ALTERNATIVE DIESEL FUELS

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ABSTRACT

Petroleum-based motor fuels gave 97 % of the 2005's energy used in transport worldwide. These fuels have already undergone substantial improvement. Many specifications have been enforced. In 2003, the transport sector consumed 1.5 Mt worldwide, from which only 3 % represented alternative motor fuels, such as natural gas for vehicles, liquefied petroleum gas and biodiesel. Alternative diesel fuels, such as water-in-fuel emulsions, have been proved to be a method for reducing diesel PM and other emissions from diesel engines. There was a 20 % emission reduction in comparison testing with other diesel fuels. The use of alternative diesel fuels to achieve emission reductions is best suited for application to fleets, stationary engines, and equipment, which have access to a centralized fueling station.

KEYWORDS: emulsion, biodiesel

1. FUEL/WATER EMULSIONS

A-55, Incorporated, has patented diesel/water and naphtha/water emulsion fuels for use in compression ignition (CI or Diesel) engines. The diesel/water fuel patented by A-55 consists of about 30 percent water and about 70 percent petrodiesel. Small amounts (less than 1 percent) of a proprietary additive are included to maintain the emulsion, enhance the lubricity, inhibit corrosion, protect against freezing, and limit foaming potential. The diesel fraction of the emulsion can be either a naphtha cut or finished diesel fuel.

The presence of water in the emulsion reduces both diesel PM and NO_x emissions in diesel engines. The water causes lower combustion temperatures, which reduces NO_x emissions. The NO_x emissions reductions increase as the water content of the emulsion increases. Also, for a certain water content, the NO_x reductions are greater for diesel/water emulsions than for diesel/naphtha emulsions. The water also produces a different combustion pattern, which causes the carbon in the fuel to burn more completely, producing lower diesel PM emissions.

Tests in a transit bus showed NO_x reductions of 53 percent and diesel PM reductions of 20 percent.

There does not appear to be any loss of engine power or degradation in performance from the use of diesel/water or naphtha/water emulsions.

Testing has shown that power and torque curves with the emulsions are comparable to those of No. 2-D fuel. Peak cylinder pressures are also comparable. Diesel/water emulsions appear to result in slightly greater thermal efficiency.

The presence of water decreases the volumetric energy content, which is translated into a reduction in VFE (miles per gallon). However, there appears to be little difference, or perhaps a slight increase, in the fuel economy, on a miles-per-BTU basis with the emulsion. Because of the reduced volumetric fuel economy, the range is reduced.

Also, on some applications, the volumetric flow rate to the engine is increased, necessitating modifications to the fuel metering system.

The need for those modifications is an obstacle that has to be overcome before diesel/water emulsions could be considered feasible on a wide spread basis for all diesel vehicles.

The use of diesel/water and naphtha/water emulsions has been demonstrated in some bus fleet applications. The regional transit agency in Reno has three urban transit buses operating on diesel/water and naphtha/water emulsions, and the Washoe County School District became the first school district to approve the use of the fuels in four school buses. More recently, two para-transit buses in Sacramento were operated on A-55.

The Lubrizol Corporation has also been developing diesel/water emulsions for use in diesel engines. Lubrizol calls its fuel Puri NO_x Performance Systems fuel (Puri NO_x). Puri NO_x is a diesel/water emulsion in which the diesel fuel is the continuous phase and the water is emulsified.

The water content of Puri NO_x is about 20 percent and the diesel fuel content is about 80 percent. Surfactants and other additives make up less than 1 percent. Lubrizol has reported a NO_x reduction of 15 percent, and a diesel PM reduction of 51 percent, in eight-mode emission testing of Puri NO_x in a eight-cylinder, 34.5-liter diesel engine. The table below summarizes the reported emission reductions.

Table 1. Emission Reductions from Engine Testing of Puri NO_x

Pollutant	Reductions (%)
NO_x	15
THC	14
CO	9
Diesel PM	51

Lubrizol has also conducted a chassis dynamometer test on a Euro II Olympian bus in which Puri NO_x was used in combination with a diesel oxidation catalyst. Over the Millbrook London Transport Bus (MLTB) Cycle, the combined use of the diesel oxidation catalyst and Puri NO_x achieved a NO_x reduction of 21 percent and a diesel PM reduction of 70 percent.

The baseline diesel fuel and the emulsion-base diesel fuel were the same, and had a sulphur content of less than 50 ppm w and a T_{95} of less than 345^{o}C. The table below summarizes the observed emission reduction.

Table 2. Emissions and Emission Reductions from Chassis Testing of a Bus with Diesel Oxidation Catalyst and Puri NO_x

Pollutant	Baseline emissions (g/km)	Emissions w/doc+ Puri NO_x (g/km)	Emission reduction (%)
NO_x	14.0	11.1	21
THC	0.654	0.055	92
CO	1.516	0.046	97
Diesel PM	0.182	0.055	70

2. ETHANOL/DIESEL MICRO-EMULSIONS

Ethanol itself is the foremost biofuel in terms of consumption, and the world leading alternative energy. In 2003, USA and Brazil were the main manufacturers.

Emulsions between ethanol and diesel recently have shown promise as an emission reduction technology for diesel engines. In ethanol-diesel emulsions, globules of ethanol are dispersed within the diesel fuel. Most of the research to date has focused on formulations with aqueous ethanol, that is, solutions of water and ethanol. The aqueous ethanol content of the emulsions is typically 12 to 24 percent by weight.

