of the carbon released into the rhizosphere, 35-51% is assimilated by micro-organisms in the soil.

Reicosky (1994) and Galinato, et al. (1987) examine field reclamation principles and post-harvest use of excess crop material. Reicosky (1994) examines various physical and chemical processes that occur in the field after harvest, including post-harvest soil condition in which carbon plays an important role. The three important agricultural cycles (carbon, water, nitrogen) and their interdependence are discussed (Fig. 11-1), which includes a brief look at the processes carbon matter takes part in when it is left in the soil such as microbial decomposition. Galinato et al. (1987) discuss present and possible future uses of residual crop biomass, which present alternative pathways the carbon may take.

Ellington and Meo (1992) present a quantitative method that accounts for all greenhouse gases emitted from technical systems. They use a systems approach to compute the total warming related to the total lifetime useful output of the system to yield an index of performance that they call the Greenhouse Warming Index. They calculate 160 kg of CO₂ emitted for every 10⁹ J of methanol produced by the system and another 69 kg of CO₂ are emitted for every 10⁹ J of methanol burned in an engine.

Peterson (1986), Peterson et al. (1983), Clark et al. (1984), Strayer et al. (1983), Klopfontstein et al. (1983), Mittelbach and Tritthart (1988) and Nye et al. (1983) all discuss to some degree the extraction and processing techniques that vegetable oil undergoes before it is used as fuel. Peterson et al. (1983) report on using a screw press to extract raw oil from rapeseed achieving an efficiency of 77%. Also, to reduce viscosity, diesel oil can be mixed with the vegetable oil, a process which introduces carbon from an outside source. This technique is also examined by Strayer et al. (1983). Other forms of processing, filtration, and fuel storage were examined again by Peterson (1986).

Ward et al. (1985), Robbelen et al. (1989) and Peterson et al. (1983) discuss applications for the meal that is left over after the oil is removed from the seeds. Since the leftover meal contains carbon from the plant, what the meal is used for enters into the carbon cycle equation. Present uses for the meal include biomass fuel for direct combustion, fertilizer, and livestock feed.

Peterson (1986), Mittelbach and Tritthart (1988), Clark et al. (1984) Klopfenstein et al. (1983), and Nye et al. (1983) all discuss the process of transesterification, which conveniently produces an oil much lower in viscosity than that of the neat oils. Transesterification directly affects the carbon cycle because both the alcohol used in the process and the glycerol that separates from the ester as a result of the process contain carbon.

Springer (1973), Obert (1973), Liljedahl et al. (1979), and Henein and Patterson (1972) examine the combustion processes of internal combustion (IC) engines. Engine fundamentals including combustion principles, chemistry, and differences between actual and ideal combustion are examined in these references. Formation of emissions, their composition, measurement techniques, reduction processes (emission controls), and comparison of emission output between different engine and fuel types are covered.

Peterson and Reece (1994), Geyer et al. (1984), and Mittelbach and Tritthart (1988), look at the emissions from vegetable oil fuels and compare them to emissions from petroleum based fuel. Results from these tests show reduced CO and HC and essentially unchanged PM and NOx when using Biodiesel compared to petroleum diesel.

Warner (1976) examines air pollutants in detail, citing causes, hazards, measurement techniques and environmental effects. Attention is also given to the natural cycle of some of these compounds, looking at both production and degradation. Stephenson (1949), Hopper (1978), and Cripps and Watkinson (1978) examine ways in which microorganisms biodegrade organic compounds, which include emissions from IC engines. The microorganism processes, required inputs, and resulting products are discussed.

Robbelen et al. (1989) and Ward et al. (1985) discuss properties of oilseed rape, although primarily producing oil for food products. Included in their material are various uses of rapeseed oil and meal. Properties of rape compared to other oilseeds are briefly discussed as well.

Peterson et al. (1995) examine the possibilities for agriculturally produced fuels. They assert that there is significant potential for energy production agriculturally, but that it will require a large initial capital investment. Vegetable oils, ethanol and collected animal wastes are three of the most promising sources of energy.

Stephens (1994) gives a very good description of the global warming problem and the carbon cycle.

PHOTOSYNTHESIS

One of the first principles of physics is that matter cannot be created nor destroyed. Thus, all the carbon is presently on the earth that ever has been or ever will be (space exploration and nuclear physics excepted). All naturally occurring hydrocarbons were fixed by the photosynthesis process. In the case of petroleum, the process occurred millions of years ago. It can be speculated that the earth had a carbon dioxide rich atmosphere which was removed by plants in the process of photosynthesis. These plant materials were subsequently subjected to heat and pressure to create the rich resources of petroleum found below the surface of the earth. As this petroleum is utilized, the carbon dioxide is returned to the atmosphere where it originated (Fig. 11-2). This freeing of carbon dioxide is one of the issues of concern with regard to global change.

Consideration of all the issues related to global change is not a simple process. In an attempt to study the full implications of the causes and effects of global change the current request for funds by the US Geological Survey Global Change Research Program is 1.8 billion dollars. This brief paper then is obviously limited in scope. We can only hope to provide insight on the concept of Biodiesel substitution for diesel fuel and the process of fixing carbon for the Biodiesel fuel.

Biodiesel produced from rapeseed oil is a cyclical process (Fig. 11-3). The carbon dioxide released to the atmosphere was fixed by the plant in a recent year (perhaps the same year as the combustion). New rapeseed plants grown for future Biodiesel production are fixing carbon during the current growth cycle. According to the ASU (Arizona State University) Photosynthesis center, "Photosynthesis is arguably the most important biological process on earth. By liberating oxygen and consuming carbon dioxide, it has transformed the world into the hospitable environment we know today. Directly or indirectly, photosynthesis fills our food requirements and many of our needs for fiber and building materials. The energy stored in petroleum, natural gas and coal all came from the sun via photosynthesis, as does the energy in firewood, which is a major fuel in many parts of the world. ...If we can understand and control the intricacies of the photosynthetic process, we can learn how to increase crop yields of food, fiber, wood, and fuel, and how to better use our lands. The energy-harvesting secrets of plants can be adapted to man-made systems which provide new, efficient ways to collect and use solar energy. ...All of our biological energy needs are met by the plant kingdom, either directly or through herbivorous animals. Plants in turn obtain the energy to synthesize foodstuffs via photosynthesis. Although plants draw necessary materials from the soil and water and carbon dioxide from the air, the energy needs of the plant are filled by sunlight. Sunlight is pure energy. ...To be beneficial, the energy in sunlight must be converted to other forms. This is what photosynthesis is all about. It is the process by which plants change the energy in sunlight to kinds of energy which can be stored for later use. Plants carry out this process in photosynthetic reaction centers. These tiny units are found in leaves, and convert light energy to chemical energy, which is the form used by all living organisms.

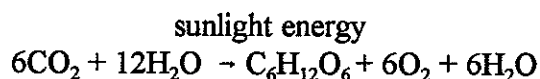
One of the major energy-harvesting processes in plants involves using the energy of sunlight to convert carbon dioxide from the air into sugars, starches, and other high-energy carbohydrates. Oxygen is released in the process. Later, when the plant needs food, it draws upon the energy stored in these carbohydrates. We do the same. When we eat ..., our bodies oxidize or "burn" the starch allowing it to combine with oxygen from the air. This produces carbon dioxide, which we exhale, and the energy we need to survive. ...One of the carbohydrates resulting from photosynthesis is cellulose, which makes up the bulk of dry wood and other plant material. When we burn wood, we convert the cellulose back to carbon dioxide and release the stored energy as heat. Burning fuel is basically the same oxidation process that occurs in our bodies; it liberates the energy of "stored sunlight" in a useful form, and returns carbon dioxide to the atmosphere. Energy from burning "biomass" is important to many parts of the world. In developing countries, firewood continues to be critical to survival. Ethanol (grain alcohol) produced from sugars and starches by fermentation is a major automobile fuel in Brazil, and is added to gasoline in some parts of the United States to help reduce emissions of harmful pollutants.

"Our major sources of energy, of course, are coal, oil and natural gas. These materials are all derived from ancient plants and animals, and the energy stored within them is chemical energy that originally came from sunlight through photosynthesis. Thus, most of the energy we use today was originally solar energy.

"Currently, there is much discussion concerning the possible effects of carbon dioxide and other "greenhouse gases" on the environment. As previously mentioned, photosynthesis converts carbon dioxide from the air to carbohydrates and other kinds of "fixed" carbon and releases oxygen to the atmosphere. When we burn firewood, ethanol, or coal, oil and other fossil fuels, oxygen is consumed, and carbon dioxide is released back into the atmosphere. Thus, carbon dioxide which was removed from the atmosphere over millions of years is being replaced very quickly through our consumption of these fuels."

CARBON FIXATION BY THE RAPE PLANT

Rape, like all other plants, uses the process of photosynthesis to capture light energy and convert it into chemical energy that the plant can utilize. Photosynthesis is the process in which plants absorb carbon dioxide and water, and use light energy from the sun to convert them into glucose sugar (Britannica, 1993). Oxygen and water are created as secondary products and released back into the atmosphere. The plant uses the glucose, in combination with nutrients absorbed from the soil, for growth and development. The following equation describes the process in terms of a balanced chemical formula (Thomas, 1984):



The important observation with regard to the carbon cycle is that the plant absorbs all of its carbon from atmospheric carbon dioxide (Britannica, 1993).

Studies show, however, that not all of the carbon dioxide fixed by the plant stays within it. Shepherd and Davies (1993) performed a study on rape seedlings (*Brassica Napus* L.) in which they concluded 17-19% of the fixed CO₂ was translocated to the roots over a period of two weeks. 23-24% of that was released into the atmosphere as CO₂, and 30-34% was released into the rhizosphere (soil). 35-51% of the carbon released into the rhizosphere was used by micro-organisms (Shepherd et al., 1993). This leaves 30-40 % of the carbon translocated to the roots in the soil. Thus the plant takes in more CO₂ than is accumulated in the plant biomass.

A rapeseed yield of 1 ton/acre (2.24 t/ha) will yield approximately 100 gal/acre (935 L/ha) of oil and 1250 lb/acre (1400 kg/ha) of meal and 5000 lb/acre (5,600 kg/ha) of biomass (Peterson et al., 1995). Rapeseed oil, rapeseed, rapeseed meal, rapeseed biomass and wheat have been analyzed for carbon content by a commercial laboratory as follows:

| | | |
|--------------|---------------|---------------|
| Rapeseed oil | 17,370 Btu/lb | 79.48% carbon |
| Rapeseed | 11,735 Btu/lb | 58.39% carbon |
| Rape meal | 8,934 Btu/lb | 46.54% carbon |
| Rape residue | 7,109 Btu/lb | 41.37% carbon |
| Wheat | 6,788 Btu/lb | 41.18% carbon |

The residue (composed of approximately 2/5 (41.37%) carbon) is generally left in the field, where tillage and soil conservation techniques incorporate it back in to the soil so it can be processed by micro-organisms. These micro-organisms assimilate the carbon from the residue, retain some of it, and return the rest back into the atmosphere as CO₂ via respiration (Reicosky, 1994).

Another possible use for the residue that may be considered economically is to collect the residue and use it as a biomass fuel resource. This has been studied with various other crops, including wheat, barley, and corn (Galinato et al., 1987). Rapeseed residue, as when the rapeseed meal is used for fuel, returns the carbon to the atmosphere in the form of exhaust gases from combustion.

An estimation of the carbon fixed by an average crop of rapeseed producing one ton per acre is:

| Product | lb/acre | % Carbon | lb C/acre | lb CO ₂ /acre |
|------------------|---------|----------|-----------|--------------------------|
| Rapeseed Oil | 750 | 0.7948 | 596.1 | 2185.7 |
| Rapeseed Meal | 1250 | 0.4654 | 581.8 | 2133.1 |
| Rapeseed | 2000 | 0.5839 | 1167.8 | 4281.9 |
| Rapeseed Biomass | 5000 | 0.4137 | 2068.5 | 7584.5 |

Processing

During processing of rapeseed the carbon cycle becomes considerably more sophisticated and complex, due the various number of processing techniques that may be utilized. The basic initial step for processing, is the extraction of the oil from the seeds. From the above table, the seed has a carbon content of 58.4 %. Extraction can be performed mechanically, chemically, or by combination of the two methods (Peterson, 1986). After the oil is extracted, the resultant meal (with carbon content of 46.5%) may be disposed of in various ways. It can be used as a biomass fuel source, organic fertilizer, or feed for livestock, although there are limitations with this last application (Ward, 1985, Robbelen, 1989; Peterson et al., 1983).

After retrieving the oil, the next step is purification. This involves removing impurities and glycerol from the raw oil. Any of a number of processing techniques may be applied, depending on exact characteristics desired in the fuel. Filtration is done by placing the oil in settling tanks, forcing the oil through elements, or both (Peterson, 1986). Degumming procedures may then be applied, such as flushing the oil with warm water (Peterson, 1986, Strayer et al., 1983).

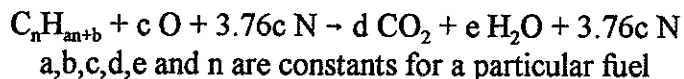
Processing the oil into Biodiesel requires transesterification. This consists of reacting the triglycerides in the oil with an alcohol to produce esters of both glycerols and fatty acids (Peterson, 1986). Generally, methanol or ethanol is used, forming methyl and ethyl ester, respectively, though butanol which forms butyl esters has also been used (Klopfenstein et al., 1983, Nye et al., 1983).

Certain advantages of transesterification include a higher cetane rating and lowered fuel viscosity, which leads to less trouble with the engine (Clark 1984, Peterson 1986). It is important to note that the addition of alcohol to the process also brings with it additional carbon.

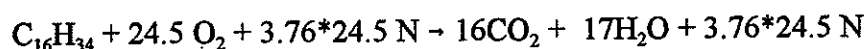
COMBUSTION

Liljedahl et al. (1979) states "In general, all crude petroleum is made up of combined carbon and hydrogen in approximately the proportion of 86% carbon to 14% hydrogen. The atoms of carbon and hydrogen may be combined in many different ways to form many different hydrocarbon compounds in crude oil."

The combustion equation for any hydrocarbon is of the form (Obert, 1968):



For example, a typical diesel fuel, $C_{16}H_{34}$, has a theoretical combustion equation of:

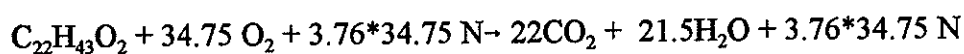


This equation shows that 3.11 lbs of CO_2 is produced for each pound of diesel used as fuel.

Reece (1995) computed the following hypothetical formulas's for the methyl and ethyl esters of rapeseed and canola oils:

| <u>Fuel</u> | <u>Hypothetical Formula</u> | <u>Molecular Weight</u> |
|-------------|-----------------------------|-------------------------|
| RME | $C_{21}H_{38}O_2$ | 323.38 |
| CME | $C_{19}H_{35}O_2$ | 295.29 |
| REE | $C_{22}H_{43}O_2$ | 340.12 |
| CEE | $C_{20}H_{37}O_2$ | 309.38 |

Note that the esters of these oils are oxygenated, with oxygen making up 10%, carbon 78%, and hydrogen 12% by weight. The combustion equation for REE is:



This equation shows that 2.86 pound of CO_2 is produced for each pound of REE used as fuel.

In the theoretical combustion equation all of the carbon goes to carbon dioxide and the nitrogen from the air goes through the process unaffected. In the actual combustion process, part of the carbon remains as various hydrocarbons, part of the carbon forms carbon monoxide and aldehydes, and part of the nitrogen is converted to NO_x . In recent tests at the Los Angeles Metropolitan Transit Authority Emissions Test Facility (LA-MTA ETF), the following emissions were measured from typical tests (Peterson and Reece, 1994):

| <u>Fuel</u> | <u>lb HC/ lb fuel</u> | <u>lb CO/ lb fuel</u> | <u>lb NO_x / lb fuel</u> | <u>lb CO_2 / lb fuel</u> | <u>lb PM / lb fuel</u> |
|-------------|---------------------------|---------------------------|---|---|----------------------------|
| 100RME | 0.003032 | 0.010027 | 0.030419 | 3.389756 | 0.002441 |
| 100REE | 0.001714 | 0.012286 | 0.030336 | 3.366879 | 0.001363 |
| Diesel | 0.004748 | 0.033727 | 0.03708 | 3.721776 | 0.001729 |

It is easily seen that most of the carbon (99% plus) goes to carbon dioxide. While emissions of HC, CO and aldehydes constitute only a small percentage of the carbon output from combustion. These are important because of their environmental effects. Biodiesel may help reduce both regulated and non-regulated emissions. As far as the carbon cycle is concerned these intermediate compounds constitute only a minor part of the picture. A full discussion of the emissions aspects of the carbon cycle is beyond the scope of this paper and is for practical consideration beyond the scope of currently available data. These intermediate products

eventually return to CO_2 through the action of microbes and various other degradation processes. Reaction rates vary however, and for certain compounds such as the free carbon in the PM, for example, the degradation may occur over a very long time.

It can be concluded, that if combustion were complete, all of the carbon in the fuel would be converted to CO_2 and released to the atmosphere. Further, the intermediate products of combustion would also eventually return to the atmosphere as CO_2 . Diesel produces 8.7 percent more CO_2 per pound than does Biodiesel; but diesel has 12.3 percent more energy per pound than Biodiesel, thus less fuel is required to do the same work. The Biodiesel is an oxygenated fuel and according to some reports has a slightly higher thermal efficiency, however, as a practical matter, it can be assumed that per unit of work done, the amount of CO_2 produced would be nearly the same whether using diesel fuel or Biodiesel.

CARBON DIOXIDE REDUCTION FOR USING BIODIESEL

Carbon dioxide exchange between diesel and Biodiesel will be discussed on two levels. First, a simple exchange of Biodiesel for diesel fuel and second, a discussion of the relevant factors affecting the exchange which could be considered due to production, processing, and transportation of the two fuels.

1. Carbon Dioxide to the atmosphere when Diesel is replaced by Biodiesel

As previously demonstrated, 3.11 pounds of carbon dioxide are produced for each pound of diesel fuel used and approximately the same amount would be produced for an equivalent energy content of Biodiesel. Peterson and Reece (1995) report that rapeseed ethyl ester has a gross heat of combustion of 17,500 Btu/lb and Diesel 19,652 Btu/lb. This means that it takes 12.3 percent more REE (mass basis) to produce the same energy as Diesel whereas the theoretical carbon balance shows 8.7 percent more REE will produce the same amount of carbon dioxide. The difference is due to a) the oxygen in the Biodiesel and b) theoretical versus actual substances.

Transesterification requires an addition of methyl or ethyl alcohol CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ and the removal of glycerin $\text{C}_3\text{H}_8\text{O}_3$. Approximately 10 percent alcohol is required and approximately 10 percent by weight glycerin is removed so the amount of ester produced per acre is essentially equivalent to the oil produced. Ethyl ester is 78 percent carbon by weight, weighs 7.31 pounds per gallon, and has a heat of combustion of 17,500 Btu/lb. Typically an acre of rapeseed produces 100 gal of REE which can replace approximately 92 gallons of diesel fuel and would replace 2024 pounds of carbon dioxide from petroleum with 2090 pounds of carbon dioxide from a renewable plant source. Further, the plants on each acre would process 11,850 pounds of carbon dioxide including the 18 percent estimated to be transported to the soil through the root system. Figure 11-3 shows the various carbon pathways. Most of this would eventually be returned to the atmosphere as carbon dioxide through the processes of

biodegradation. However some may be fixed as free carbon, and some is stored in less biodegradable forms. The renewable fuel thus potentially removes more carbon dioxide than the simple exchange of fuel combustion equivalents would suggest.

Peterson et al. (1995) estimates that 68 million acres of cropland in the U.S is idle and that land could produce about 6.8 billion gallons of vegetable oil per year or 27% of the diesel used in transportation. They report an additional 62 million acres in the U.S. is used for producing exports and that at least part of that land could be used to produce Biodiesel. Another 1.25 billion gallons of oil is produced in the U.S. from tallow, grease, butter as fat, lard and fish oil, 34% of which is exported. Thus a total production in the order of 12-15 billion gallons, approximately 50 percent of transportation diesel is possible. The impact on carbon dioxide released to the atmosphere from petroleum versus renewable sources would be in the order of 250 billion to 300 billion pounds per year.

2. Factors affecting the exchange which could be considered due to production, processing, and transportation of the two fuels.

A further discussion of the carbon dioxide emissions from Biodiesel compared to diesel fuel would require an analysis of the total system. Biodiesel is grown on agricultural land requiring inputs of energy for tillage, chemical applications, chemical production, machinery production, harvesting, crop transport, storage and labor. Processing requires energy to operate mixers and pumps, production of storage vessels, and labor. The fuel would also require transportation to it's point of use. Auld and Peterson (1989) estimated that 4.2 units of energy were produced by rapeseed oil for every unit of energy input. Other researchers have variously estimated from 3 to 4 units of energy output for each unit of energy input for Biodiesel.

It should also be noted that land is not bare when not growing vegetable oil crops. How does the carbon dioxide utilization for rapeseed compare to another crop such as wheat? Some land is not in actual production such as land in the Conservation Reserve Program (CRP). Much of the CRP land is pasture having few inputs. Some crops such as sugarbeets or vegetable oil crops are very intensively cultivated. As an example consider an 80 bushel per acre wheat crop which would produce about 8000 pounds of straw biomass (Wilkens et al., 1989). The following table provides a carbon dioxide processing estimate for an 80 bushel per acre wheat crop.

| Product | lb/acre | % Carbon | # C/acre | # CO2/acre |
|----------------------|---------|----------|----------|------------|
| wheat seed | 4800 | 0.4118 | 1976.6 | 7247.7 |
| wheat straw | 8000 | 0.4137 | 3309.6 | 12135.2 |
| transported by roots | | | | 3488.918 |
| Total | | | | 22871.8 |

Assuming the biomass in wheat straw contains carbon equivalent to rapeseed biomass, the wheat crop would process about 22,800 pounds of carbon dioxide compared to the 11,850 pounds for rapeseed. The purpose of this show is that some plants may remove more carbon dioxide than rapeseed, while at the same time a very low biomass producing crop could process considerably less.

Diesel fuel also requires energy inputs for exploration, drilling, pumping, transportation, processing and storage. No estimates of the total energy required for producing diesel fuel have been found in the literature search. If we assume it is approximately the same as for Biodiesel the estimates of carbon dioxide exchange given above are adequate. Projected refinery energy usage for the U.S. refinery industry simulated by three clusters in three selected regions of the U.S. is given below:

Refinery Energy Usage - 1985
(Sittig, 1978 projection)

| | East Coast | Gulf Coast | West Coast | Total |
|---|------------|------------|------------|-------|
| Crude Run, 10 ³ BPD | 198 | 218 | 164 | 580 |
| Refinery Fuel, FOE ¹ /day | | | | |
| Gas | 6990 | 6880 | 7500 | 21370 |
| Oil | 9640 | 10700 | 11690 | 32030 |
| Total Fuel, FOE/day | 16630 | 17580 | 19190 | 53400 |
| Purchased Steam, 10 ⁶ lb/day | 5.7 | 0.5 | 0 | 6.2 |
| Electricity, 10 ³ kWh/day | 838.7 | 875 | 897.3 | 2611 |

¹FOE = Fuel Oil Equivalent, 6.3×10^6 Btu

Sittig (1978) reports that the fuel consumed by a refinery in the processing of crude to finished product is in the order of 8 to 11 percent of the crude run. Additional fuel would be required for pumping, storage and transportation.

USDOE (1995) says that for every barrel of oil produced to date in the U.S., two have been left behind. The U.S. oil industry has produced 160 billion barrels, but some 350 billion barrels remain. Most of the remaining oil is difficult to produce. It is locked in complex geologic structures or is simply beyond the capability of today's recovery processes. U. S. crude oil supplies are becoming heavier and of higher sulfur content. This creates new challenges for refiners to produce light-end motor fuels and other products. The U.S. exploration and production industry faces ever tightening environmental regulations and is spending more than \$1.5 billion per year to comply with EPA requirements. If environmental regulations are not made more "risk-based, site-specific and scientifically grounded" production may be reduced by 330,000 barrels per day or 120 million barrels per year in 2020.

This data demonstrates that while Biodiesel production requires outside resources, production of petroleum diesel also requires outside resources. It is difficult to place a comparable

quantity on each, however petroleum diesel probably requires 15-20 percent of the energy produced to create the product while Biodiesel requires from 25 to 33 percent to create the product. In terms of the carbon cycle this means that an additional 5 to 15 percent Biodiesel would be required to compensate for each gallon of diesel replaced.

CONCLUSIONS

Complete combustion converts hydrocarbon fuels to carbon dioxide and water. Diesel fuel represented by $C_{16}H_{34}$ releases 3.11 pounds of CO_2 per pound of fuel used in combustion. Biodiesel releases 2.86 pounds of CO_2 per pound of fuel used in combustion. Incomplete combustion can result in small amounts of carbon monoxide and aldehydes which eventually also degrade into carbon dioxide.

In its most simple form the carbon cycle consists of the fixation of carbon and release of oxygen by plants through the process of photosynthesis, then the recombining of oxygen and carbon to form CO_2 through processes of combustion or respiration. The carbon dioxide released by petroleum diesel was fixed from the atmosphere during the formative years of the earth. Carbon dioxide released by Biodiesel is fixed by the plant in a recent year and is recycled by the next generation of crops.

Many scientists believe that global warming is occurring because of the rapid release of CO_2 through combustion of stored carbon such as petroleum diesel. Replacing petroleum diesel with Biodiesel could reduce the CO_2 accumulation in the atmosphere. The reduction is not an exact one-to-one replacement. It is estimated that each gallon of Biodiesel releases 1.1 to 1.2 times the CO_2 released in the atmosphere by one gallon of petroleum diesel but the Biodiesel CO_2 will be recycled by a future rapeseed plant.

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CYCLES IN AGRICULTURAL ECOSYSTEMS

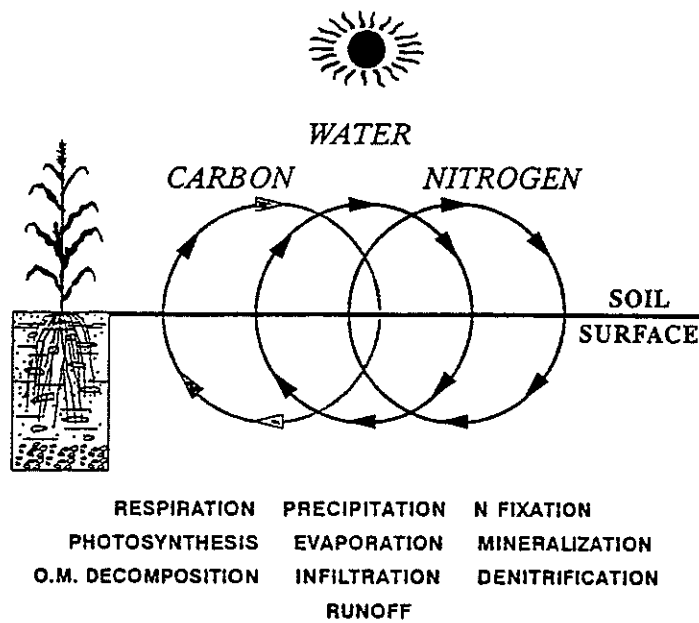


Figure 11-1. Carbon, water and nitrogen cycles from Reicosky (1994).

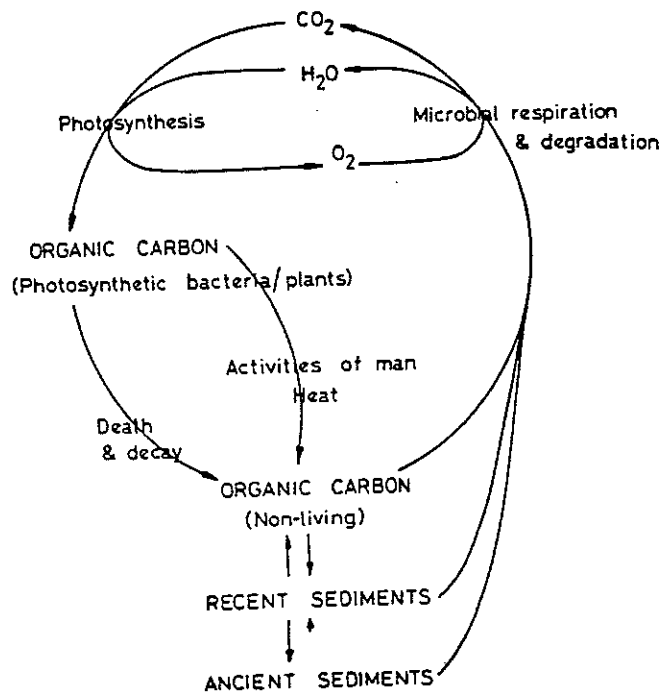


Figure 11-2. Carbon Cycle from Cripps and Watkinson (1978).

Theoretical Carbon Cycle

(Based on a 2000 pounds/acre yield of Rapeseed)

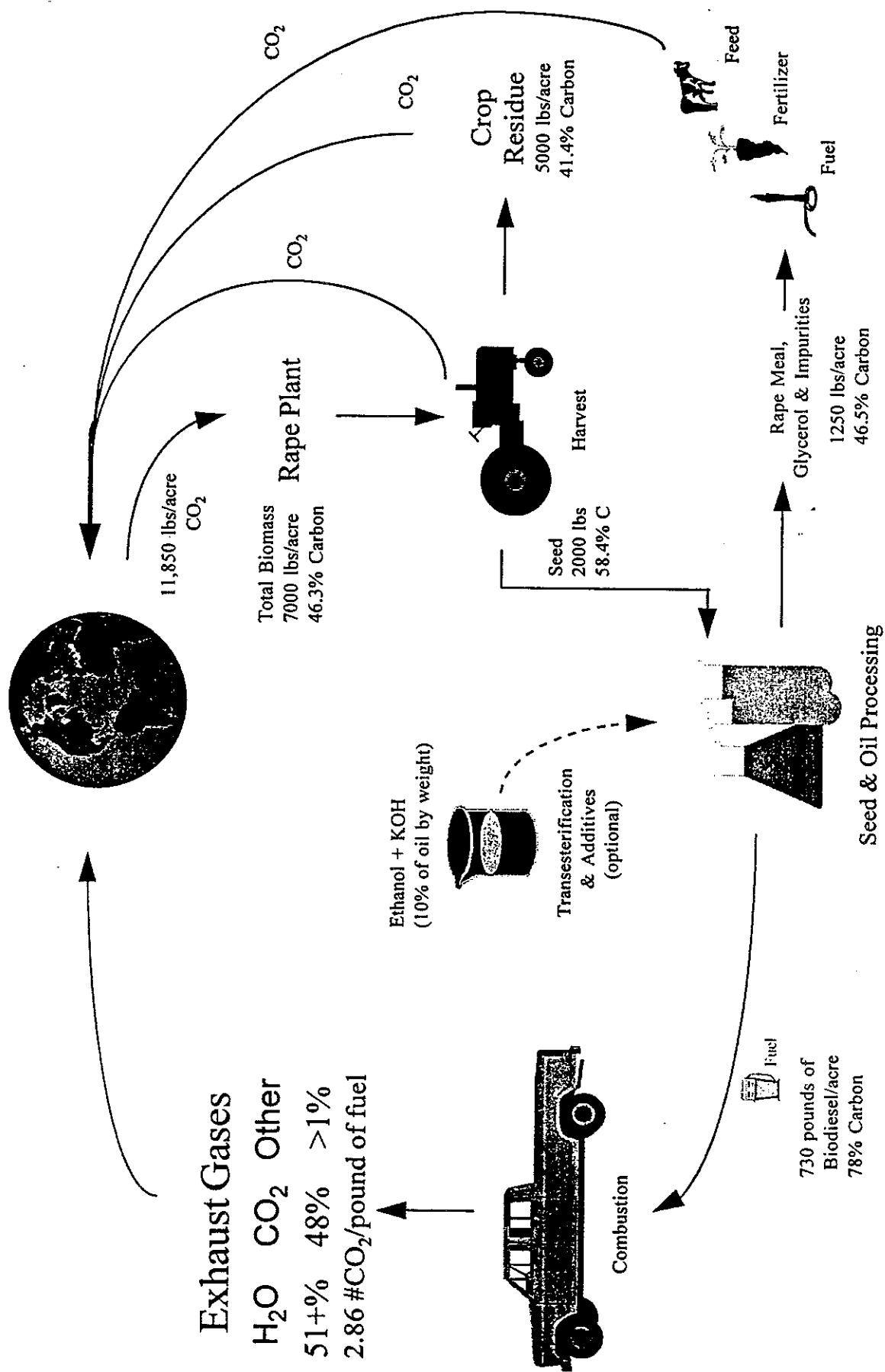


Figure 11-3. The rapeseed oil carbon cycle.

Pour Point Depressant Screening

The cloud and pour points of Rapeseed Ethyl Ester (REE) and Hydro Soy Ethyl Ester (HySEE) were evaluated using a winterization method and a number of pour point depressants and compared to the baseline values for each fuel. ASTM standards D 2500 and D97 were followed to measure cloud and pour points respectively. The following is a list of the products and methods.

A = Lubrizol #110050A

B = Lubrizol #110050B

C = Lubrizol #22777AM

CO₂ = Carbon Dioxide

D = Dupont (Fuel oil additive #2)

DBE = Dupont DBE-5 (Dimethyl Glutarete #1119-40-0)

E = Ethanol (200 proof)

J = Jet A Fuel

M = Methanol

P = Propanol

R = Rohm-Tech (Viscoplex, type 10-310)

2D = #2 Diesel Fuel

U = 2,2,4-Trimethylpentane

V = tert-Butyl methyl ether

W = Winterized (chilled to let high mol. wt. crystals drop out)

X = 2-Ethoxyethanol

Y = 2-Butoxyethanol

Z = 1-tert-Butoxy-2-ethoxyethane

Table 12-1. Pour point depressant trials with HySEE.

| Fuel | PPD | Concentration | Cloud Pt. | Pour Pt. |
|-------|----------|---------------|-----------|----------|
| HySEE | Baseline | (%) | 10 | 6 |
| HySEE | A | 0.5 | 10 | 6 |
| HySEE | E | 10 | 4 | 3 |
| HySEE | M | 10 | 5 | 3 |
| HySEE | J | 20 | 4 | 3 |
| HySEE | 2D | 30 | 4 | 3 |
| HySEE | 2D | 50 | -1 | -3 |
| HySEE | 2D | 80 | -9 | -15 |
| HySEE | P | 10 | 2 | 3 |
| HySEE | P | 20 | 4 | 0 |
| HySEE | J | 20 | 9 | 0 |
| HySEE | J | 30 | 4 | 0 |
| HySEE | J | 50 | -7 | |
| HySEE | U | 20 | 0 | 0 |
| HySEE | V | 10 | 3 | 3 |
| HySEE | V | 20 | 0 | 0 |
| HySEE | X | 10 | 7 | 3 |
| HySEE | Y | 10 | 7 | 3 |
| HySEE | Z | 10 | 6 | 3 |
| HySEE | RME | 20 | 5 | 6 |
| HySEE | REE | 20 | 5 | 6 |
| HySEE | REE | 50 | 1 | 0 |
| HySEE | REE+R@1% | 20 | 3 | 0 |
| HySEE | REE+R@1% | 50 | -1 | -6 |
| HySEE | RME+R@1% | 20 | 3 | 3 |
| HySEE | R | 0.5 | 8 | 6 |
| HySEE | W | | 0 | 0 |
| HySEE | W+R | 0.5 | -1 | 0 |
| HySEE | DBE | 1 | 7 | 6 |
| HySEE | DBE | 5 | 6 | 3 |
| HySEE | DBE | 10 | 5 | 3 |

Table 12-2. Pour point depressant trials with REE.

| Fuel | PPD | Concentration | Cloud Pt. (°C) | Pour Pt. (°C) |
|------|---------------------|---------------|-------------------|------------------|
| REE | Baseline | (%) | -2 | -10 |
| REE | R | 0.5 | -4 | -24 |
| REE | A | 0.5 | -1 | -24 |
| REE | B | 0.5 | -2 | -24 |
| REE | C | 0.5 | -3 | -24 |
| REE | R | 1 | -4 | -27 |
| REE | A | 1 | -2 | -27 |
| REE | B | 1 | -2 | -27 |
| REE | C | 1 | -4 | -27 |
| REE | W | | -9 | -15 |
| REE | W + R | 0.5 | -13 | -30 |
| REE | CO ₂ | 0.5 | -1 | -12 |
| REE | R + CO ₂ | 0.5 | -4 | -27 |
| REE | D | 0.5 | -3 | -24 |

The commercial pour point depressants did not lower the pour point to an acceptable value. The pour point depressant for the HySEE EMA test, biodegradability studies, and acute aquatic toxicity tests was number one diesel fuel.

UNIVERSITY OF IDAHO

Material Safety Data Sheet

EMERGENCY PHONE: CHEMTREC 800-424-9300

MSDS REFERENCE: RME(Rapeseed Methyl Ester)

SECTION I - IDENTIFICATION

PRODUCT: RME - METHYL ESTER OF RAPESEED
SYNONYMS:
CHEMICAL: METHYL ESTER
CAS No:
SARA HAZARD: NONE NOTED (SECTION 311/312) TITLE III SECTION 313 - NOT LISTED

SECTION II - INGREDIENTS AND HAZARD CLASSIFICATION

| <u>FATTY ACID COMPOSITION</u> | <u>%</u> | <u>PEL/TEV</u> | <u>HAZARD</u> |
|-------------------------------|----------|----------------|---------------|
| PALMITIC (16:1) | 2.8 | NONE/NONE | NONE NOTED |
| STEARIC (18:0) | 1 | NONE/NONE | NONE NOTED |
| OLEIC (18:1) | 12.5 | NONE/NONE | NONE NOTED |
| LINOLEIC (18:2) | 12.1 | NONE/NONE | NONE NOTED |
| LINOLENIC (18:3) | 8.0 | NONE/NONE | NONE NOTED |
| EICOSENOIC (20:1) | 7.4 | NONE/NONE | NONE NOTED |
| ERUCIC (22:1) | 49.8 | NONE/NONE | NONE NOTED |
| MISC | 6.4 | NONE/NONE | NONE NOTED |

SECTION III - HEALTH INFORMATION

INHALATION: UNKNOWN
INGESTION: LD50:>50ML/KG (ALBINO RATS)
EYE CONTACT: SIMILAR PRODUCTS WERE NOT CLASSIFIED AS EYE IRRITANTS
SKIN CONTACT: RME WAS NOT CLASSIFIED AS A PRIMARY SKIN IRRITANT OR CORROSIVE MATERIAL

SECTION IV - OCCUPATIONAL EXPOSURE LIMITS

PEL: NO OSHA PEL
TLV: NO ACGIH TLV

SECTION V - EMERGENCY FIRST AID PROCEDURE

FOR OVEREXPOSURE BY SWALLOWING: CALL A PHYSICIAN OR POISON CONTROL CENTER PROMPTLY

FOR OVEREXPOSURE BY SKIN CONTACT: WASH AFFECTED AREA

FOR OVEREXPOSURE BY EYE CONTACT: IMMEDIATELY FLUSH EYES WITH PLENTY OF WATER FOR AT LEAST 15 MINUTES. DO NOT LET VICTIM RUB EYES.

FOR OVEREXPOSURE BY INHALATION: IMMEDIATELY REMOVE VICTIM TO FRESH AIR. IF VICTIM HAS STOPPED BREATHING, GIVE ARTIFICIAL RESPIRATION, PREFERABLY BY MOUTH-TO-MOUTH. GET MEDICAL ATTENTION IMMEDIATELY.

SECTION VI - PHYSICAL DATA

BOILING POINT: OVER 400°F (204°C) AT 760 MM HG PRESSURE

MELTING POINT: NOT DETERMINED

VAPOR PRESSURE: LESS THAN 1 MM HG PRESSURE AT 72°C

SPECIFIC GRAVITY: 0.88 AT 25°C

SOLUBILITY IN WATER: NEGLIGIBLE AT ROOM TEMPERATURE

APPEARANCE AND COLOR: YELLOW LIQUID AT ROOM TEMPERATURE

SECTION VII - FIRE AND EXPLOSION HAZARDS

FLASH POINT & METHOD USED: 355°F (180°C) (PMCC)

FLAMMABILITY LIMITS IN AIR, % BY VOL. LOWER: NOT APPLICABLE

FLAMMABILITY LIMITS IN AIR, % BY VOL. UPPER: NOT APPLICABLE

NFPA RATING: NO NFPA RATING

HMIS RATING: HEALTH (0) FIRE (1) REACTIVITY (0)

SPECIAL FIRE FIGHTING PROCEDURES & PRECAUTIONS:

(INDIVIDUALS SHOULD PERFORM ONLY THOSE FIGHTING PROCEDURES FOR WHICH THEY HAVE BEEN TRAINED). USE WATER SPRAY, DRY CHEMICAL, FOAM OR CARBON DIOXIDE. WATER MAY BE INEFFECTIVE BUT SHOULD BE USED TO KEEP FIRE-EXPOSED CONTAINERS COOL. IF A SPILL OR LEAK HAS NOT IGNITED, USE WATER TO DISPERSE THE VAPORS. WATER SPRAY MAY BE USED TO FLUSH SPILLS AWAY FROM HERE.

USUAL FIRE & EXPLOSION HAZARDS:

FIRE FIGHTERS SHOULD WEAR SELF-CONTAINED BREATHING APPARATUS IN THE

POSITIVE-PRESSURE MODE WITH A FULL FACE PIECE WHEN THERE IS A POSSIBILITY OF EXPOSURE TO SMOKE, FUMES OR HAZARDOUS DECOMPOSITION PRODUCTS.

SECTION VIII - REACTIVITY

STABILITY: GENERALLY STABLE

HAZARDOUS POLYMERIZATION: NONE LIKELY

CONDITIONS & MATERIALS TO AVOID: AVOID CONTACT WITH STRONG OXIDIZING AGENTS

HAZARDOUS DECOMPOSITION PRODUCTS: DECOMPOSITION MAY PRODUCE CARBON MONOXIDE AND CARBON DIOXIDE

SECTION IX - EMPLOYEE PROTECTION

CONTROL MEASURES: HANDLE IN THE PRESENCE OF ADEQUATE VENTILATION

RESPIRATORY PROTECTION: RECOMMENDED EXPOSURE LIMITS (I.E., OSHA-PEL AND ACGIH-TLV) HAVE NOT BEEN ESTABLISHED FOR THIS MATERIAL. WHETHER THERE IS A NEED FOR RESPIRATORY PROTECTION UNDER YOUR CONDITIONS OF HANDLING OF THIS MATERIAL SHOULD BE EVALUATED BY A QUALIFIED HEALTH SPECIALIST.

PROTECTIVE CLOTHING: NO NEED ANTICIPATED.

EYE PROTECTION: WEAR SAFETY GLASSES MEETING SPECIFICATIONS OF ANSI STANDARD Z87.1.

SECTION X - ENVIRONMENTAL PROTECTION

ENVIRONMENTAL PRECAUTIONS: AVOID UNCONTROLLED RELEASES OF THIS MATERIAL WHERE SPILLS ARE POSSIBLE, A COMPREHENSIVE SPILL RESPONSE PLAN SHOULD BE DEVELOPED AND IMPLEMENTED.

SPILL OR LEAK PRECAUTIONS: WEAR APPROPRIATE RESPIRATORY PROTECTION AND PROTECTIVE CLOTHING AS DESCRIBED IN SECTION IX. CONTAIN SPILLED MATERIAL TRANSFER TO SECURE CONTAINER. WHERE NECESSARY, COLLECT USING ABSORBENT MEDIA. IN THE EVENT OF AN UNCONTROLLED RELEASE OF THIS MATERIAL, THE USER SHOULD DETERMINE IF THE RELEASE IS REPORTABLE UNDER APPLICABLE LAWS AND REGULATIONS.

WASTE DISPOSAL: ALL RECOVERED MATERIAL SHOULD BE PACKAGED, LABELED, TRANSPORTED AND DISPOSED OR RECLAIMED IN CONFORMANCE WITH APPLICABLE LAWS AND REGULATION AND IN CONFORMANCE WITH GOOD ENGINEERING PRACTICES. AVOID LAND FILLING OF LIQUIDS. RECLAIM WHERE POSSIBLE.

SECTION XI - REGULATORY CONTROLS

DEPARTMENT OF TRANSPORTATION:

DOT CLASSIFICATION: NOT REGULATED
DOT PROPER SHIPPING NAME:
OTHER DOT INFORMATION:

OTHER REGULATORY REQUIREMENTS: LISTED IN TSCA INVENTORY

SECTION XII - PRECAUTIONS: HANDLING, STORAGE AND USAGE

NO SPECIAL PRECAUTIONS NECESSARY.

The information presented herein is believed to be factual as it has been derived from the works and opinions of persons believed to have qualified experts; however, nothing contained in this information is to be taken as a warranty or representation for which the University of Idaho bears legal responsibility. The user should review any recommendation in the specific context of the intended use to determine they are appropriate.

UNIVERSITY OF IDAHO

Material Safety Data Sheet

EMERGENCY PHONE: CHEMTREC 800-424-9300

MSDS REFERENCE: REE(Rapeseed Ethyl Ester)

SECTION I - IDENTIFICATION

PRODUCT: REE - ETHYL ESTER OF RAPESEED
SYNONYMS:
CHEMICAL: ETHYL ESTER
CAS No:
SARA HAZARD: NONE NOTED (SECTION 311/312) TITLE III SECTION 313 - NOT LISTED

SECTION II - INGREDIENTS AND HAZARD CLASSIFICATION

| <u>FATTY ACID COMPOSITION</u> | <u>%</u> | <u>PEL/TEV</u> | <u>HAZARD</u> |
|-------------------------------|----------|----------------|---------------|
| PALMITIC (16:1) | 2.8 | NONE/NONE | NONE NOTED |
| STEARIC (18:0) | 1 | NONE/NONE | NONE NOTED |
| OLEIC (18:1) | 13.8 | NONE/NONE | NONE NOTED |
| LINOLEIC (18:2) | 11.6 | NONE/NONE | NONE NOTED |
| LINOLENIC (18:3) | 8.0 | NONE/NONE | NONE NOTED |
| EICOSENOIC (20:1) | 7.4 | NONE/NONE | NONE NOTED |
| ERUCIC (22:1) | 49.7 | NONE/NONE | NONE NOTED |
| MISC | 5.7 | NONE/NONE | NONE NOTED |

SECTION III - HEALTH INFORMATION

INHALATION: UNKNOWN
INGESTION: LD50:>50ML/KG (ALBINO RATS)
EYE CONTACT: SIMILAR PRODUCTS WERE NOT CLASSIFIED AS EYE IRRITANTS
SKIN CONTACT: REE WAS NOT CLASSIFIED AS A PRIMARY SKIN IRRITANT OR CORROSIVE MATERIAL

SECTION IV - OCCUPATIONAL EXPOSURE LIMITS

PEL: NO OSHA PEL
TLV: NO ACGIH TLV

SECTION V - EMERGENCY FIRST AID PROCEDURE

| | |
|---|--|
| FOR OVEREXPOSURE BY <u>SWALLOWING</u> : | CALL A PHYSICIAN OR POISON CONTROL CENTER PROMPTLY |
| FOR OVEREXPOSURE BY <u>SKIN CONTACT</u> : | WASH AFFECTED AREA |
| FOR OVEREXPOSURE BY <u>EYE CONTACT</u> : | IMMEDIATELY FLUSH EYES WITH PLENTY OF WATER FOR AT LEAST 15 MINUTES. DO NOT LET VICTIM RUB EYES. |
| FOR OVEREXPOSURE BY INHALATION: | IMMEDIATELY REMOVE VICTIM TO FRESH AIR. IF VICTIM HAS STOPPED BREATHING, GIVE ARTIFICIAL RESPIRATION, PREFERABLY BY MOUTH-TO-MOUTH. GET MEDICAL ATTENTION IMMEDIATELY. |

SECTION VI - PHYSICAL DATA

| | |
|-----------------------|--|
| BOILING POINT: | OVER 400°F (204°C) AT 760 MM HG PRESSURE |
| MELTING POINT: | NOT DETERMINED |
| VAPOR PRESSURE: | LESS THAN 1 MM HG PRESSURE AT 72°C |
| SPECIFIC GRAVITY: | 0.87 AT 25°C |
| SOLUBILITY IN WATER: | NEGLIGIBLE AT ROOM TEMPERATURE |
| APPEARANCE AND COLOR: | YELLOW LIQUID AT ROOM TEMPERATURE |

SECTION VII - FIRE AND EXPLOSION HAZARDS

| | |
|---|------------------------------------|
| FLASH POINT & METHOD USED: | 365°F (185°C) (PMCC) |
| FLAMMABILITY LIMITS IN AIR, % BY VOL. LOWER: | NOT APPLICABLE |
| FLAMMABILITY LIMITS IN AIR, % BY VOL. UPPER: | NOT APPLICABLE |
| NFPA RATING: | NO NFPA RATING |
| HMIS RATING: | HEALTH (0) FIRE (1) REACTIVITY (0) |
| SPECIAL FIRE FIGHTING PROCEDURES & PRECAUTIONS: | |

(INDIVIDUALS SHOULD PERFORM ONLY THOSE FIGHTING PROCEDURES FOR WHICH THEY HAVE BEEN TRAINED). USE WATER SPRAY, DRY CHEMICAL, FOAM OR CARBON DIOXIDE. WATER MAY BE INEFFECTIVE BUT SHOULD BE USED TO KEEP FIRE-EXPOSED CONTAINERS COOL. IF A SPILL OR LEAK HAS NOT IGNITED, USE WATER TO DISPERSE THE VAPORS. WATER SPRAY MAY BE USED TO FLUSH SPILLS AWAY FROM HERE.

USUAL FIRE & EXPLOSION HAZARDS:

FIRE FIGHTERS SHOULD WEAR SELF-CONTAINED BREATHING APPARATUS IN THE POSITIVE-PRESSURE MODE WITH A FULL FACE PIECE WHEN THERE IS A POSSIBILITY OF EXPOSURE TO SMOKE, FUMES OR HAZARDOUS DECOMPOSITION PRODUCTS.

SECTION VIII - REACTIVITY

STABILITY: GENERALLY STABLE

HAZARDOUS POLYMERIZATION: NONE LIKELY

CONDITIONS & MATERIALS TO AVOID: AVOID CONTACT WITH STRONG OXIDIZING AGENTS

HAZARDOUS DECOMPOSITION PRODUCTS: DECOMPOSITION MAY PRODUCE CARBON MONOXIDE AND CARBON DIOXIDE

SECTION IX - EMPLOYEE PROTECTION

CONTROL MEASURES: HANDLE IN THE PRESENCE OF ADEQUATE VENTILATION

RESPIRATORY PROTECTION: RECOMMENDED EXPOSURE LIMITS (I.E., OSHA-PEL AND ACGIH-TLV) HAVE NOT BEEN ESTABLISHED FOR THIS MATERIAL. WHETHER THERE IS A NEED FOR RESPIRATORY PROTECTION UNDER YOUR CONDITIONS OF HANDLING OF THIS MATERIAL SHOULD BE EVALUATED BY A QUALIFIED HEALTH SPECIALIST.

PROTECTIVE CLOTHING: NO NEED ANTICIPATED.

EYE PROTECTION: WEAR SAFETY GLASSES MEETING SPECIFICATIONS OF ANSI STANDARD Z87.1.

SECTION X - ENVIRONMENTAL PROTECTION

ENVIRONMENTAL PRECAUTIONS: AVOID UNCONTROLLED RELEASES OF THIS MATERIAL WHERE SPILLS ARE POSSIBLE, A COMPREHENSIVE SPILL RESPONSE PLAN SHOULD BE DEVELOPED AND IMPLEMENTED.

SPILL OR LEAK PRECAUTIONS: WEAR APPROPRIATE RESPIRATORY PROTECTION AND PROTECTIVE CLOTHING AS DESCRIBED IN SECTION IX. CONTAIN SPILLED MATERIAL TRANSFER TO SECURE CONTAINER. WHERE NECESSARY, COLLECT USING ABSORBENT MEDIA. IN THE EVENT OF AN UNCONTROLLED RELEASE OF THIS MATERIAL, THE USER SHOULD DETERMINE IF THE RELEASE IS REPORTABLE UNDER APPLICABLE LAWS AND REGULATIONS.

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SECTION XI - REGULATORY CONTROLS

DEPARTMENT OF TRANSPORTATION:

DOT CLASSIFICATION: NOT REGULATED
DOT PROPER SHIPPING NAME:
OTHER DOT INFORMATION:

OTHER REGULATORY REQUIREMENTS: LISTED IN TSCA INVENTORY

SECTION XII - PRECAUTIONS: HANDLING, STORAGE AND USAGE

NO SPECIAL PRECAUTIONS NECESSARY.

The information presented herein is believed to be factual as it has been derived from the works and opinions of persons believed to have qualified experts; however, nothing contained in this information is to be taken as a warranty or representation for which the University of Idaho bears legal responsibility. The user should review any recommendation in the specific context of the intended use to determine they are appropriate.

SOUTHWEST RESEARCH INSTITUTE EMISSIONS TESTING

One hundred fifty gallons of REE (3-55 gallon drums) and one hundred gallons of RME (2-55 gallon drums) were produced and shipped to Southwest Research Institute (SwRI) for emissions testing, fuel characterization and lubricity testing. Samples of the fuel were also sent to Phoenix Chemical Labs and Diversified Labs for fuel characterization. Results from these laboratories are listed in Table 13-1.

Table 13-1. Fuel Characterization Data

| | REE (P) | REE (S) | RME (P) | RME (S) |
|----------------------------------|---------|---------|---------|---------|
| Fuel Specific Properties | | | | |
| Specific Gravity, 60/60 | 0.876* | 0.875 | 0.8802* | 0.879 |
| Viscosity, cSt @ 40°C | 6.17* | 6.07 | 5.65* | 5.51 |
| Cloud Point, °C | -2* | -4 | 0* | -6 |
| Pour Point, °C | -10* | -18 | -15* | -12 |
| Flash Point, °C | 170* | 207 | 179* | 200 |
| Boiling Point, °C | 160 | 339 | 210 | 240 |
| Water and Sediment, % Vol. | <0.005 | | <0.005 | |
| Carbon Residue, % mass | 0.04 | | 0.04 | 0.458 |
| Ash, % mass | 0.001 | 0.001 | 0.001 | 0.003 |
| Sulfur, wt% | 0.028 | <0.001 | <0.005 | <0.001 |
| Cetane Number | | 60.7 | | 58.7 |
| Heat of Combustion, Gross, MJ/kg | 40.51* | 40.67 | 40.54 | 40.38 |
| Copper Corrosion | 1A | | 1A | |
| Karl Fischer Water, ppm | 1181 | | 563 | |
| Particulate Matter, mg/L | | | | |
| Total | 2.32 | | 1.69 | |
| Non-Combustible | 0.46 | | 0.45 | |
| Elemental Analysis | | | | |
| Carbon, % | 79.03 | 78.2 | 78.79 | 77.7 |
| Hydrogen, % | 13.40 | 12.6 | 12.78 | 12.4 |
| Oxygen, % (by difference) | 7.54 | 9.2 | 8.43 | 9.9 |

* Tests performed by the Department of Biological and Agricultural Engineering

Jeff Taberski flew to SwRI to participate in the blending of the fuels. The four blends of fuel (two 50-gallon drums for each blend) were to be mixed as follows:

| | |
|-------|-------------------|
| REE50 | 50% REE / 50% 2-D |
| REE20 | 20% REE / 80% 2-D |
| RME50 | 50% RME / 50% 2-D |
| RME20 | 20% RME / 80% 2-D |

The two REE blends were mixed Monday, Oct. 9. Due to a missing drum of RME (the drum was damaged in shipping and another one was shipped), the mixing was not completed until another RME drum had been received.

The mixing method used specific gravity readings to determine a weight for each volume of fuel required, yielding a % by volume mixture. Chris Sharp of SwRI calculated the weights for each fuel mixture based on the specific gravities measured by SwRI.

| <u>Fuel</u> | <u>S.G.</u> | <u>API</u> |
|--------------------|-------------|------------|
| 2-D (0.05% sulfur) | 0.8446 | 36.0 |
| REE | 0.8752 | 30.2 |
| RME | 0.8796 | 29.4 |

The following weights were used in mixing. The final API numbers shown were used as a final check (see step 6, below).

| <u>Blends</u> | <u>2-D</u> | <u>Ester</u> | <u>Total</u> | <u>API</u> |
|-------------------|------------|--------------|--------------|------------|
| 50% REE / 50% 2-D | 176.3 | 182.5 | 358.8 | 33.1 |
| 20% REE / 80% 2-D | 282.0 | 73.0 | 355.0 | 34.8 |
| 50% RME / 50% 2-D | 176.3 | 183.5 | 359.8 | 32.7 |
| 20% RME / 80% 2-D | 282.0 | 73.4 | 355.4 | 34.7 |

The technicians followed the blending procedure below, as instructed by Chris Sharp.

1. Place empty drum on scale
2. Tare scale with empty drum
3. Add 2-D fuel to drum until scale reads the 2-D weight for the given blend
4. Add REE or RME, depending on the blend, until scale reads the "total" weight
5. Seal and label drum, place on drum mixer for one hour
6. Check API gravity of each blended drum

A draft copy of the final report of the emissions study has been circulated and the final copy is in the final process.

A SUMMARY OF THE UNIVERSITY OF IDAHO CONFERENCE COMMERCIALIZATION OF BIODIESEL - ESTABLISHMENT OF ENGINE WARRANTIES

The University of Idaho, Department of Agricultural Engineering with assistance from The National Center for Advanced Transportation, The PNW and Alaska Regional Bioenergy Program, the Idaho Department of Water Resources Energy Division and the ASAE T-11, Energy Committee sponsored an invited, focused workshop on Commercialization of Biodiesel, Establishment of Engine Warranties. Participants were invited from all segments of the Biodiesel industry but engine manufacturers and users were particularly targeted. Representatives from Detroit Diesel, Navistar, Cummins, Mercedes Benz, the National Biodiesel Board, the Austrian Biodiesel Industry, Link Transportation, Spokane Transit plus other interested research workers and individuals participated in the conference. The conference had two goals 1) development of a brief statement on the current status of the effect of Biodiesel on Engine Warranties 2) development of a strategic plan for making Biodiesel a recognized fuel acceptable by engine manufacturers for use in their engines. This paper will summarize the presentations of the conference, will discuss the draft statement on where we are today on warranty for use of Biodiesel and the issues related to warranty which the engine manufacturer's and users developed as part of the conference.

A complete proceedings of the warranty conference is available from the National Center for Advanced Transportation Technology at the University of Idaho.

The workshop was organized to bring together Biodiesel users, research workers, representatives of the National Biodiesel Board and other interested parties to explore the current status of Biodiesel, its effect on engine warranties and what issues remain to be resolved before Biodiesel can be thought of as a legitimate fuel for diesel engines. The workshop format included brief "state-of-the-art" presentations by researchers, NBB, DOE and Biodiesel users, followed by group sessions which developed a statement of where we are now with engine warranties and a statement of issues that need to be resolved to bring Biodiesel under full warranty coverage equivalent to diesel.

The University of Idaho, Department of Agricultural Engineering; the National Center for Advanced Transportation Technology (NCATT), the Pacific Northwest and Alaska Regional Bioenergy Program, The Idaho Department of Water Resources, Energy Division and the ASAE T-11 Energy Committee were the principal underwriters for this workshop. The planning committee included Craig Chase (a consultant to DOE), Jim Butler (consultant to NBB), Steve Howell (Director of Research at NBB), and Dave Woodall (Associate Dean, College of Engineering, University of Idaho).

NCATT

The National Center for Advanced Transportation Technology (NCATT) was founded in 1991 through an act of Congress. It received funding to construct a new engineering and physics building and a mandate to develop a transportation center with a focus on the needs and agenda of industry. During the past two years, it has organized its efforts around five technology working groups, including hybrid electric vehicles, advanced materials and manufacturing, power electronics, traffic control systems, and alternative fuels. While the center is still relatively new, its work during the past two years has generated about \$1.5 million in external research funding involving nearly 100 University of Idaho faculty and students. The work at the center is guided by three primary customers: private industry and governmental agencies with a direct stake in our nation's transportation system, engineering students, and faculty at the University of Idaho.

PROGRAM

Welcome and Introductions:

Charles L. Peterson, Agricultural Engineering Department, University of Idaho
Dave Woodall, College of Engineering, University of Idaho

Mike Kyte, National Center for Advanced Transportation Technology, University of Idaho.

Biodiesel Research:

Jim Butler, P.E. -- Moderator
Earle E. Gavett, National Biodiesel Board
Mehboob Sumar, Ortech
Bill Marshall, National Institute for Petroleum and Energy Research
Mark Russell, University of Missouri
Charles L. Peterson, University of Idaho
Werner Korbitz, Korbitz Consulting, Austria

Transit System and Other Use of Biodiesel

Craig Chase -- Moderator
Dick Yost, Spokane Transit
Todd Daniel, Link Transit
Howard Haines, Montana Department of Natural Resources

Luncheon Speakers

Jeffrey James, U.S. Department of Energy
Jerry Allsup, U.S. Department of Energy

Engine Warranty Policy

Steve Howell -- Moderator

Rodica Baranescu, Navistar, Engine Manufacturers Association

Karl Koontz, Cummins Engine Co., Inc.

Ansgar Shafer, Mercedes Benz

Lester Walker, Detroit Diesel

Madan R. Goyal, Deere Power Systems Group (written only)

Industry and Biodiesel

George Durany, J.R. Simplot Co.

Group Sessions: Questions and Answers.

INTRODUCTORY REMARKS

This was a focused workshop on commercialization of Biodiesel and the establishment of engine warranties. There are many Biodiesel issues that are important, but this conference was to focus on engine warranties.

During a trip some time ago in Europe several pieces of advertising literature were found which recognized Biodiesel as an engine fuel. A Mercedes Benz "Unimog" advertisement says, "Attention: New Information for Agriculture! I have RME in my tank. It can be used in diesel engines. It can be mixed with diesel. There's no effect on the engine. There's no effect on the engine warranty." In Europe there are other manufacturers who do warrant engines, and state so in their advertising literature. Deutz Fahr, for example, in an advertisement says "Environmentally Friendly, Energy Sparing with Deutz Fahr Tractors," referring to use of rape methyl ester. An advertisement from an Agricultural show in Frankfurt for Deutz Fahr rape methyl ester. An advertisement from an Agricultural show in Frankfurt for Deutz Fahr tractors says "RME Usable" directly under the Deutz Fahr tractor model listing on the display. There are many other manufacturers that warrant their engines operating on Biodiesel in Austria.

This conference focused on the issue of establishment of engine warranties in the United States. The issues are where we are currently and what we have to do. There were two goals for the final product from this meeting. First, a brief statement on the status of Biodiesel today with respect to engine warranties. In many of the publications from the University of Idaho notices are included stating that this is a research report and that we are not advocating use of Biodiesel in personal vehicles. We would like to rewrite that statement. When Biodiesel is used in a vehicle we want the owner to know what effect that will have on their engine warranty. Second, to develop a strategic plan for what needs to be done to establish full warranty of engines fueled with Biodiesel. The goal is for Biodiesel, as a recognized fuel, to be accepted by the engine manufacturers, removing the concern for engine warranty. At

this meeting were engine manufacturers, Biodiesel producers, and research teams. They all need to be part of the strategic plan. The goal was to develop the plan while they were together.

BIODIESEL RESEARCH

For lack of space the Biodiesel Research results will not be included in any depth. Most of the research has been or will be presented elsewhere. Biodiesel is used to describe esters of lipids from a variety of feedstocks.

Specific Conclusions noted during the Conference from a variety of feedstocks: Biodiesel has been found to be an acceptable substitute for diesel fuel, performing normally in unmodified diesel engines. Recipes for producing Biodiesel have been developed and used to produce demonstration quantities of fuel. Biodiesel is safer because the flashpoint is over 56°C (100°F) higher than that of diesel. Engine durability tests of up to 1000 hours have generally shown Biodiesel to be equivalent to diesel fuel. Biodegradability of Biodiesel was higher than the biodegradability of reference dextrose and much higher than diesel fuel. Toxicity of Biodiesel was at least 15 times less than diesel and probably even much lower. Smoke, as measured by an opacity meter, has generally been found to be 33% to 65% lower than from diesel fuels. Emissions test have shown a reduction in HC and CO₂ and an increase in CO₂. Results for PM and NO_x are mixed. Much more work on emissions with Biodiesel is required.

TRANSIT SYSTEM AND OTHER USE OF BIODIESEL

Spokane Transit, Dick Yost

Spokane Transit has a bus fleet of 144 heavy duty coaches that are operated in the city of Spokane and surrounding area. The main base is in the downtown area where approximately 124 busses are stored. A satellite facility is in the Spokane valley. The facility in the valley is where the year-long test on biofuel was conducted. The test was divided into two six-month segments: the first six months the coaches used a 70% blend of #1 diesel with a 30% soy-based oil. For the second six-month period the fuel was changed to an 80% #1 fuel with a 20% soy-oil. The engines in the coaches designated for the test are all Detroit diesels with several different engine types: six V-71's; six V-92's; six L-71's. The coaches are from various years ranging from 1974 to 1992.

The test was conducted from October, 1993 to October, 1994. Particulate levels were tested with a Bosch smoke analyzer, which is what the State of Washington uses for testing particulate matter. Oil analysis tests were taken at different times during the test. Three months into the test the injectors were removed from two coaches, both an electronic injector and a mechanical injector, which were sent to Salt Lake City, Utah by Spokane Detroit. No

problems were found with any injectors at any point in the test. There also were no mechanical problems. The results from the test were really very positive. They reported a clean burning fuel. The particulate level decreased about 12% and they had an average of about 0.2 kilometer/liter (0.5 miles per gallon) better fuel mileage with the biofuel than with the straight diesel.

During the first six months, the soybean association provided the fuel; during the second six months they purchased the fuel. They were hoping from a maintenance standpoint to continue with the fuel, but the cost was too high. The cost was about \$0.76 per liter (\$2.89 a gallon) for the soy fuel and \$0.19 per liter (\$.73 per gallon) for diesel. The increase in the annual fuel cost was 59%. Even with the advantages of Biodiesel they are not able to justify the extra cost to the Board of Directors.

Link Transit Biodiesel Demonstration Project, Todd Daniel

On December 16, 1994 Link will celebrate three years of providing public transit in Chelan and Douglas county. They are a fare free system, one of just three in the state of Washington. Because of the high monthly fleet mileage they elected to try a fleet-wide, one month, 161,000 kilometer (100,000 mile), Biodiesel demonstration. The biodiesel fuel was supplied free of charge from farmer checkoff dollars and regulated by the National Biodiesel Board. A 20% blend with number two low sulfur diesel powered their diesel fleet for twenty-eight days, or the entire month of February, 1994.

A few points of interest that were recorded during the demonstration were total fleet miles recorded at 167,000 kilometer (104,000 miles) on the 20% blend: oil sample results did not reflect anything unusual, there was no change in fuel economy, the average temperature was 12°C (22°F) with no fuel clouding; emission levels (smoke) were lowered 17% fleet wide and finally, they received very positive public response. The Link Biodiesel demonstration was called a success. Public and staff involvement, along with lower emissions, were the ingredients. National news coverage was an added benefit. It is their hope that better pricing and availability will develop and breed life into Biofuels!

"Truck in the Park" Demonstration, Howard Haines

The Montana Department of Natural Resources and Conservation (DNRC) in cooperation with the National Park Service (NPS) and the U.S. DOE Pacific Northwest and Alaska Regional Bioenergy Program will conduct an operational demonstration of a diesel truck powered by rape ethyl ester (REE). This fuel is produced by the University of Idaho (U of I) for use in tourism-related service in Yellowstone National Park. DNRC will assist the Park Service and private industry in developing options for managing the impact of the growth in tourism while preserving scenic resources.

Project Goals, Objectives, and Approach

The goals of this project are to:

- Develop a biomass-derived transportation fuel that is attractive for use in tourism-related industries and others that operate in environmentally sensitive areas.
- Provide a beachhead market for a developing industry, to encourage the development, production, and use of this biofuel within the region.
- Determine the feasibility of using Biodiesel at high elevation.

INDUSTRY

Navistar, Rodica Baranescu

Between 1991 and 1993 Navistar made 88,000 medium and heavy duty trucks. Last year they produced 178,300 engines. They are the largest producer of diesel engines in North America. Navistar has a statement for Biodiesel fuel use, it reads: "Use of 100% Biodiesel fuel is not recommended due to performance and potential reliability issues." By Biodiesel, they imply mostly methyl esters of vegetable oil. As to warranty position on this issue Navistar says, "Blends of Biodiesel with conventional diesel fuel in amounts up to 20% may be suitable for use. However, the user assumes warranty liability for any failure directly resulting from the suitability of a 'BIO' fuel blend and/or associated additives." They state that "This position is consistent with the use of any fuel additive." The Warranty Procedures and Administrative Policies procedure reads " ...If the use of additives causes a failure, the cost to repair or replace the failed part or component is not reimbursable. User and fuel suppliers maintain a responsibility for the quality of fuel regardless of Biodiesel impacts. Further, durability and emissions impact testing will be required to better assess the vulnerabilities of Biodiesel fuel usage in International engines.." In one of the warranty statements it states "Warranty coverage will not be voided by installation or use of special equipment additives or other chemicals designed to improve vehicle performance, non-Navistar parts, or by modification of any part of the vehicle. However, if the use of such devices, modifications or additives causes a failure the cost to repair or replace the failed part or component is not reimbursable." We believe we don't know enough today about the behavior, especially the long term behavior, of Biodiesel fuel.

The Engine Manufacturers Association brainstorming session identified the following critical issues in the development and commercialization of Biodiesel: fuel characteristics, water absorption and additive compatibility, cold flow characteristics of the fuel, fuel specifications for Biodiesel, engine performance and emissions, engine certification for Biodiesel, engine optimization for Biodiesel, emissions speciation for Biodiesel, compatibility with engine materials, effects of the fuel on lubricating oil, maintenance of Biodiesel engines in comparison to diesel engines, economics and infrastructure needs, availability of the fuel and potential markets.

Cummins Engine Co. Karl Koontz

Cummins is celebrating the 75th year of building engines. Cummins produced 250,000 diesel engines last year. In the U.S., Cummins is number one in engines over 200 horsepower and number five over-all in diesel engine production.

The Cummins fuel specification bulletin lists recommended fuel specifications as well as alternative fuel specifications, and basically says that alternatives are not normally used in Cummins engines and may be used only where a recommended fuel is not available. Biodiesel is generally placed in the alternative fuel category at this time. Our standard fuel recommendation is No. 2 diesel blending for winter requirements.

The owner is responsible for the operation and maintenance of the engine as specified in the Operation and Maintenance manual, providing proof of that maintenance. Under limitations, "We are not responsible for failure or damage resulting from abuse, neglect," and "not responsible for failures caused by incorrect fuels, by water or dirt, or other contaminants in the fuel." Our warranty covers defects in Cummins workmanship and materials; we have built the engines with good parts that have been assembled properly and tested. It doesn't say you can't wear it out; it doesn't say you can't damage it. We look at the fine line as those consumables such as fuel and oil as user's choices, and at different times and emergencies, it may be necessary to deviate from our recommendations; however, all our engines are designed, tested, proven, and fully warranted to run on our recommended consumables: fuel, oil, and coolant. So, in short, the choice of these things implies acceptance of responsibility by the operator. These will not cancel our warranty. We follow ASTM recommended No. 2-D diesel fuel and recommend blends of Numbers 2-D and 1-D in the winter. This fuel needs to be kept above 1.3 degrees centigrade to provide adequate lubrication to the fuel system.

Cummins Concerns and Questions dealing with warranties:

- | | |
|--|---|
| 1. Fuel properties | 9. Effect on power and fuel consumption |
| 2. Cold flow issue | 10. Effect on each of the seven Cummins engine families |
| 3. Seal and gasket compatibility | 11. Reliability |
| 4. Engine deposits | 12. Emissions testing |
| 5. Oil acidity | 13. Durability, wear and deposits |
| 6. Ignition delay | 14. Experience in 240,000-320,000 kilometer (150,000 - 200,000 miles) |
| 7. Effect on combustion and engine temperature | |
| 8. Effect on fuel systems | |

Mercedes Benz, Ansgar Shafer

Mercedes Benz employs 200,000 people world-wide. The U.S. affiliate is Freightliner. Mercedes Benz has world-wide, the largest market share of heavy duty trucks.

Almost 14 to 15 years ago they found that vegetable oils themselves are not suitable alternative fuels. The transesterification of vegetable oils into methyl esters is a well known, optimized and commercially used large-scale standard process in the chemical industry. These esters are usable in all existing CI engines. If any, only minor engine modifications are required (e.g. elastomeric materials for fuel lines). This is the best researched and most developed vegetable oil based alternative fuel. The reality of transesterification is that there are all types of impurities. For example there are non-reacted triglycerides, partially reacted monoglycerides and diglycerides, free fatty acids, and glycerol. There is also methanol, water, monoglycerides and diglycerides, free fatty acids, and glycerol. There is also methanol, water, and the rest of the catalyst. all these things have to be removed because they all are threatening the engine. For example the unreacted material, triglycerides, are building materials for (injector) deposit formation. The free fatty acids are very dangerous for bearing metals, by so-called dry corrosion. The same thing applies to the free glycerol and the monoglycerides because they are very eager to react with bearing metals. The catalysts form ash. Methanol lowers the flash point.

A few important results from long term tests on different vegetable oil esters at Mercedes Benz. (These are tests of rapeseed oil methyl ester and palm oil methyl ester):

- No sludging is apparent with a suitable lubricating oil;

- Oil dilution is within relatively tight limits; no serious effects on relevant lubricating oil characteristics;

- Inlet valves show a slight tendency to coke when the content of glycerides in the ester is too high;

- The cylinder gap has a slight tendency to burn, but these were within acceptable limits;

- The fuel injection system can remain unchanged; no nozzle coking is found when fuel quality is adequate: too high a glyceride content causes nozzle coking;

- Some elastomeric materials (e.g. some fuel lines) are not sufficiently resistant to vegetable oil esters; the materials have to be changed;

- The unusual exhaust gas smell is troublesome (some employees and customers could not tolerate the odor); an oxidation catalyst significantly diminishes the respective inconvenience.

Based on these experiences with methyl esters, Mercedes Benz has produced a service information bulletin regarding the use of rapeseed oil methyl ester produced according to the specification shown earlier. It is not for Biodiesel, because Biodiesel is not clearly defined. This service information is being circulated world-wide to all our affiliates, service centers, and dealers.

Mercedes-Benz trucks (not passenger cars) produced since 1988 with series 300 and 400 engines (DI CI) can be fuelled with RME.

The leak fuel lines of the injection nozzles on series 400 engines have to be replaced by an RME-resistant version and connected to the fuel feed line.

If RME is used in older vehicles, there is a risk that hoses and seals impaired by many years contact with diesel fuel will be attacked by RME and thus become leaky.

Commercial vehicles with MB series 600 engines (vans and pick-ups; IDI) cannot be operated with RME.

Mercedes-Benz does not provide warranty coverage for damage caused by using RME of inferior quality or by non-observance of the instructions for RME operation.

The same applies for industrial engines:

Industrial engines of series 300 and 400 are approved for RME operation.

The fuel should correspond to the DIN standard DIN V 51606.

Operation with fuel of inferior quality may lead to malfunctions or engine damage.

Mixed-fuel operation using RME and diesel fuel is not approved.

Supplementary heaters: Some of them must not be operated on RME, others need to be modified for RME operation, others can be operated on RME without modification provided the control unit has been programmed appropriately. Generally, the supplementary heater can be operated via a separate fuel oil or diesel fuel tank; retrofitting is possible and even advisable for winter operation.

Lester Walker, Detroit Diesel

Detroit Diesel is a well known manufacturer of diesel engines. Specification sheets and warranty documents are very similar to what has already been discussed.

"Is the use of Biodiesel covered under engine warranties?" The answer is right out of our own individual statements: "Manufacturer warranties cover defects in materials and workmanship," much as was covered by our Cummins representative, "Those warranties extend to engines burning Biodiesel. These warranties do not cover engine problems related to fuel of any kind." Then there is a follow-up statement that says, "Tests and demonstrations have shown Biodiesel to be no different than petroleum diesel in terms of engine performance and wear."

The engine warranty, in most cases, is not set up to deal specifically with the use of a fuel. It is set up to cover defects in materials and defects in workmanship; engine problems that are traceable directly to the manufacturer. It's not uncommon when there is an engine warranty question that deals with a particularly severe warranty claim, for example, for the relevant parts of that engine to be returned to the factory or for a materials meeting to be set up to review and look at the condition of the parts to try to establish whether or not there is a root cause that relates to something that the manufacturer did.

Detroit diesel has the following concerns about using Biodiesel

- Regulated emissions, especially NOx;
- Effect on fuel seals;
- Durability testing of 1000 hours duration;
- Field demonstration of over 160,000 kilometers (100,000 miles);
- Tear down of engine from 160,000 kilometer (100,000 mile) demonstration;
- Standardization of the fuel and fuel specification;
- EPA approval.

Diesel Power Systems Group, Madan R. Goyal

The Biodiesel fuels, methyl ester of rape seed oil (RME) or Methyl ester of soybean oil, are believed to be fairly good solvents. The switch over from the diesel fuel to the use of Biodiesel is very likely to dissolve deposits from the fuel tank and fuel injections system and could cause serious fuel filter plugging and/or injector plugging problems. The protective coating from the inside of the fuel tank could also be removed by the Biodiesel fuel.

The technical data in the literature discuss the following important engine durability issues:

- | | |
|------------------------------|------------------------|
| 1. Fuel Quality | 5. Phosphorus |
| 2. Material Compatibility | 6. Oil Dilution |
| 3. Long Term Storage | 7. Valve/Port deposits |
| 4. Low Temperature Operation | 8. Durability Summary |

WORKSHOP SUMMARY

Draft Statement on Where We Are Today On Warranty for Use of Biodiesel

Biodiesel (methyl or ethyl ester of plant oils or animal fats) is a new fuel which is being tested under a wide range of conditions including both neat and blended with petrodiesel. Users of this fuel should be aware, however, that currently there is not fuel specification for Biodiesel and, therefore, engine manufacturers cannot fully recognize it as equivalent to diesel. Users of this or any fuel not meeting manufacturers' published fuel specification requirements assume

warranty liability for failure of components or emission certification traceable to the fuel. Non-fuel related warranty issues are not affected by the use of Biodiesel.

CRITICAL ISSUES RELATED TO ACCEPTANCE OF BIODIESEL BY ENGINE MANUFACTURERS

- A) Fuel Characteristics and Specifications
 - standard test methods
 - fuel standard such as ASTM
- B) Engine Performance and Emissions
 - certified for use by EPA
 - many 1000 hour+and/or 160,000 kilometer (100,000 mile) engine durability tests
 - test for air toxics
- C) Fuel/Engine Interaction
 - materials compatibility tests
 - establishment of oil change intervals
 - engine manufacturer tests
- D) Economics/Infrastructure
 - supply at competitive price
 - identify uses where price is justified
- E) It is clear that development of the required data must be a joint effort of research labs, private and public; engine manufacturers; the biodiesel industry; and governmental agencies such as CARB, EPA, DOE, etc.

A SUMMARY OF THE UNIVERSITY OF IDAHO CONFERENCE COMMERCIALIZATION OF BIODIESEL -- ENVIRONMENTAL AND HEALTH BENEFITS

Mammoth Hot Springs was the site selected for a conference titled " Commercialization of Biodiesel: Environmental and Health Benefits" held May 21 and 22, 1996. This by-invitation, conference brought together Biodiesel users, research workers, representatives of the National Biodiesel Board, government workers, engine manufacturers, and others to review current regulations and research related to environment and health benefits of Biodiesel, to develop a state-of-the-art summary and a plan for further research.

Yellowstone National Park was chosen for the site because of the "Truck-in- the-Park" program; a research and demonstration program of the National Park Service, Montana Department of Environmental Quality, Wyoming Department of Commerce, University of Idaho, Dodge Truck and others. The "Truck-in-the-Park" project is studying the feasibility of using a biodegradable and environmentally friendly fuel like Biodiesel (which uses canola oil and alcohol as feedstocks) in the pristine setting of a National Park.

The conference was sponsored by those listed above plus both the Western and Pacific Northwest and Alaska Regional Bioenergy Programs and the Idaho Department of Water Resources, Energy Division. Charles Peterson , Professor of Biological and Agricultural Engineering at the University of Idaho was the conference chair, Jack Roberts and Jim Evanoff of the National Park Service were local hosts. The Universtiy of Idaho National Center for Advanced Transportation Technology managed the conference.

Topics discussed in addition to the "Truck-in-the-Park project included: Health issues, Regulation and Policy; Biodegradability and Toxicity; Exhaust Emissions and Air Quality Issues.

Richard Moorer, Associate Deputy Assistant Secretary, Office of Transportation Technology, USDOE, was the featured speaker; other speakers included: Peter Venturini, California Air Resources Board; Jurgen Krahel, Institute of Biosystemstechnik, Germany; Rodica Barenescu, Navistar International and many others.

PURPOSE

To review current regulations and research related to environment and health effects of biodiesel, to develop a state-of-the-art summary statement and a plan for further research.

SPONSORS

National Center for Advanced Transportation Technologies (NCATT), University of Idaho
Department of Biological and Agricultural Engineering, University of Idaho
U. S. Department of Energy
 Pacific Northwest and Alaska Regional Bioenergy Program
 Western Regional Biomass Energy Program
Idaho Department of Water Resources, Energy Division
National Park Service
Montana Department of Environmental Quality

PROGRAM COMMITTEE

Charles L. Peterson, Chairman
 Department of Biological and Agricultural Engineering, University of Idaho
Craig Chase, Consultant, Pacific Northwest and Alaska Regional Bioenergy Program
David Woodall, Associate Dean, College of Engineering, University of Idaho
Jim Butler, Consultant, National Biodiesel Board
Steve Howell, Director of Research, National Biodiesel Board
Jeff James, Department of Energy
Howard Haines, Montana Department of Environmental Quality
Jack Roberts, National Park Service, Yellowstone National Park
Jim Evanoff, National Park Service, Yellowstone National Park

PROGRAM

Tuesday, May 21, 1996

8:30 a.m. **Welcome and Introductions**
 Charles L. Peterson, Conference Chairman
 Professor Department of Biological and Agricultural Engineering
 University of Idaho, Moscow, Idaho

Welcome to Montana
 Mark Simonich, Director
 Montana Department of Environmental Quality
 Helena, Montana

9:00 a.m. **Welcome to Yellowstone**
 Marvin Jensen, Assistant Superintendent, Yellowstone National Park

Greening of Yellowstone

Tim Hudson, Chief of Maintenance, Yellowstone National Park

About Yellowstone and the "Truck-in-the-Park" Program

Jack Roberts, Assistant Chief of Maintenance, Yellowstone National Park

Jim Evanoff, Facilities Manager, Yellowstone National Park

10:00 a.m. **Break**

Session 1 - Compression Ignition Fuels: Health Issues, Regulations and Policy

Moderator - Craig Chase, Consultant

Pacific Northwest and Alaska Regional Bioenergy Program

Cody, Wyoming

10:15 Diesel Fuel and Diesel Fuel Exhaust - An Overview of California Programs

Peter Venturini, Director, Stationary Sources, California Air Resources Board

10:40 New Fuels and Fuel Additives, Section 211(b) Programs

Dave Kortum, Manager, Technical Analysis Group, Fuels and Energy Division
Office of Mobile Sources

U.S. Environmental Protection Agency

11:05 Environmental Effects of Biodiesel and Biodiesel Exhaust: A European
Perspective

Jurgen Krah, Institute for Biosystemstechnik, Braunschweig, Germany

11:30 An Industry Perspective

Rodica Baranescu, Ph.D., Chief Engineer

Engine Technology Analysis

Navistar International

12:00 Working Lunch (Catered by the Yellowstone Concessionaires)

Moderator -- Jeff James, Manager

Pacific Northwest and Alaska Regional Bioenergy Program

Seattle, Washington

**Luncheon Speaker - Richard Moorer, Associate Deputy Assistant Secretary, Office of
Transportation Technology, USDOE**

Session 2 - Biodegradability and Toxicity Research

Moderator -- Jim Butler, Consultant

National Biodiesel Board

Tifton, Georgia

1:30 p.m. Biodegradability of Biodiesel in the Aquatic and Soils Environment

Xiulin Zhang, Graduate Assistant

Department of Biological and Agricultural Engineering

University of Idaho

10:00 p.m. Toxicity Studies with Biodiesel

- Daryl Reece, Engineering Specialist, Department of Biol. And Ag.
Engineering, University of Idaho
2:30 p.m. COD, BOD and Toxicity of Biodiesel
Randall Haws, Quality Assurance/Project Coordinator,
Home Analytical Services, University of Idaho
3:00 p.m. Break

Session 3 - Biodegradability and Toxicity Research Part II

Moderator -- Earle Gavett, Consultant, NBB, Washington D.C.

- 3:15 p.m. Yellowstone Park Bear Attractant Study with Biodiesel
Mark Biel/Kerry Gunther
Bear Management -- Yellowstone National Park
3:45 p.m. Power, Emissions and Bioresponse of Biodiesel in a Marine Environment
Alvin Womac, Assistant Professor
Department of Agricultural Engineering
University of Tennessee
4:15 p.m. Life Cycle Analysis
John Sheehan,
NREL
4:45 p.m. Discussion

6:30 p.m. Evening Barbecue

Program -- *The Yellowstone Wolves*

Mike Phillips
Yellowstone National Park

Wednesday, May 22, 1996

Session 4 -- Emissions and Air Quality Issues

Moderator -- Howard Haines, Montana Department of Environmental Quality

- 8:30 a.m. Emissions Testing With Biodiesel
Charles L. Peterson, Professor
Department of Biological and Agricultural Engineering
University of Idaho
9:00 a.m. Toxic Compounds Studies with Ethyl and Methyl Esters
Norman Kado, Assistant Professor
Environmental Toxicology
University of California
9:30 a.m. Chemical Characteristics of Biodiesel/Low Sulfur Diesel Fuel Blends
Leon Schumacher
University of Missouri
10:00 a.m. Break

Session 5 -- Emissions and Air Quality Issues Continued

Moderator -- Steve Howell, Research Coordinator, NBB and Marc IV, Bucyrus, Kansas

10:30 a.m. Emissions With Ethyl and Methyl Esters of Biodiesel
Chris Sharp, SWRI

11:00 a.m. Emission Studies at North Dakota
Howard Haines
Montana DEQ

11:30 a.m. Environmental and Health Concerns at Mercedes Benz
Ansgar Schafer
Mercedes-Benz AG
Stuttgart, Germany

12:00 Lunch

1:30 p.m. Session 6 -- Break Out Session -- Where we are and Where We Need To Be

Moderator -- David Woodall, Associate Dean
College of Engineering
University of Idaho

Goals for the Session:

1. Develop a statement describing the current status of the Environmental and Health Benefits of Biodiesel.
2. Identify environmental and health issues that need additional research.
3. Identify those best prepared to do this research and estimate of cost of the activity.

Task 1: Each group will draft a statement to meet goal 1.

Task 2: Each group will prepare a list of issues to meet goal 2.

Task 3: Each group will select high priority issues from the lists and respond to goal 3.

4:00 p.m. Conference Summary -

Charles L. Peterson, Professor University of Idaho, Moscow, Idaho

Adjourn

CONFERENCE SUMMARY STATEMENT

Statement describing the current status of the environmental and health benefits of Biodiesel -

Biodiesel; with respect to petroleum diesel, demonstrates the potential for improved performance in the areas of safety, health and environmental protection. It offers the following benefits:

- *Improved biodegradability;
- *Reduced CO and HC emissions;
- *Reduced particulate emissions in most cases, especially soot;
- *Safer for handling in the neat form due to the high flash point;
- *Increased oxidizing catalytic converter effectiveness with organic compounds;
- *CO₂ recycling, thus reducing greenhouse gas emissions; and
- *a positive energy balance.

Biodiesel may also offer the following benefits, however, additional research data are needed for verifications:

- *Reduced oral and dermal toxicity;
- *Reduction of ozone precursors;
- *reduced PAH emissions; and
- *reduced mutagenic and carcinogenic compounds associated with Biodiesel exhaust.

The following issues need resolution:

- *increased NO_x levels associated with Biodiesel exhaust;
 - *exhaust Aldehyde levels show reductions in some tests;
 - *the insoluble nature of biodiesel clouds information on water toxicity;
 - *Some PAH's, such as Benzo(a)pyrene may be increased; and
 - *The benefits of biodiesel blends (with petroleum diesel) are less than for the neat fuel.
- Some of these effects are nonlinear.

The priority research needs for Biodiesel in the areas of environment and health are:

1. Determine the optimum blend of biodiesel based on fuel properties, engine performance and emissions, including non-regulated compounds, over a wide range of feedstocks and engine technologies.
2. Risk assessment for PM size distribution, PM-NO_x tradeoffs, emissions speciation, emissions toxicity, and influence on ozone formation in petroleum diesel vs. biodiesel blends.

3. Develop testing protocols for some emissions parameters (HC and PM for example) for biodiesel.
4. Determine the effect of biodiesel spills and exhaust gases on soil and water environments including effects on plant and animal life forms.
5. Identification of issues associated with Biodiesel solubility in both the aquatic and marine environments.
6. Development of a database on health impacts of biodiesel, biodiesel blends and air toxics from biodiesel emissions.
7. Develop fuel specifications and standard test protocols for biodiesel and biodiesel blends.
8. Confirm the effectiveness and life of the oxidizing catalytic converter for use with biodiesel.
9. Conduct a biodiesel life cycle analysis, including global warming and energy efficiency, for the major biodiesel feedstocks.
10. Determine the effect of additives, if any, used with biodiesel on health and safety.

CONCLUSION

This conference was very successful in bringing together the members of the biodiesel community to present and discuss the current issues related to the benefits of biodiesel as regards environment and health. The conference summary should be useful both as a state of the art statement and a guide to future research. A complete conference proceedings will be available in the near future and may be ordered from the University of Idaho, National Center for Advanced Transportation Technology.

TECHNICAL AND DEMONSTRATION VEHICLE DISPLAYS

Technical Presentations

The first technical presentation was at the American Oil Chemist's Society in Atlanta, Georgia in May, 1994.

The second technical presentation was at the Biodiesel '94 Conference "Biodegradability and Environmental Benefits of Biofuels" in Sioux Falls, SD April 19, 1994.

The third technical presentation, "Biodiesel feedstocks and Fuel Supply" Biodiesel '94, Sioux Falls, SD, April 19, 1994.

The fourth technical presentation was at the American Oil Chemist's Society in Atlanta, Georgia, May 11, 1994.

The fifth technical presentation was in Boise, Idaho at the National Alternative Energy Teleconference "Potential of Biodiesel as a Transportation Fuel" May 16, 1994.

The sixth technical presentation was in Reno, Nevada at the 1994 National Bioenergy Conference, October 2-6, 1994.

The seventh technical presentation was at the 1994 ASAE Winter Meeting in Atlanta, Georgia. (2 papers)

Bureau of Land Management (BLM) Energy Workshop, "Biodiesel Research and Development", May 24, 1994, Boise, Idaho.

Ag Expo '96, "Biodiesel from Rapeseed Oil and Canola", January 17, 1996, Spokane, Washington.

International Spring Fuels and Lubricants Meeting, Dearborn, Michigan, "Emission Testing with Blends of Esters of Rapeseed Oil with and without a Catalytic Converter".

Agriculture Machinery Conference, Cedar Rapids, Iowa, "Biodiesel Development and Testing", May 6, 1996.

Vehicle Demonstrations

Earth Day, Portland, Oregon April 23, 1994. Craig Chase

Kansas City, Missouri June 16, 1994 at the Second Annual Liquid Fuels, Lubricants and Additives from Biomass Conference.

The Capitol Mall in Washington D.C. June 24, 1994. The pickup was on display in front of

the Department of Energy's office in the morning and in front of the State Capitol Building in the afternoon.

The International Alternative Fuels and Clean Air Conference in Milwaukee, Wisconsin, June 29 - July 1, 1994.

First Biodiesel Conference - Commercialization of Biodiesel: Establishment of Engine Warranties, November 9-10, 1994, Moscow, Idaho.

Truck In The Park kickoff on the Montana State Capitol building grounds, Helena, Montana, April 7, 1995.

Second Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry. Portland, Oregon, August 21-24, 1995. Three papers were on display as poster presentations.

The International Alternative Fuels and Clean Air Conference in Milwaukee, WI, June 30 - July 2, 1995.

Big Sky Alternative Fueled Vehicles conference and Expo '95, Billings, Montana, August 7-9, 1995.

SAE Alternative Fuels Conference & Exposition, San Diego, California, December 6-8, 1995.

Ag Expo 96, Spokane, Washington January 16-18, 1996.

Second Biodiesel Conference - Commercialization of Biodiesel: Environmental and Health Benefits. Mammoth Hot Springs, Wyoming, Yellowstone National Park, May 21-22, 1996.

Idaho Transportation Consortium Meeting, Alternative Energy, August 29, 1994, Moscow, Idaho.

Moscow Grange Annual Meeting, "Biodiesel from Rapeseed Oil", Sept. 21, 1994, Moscow, Idaho.

1994 PNW Canola Conference, University of Idaho Biodiesel Program, Nov. 11, 1994, Spokane, Washington.

Biodiesel fueled pickup display at the Biobased Products Expo '94, Kansas City, Kansas, December 4-7, 1994.

Publications of technical Biodiesel development articles in trade, energy and environmental publications.

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