A stable emulsion is maintained with the presence of surfactants, which contain polar and non-polar ends. The polar ends point towards the interior of the globules where the ethanol molecules are found, while the non-polar ends point to the area between the globules where the diesel compounds are founds.

The globules in ethanol-diesel emulsions tend to be smaller than those found in fuel/water emulsions. Hence they are referred to as micro-emulsions. Micro-emulsions are clear, temperature-stable formulations that can be handled the same way as diesel fuel.

Ethanol-diesel emulsions are being developed as a strategy for diesel PM and NO_x emission reduction. NO_x reductions are achieved as a result of lower combustion temperatures. The combustion temperatures are reduced as a result of the high heats of vaporization of ethanol and water.

The diesel PM emissions are reduced as a result of a phenomenon referred to as steam explosion. Steam explosion refers to the sudden vaporization and expansion of the water within the globules.

This vaporization better atomizes the fuel, which promotes complete combustion. The emission reduction effects of water and ethanol are proportional to their concentration.

So-called “first generation” formulations of ethanol-diesel emulsions reduced diesel PM emissions by approximately 40 percent and NO_x emissions by approximately 10 percent. “Second generation” formulations incorporating several refinements increased the NO_x reduction somewhat, but decreased the diesel PM reductions.

Further work is being done to obtain the optimum formulation for combined NO_x and diesel PM reductions. Some tests have shown that the use of ethanol-diesel emulsions increases emissions of some pollutants. Exhaust hydrocarbon emission increases of 20 to 50 percent have been measured.

The presence of ethanol in the emulsion causes both formaldehyde and acetaldehyde to increase. The table below summarizes the emissions reductions from the use of ethanol-diesel emulsions.

Table 3. Potential Emission Benefits of Ethanol-Diesel Fuel Emulsions

Pollutant	Percent Reduction
diesel PM	30…40
NO_x	10…20
CO	0…20
HC	-20…-50
Formaldehyde	-170
Acetaldehyde	-75

Ethanol-diesel emulsions appear to have little effect on diesel-engine fuel economy. The volumetric energy content of ethanol-diesel emulsions is lower than that of diesel fuel.

This would tend to reduce the fuel economy of ethanol-diesel emulsions. However, the thermal efficiency of an engine fueled with an ethanol-diesel emulsion is somewhat higher than with diesel fuel, and this offsets the effect of lower energy content. Consequently, the net VFE with ethanol-diesel emulsions is about the same as with diesel fuel.

A number of companies are working to commercialize the ethanol-diesel emulsion technology. Pure Fuels USA, Incorporated, is working to find the optimum mix of ethanol, water, and diesel.

They are also working to optimize the amount and type of emulsifier. The use of other additives to increase cetane number, improve NO_x reductions, and lower cost is also being explored.

Pure Energy Corporation has developed an additive package that allows the emulsion to be maintained at temperatures as low as -20^{o}F. Pure Energy Corporation participated in a demonstration program by the Chicago Transit Authority in which 15 buses were operated with an ethanol-diesel emulsion.

Further development work needs to be done before ethanol-diesel emulsions can be considered a viable alternative to conventional diesel. Currently, ethanol-diesel emulsions are not cost competitive with conventional diesel, costing about $0.07 to $0.15 more per gallon to produce.

Ethanol-diesel emulsions require government subsidies in the form to tax breaks to approach cost competitiveness with conventional diesel.

Further fleet testing is required to demonstrate the lack of adverse, long-term engine and fuel system effects. Specifically, more information is needed on long-term lubricity and corrosion effects.

Also, further optimization of the emulsifier/additive package is required. In order to optimize the total emissions reductions from diesel engine, the integrated use of ethanol-diesel emulsions in engines using exhaust gas treatment technologies needs to be demonstrated.

3. BIODIESEL

Biodiesel is a mono-alkyl ester-based oxygenated fuel, a fuel made from vegetable oil or animal fats. It can be produced from oilseed plants, such as soybeans and canola, or from used vegetable oil.

It has similar properties to petroleum-based diesel fuel, and can be blended into petroleum-based diesel fuel at any ratio. It is most commonly blended into petroleum-based diesel fuel at 20 percent. This mixture is commonly referred to as "B20". Neat biodiesel is termed B100. The use of biodiesel, neat or in petroleum-based blends, does not require modifications to the engine or fuel system.

Biodiesel is registered as a fuel additive with the US Environmental Protection Agency. It has gone through the US EPA Tier I Health Effects Testing under the Clean Air Act section 211(b), which provides an inventory of environmental and human health effects attributes. Recently, B100 has been classified as an alternative fuel by the US Department of Energy, and the US Department of Transportation.

Some think there are two tipes of biofuels, one of them being ethanol, used in gasoline engine, and vegetable oil methyl esthers (VOME), used in diesel engines. One advantage of biofuels is that, blended with conventional motor fuels, they are compatible with the existing distribution system. Vehicle modifications are not required. Their cost still inhibit general use, although emissions are reduced.

Biodiesel has similar properties to petroleum-based diesel fuel; however, there are some significant differences. Biodiesel contains 11 percent oxygen by weight and contains no sulphur or aromatic hydrocarbon.

On a transient test cycle, fuel economy and power are about 10 percent lower than conventional diesel fuel; with B20 the loss is about 2 percent. Biodiesel has favorable lubricity characteristics, but will soften and degrade certain types of elastomers and natural rubber compounds over time.

Manufacturers recommend that natural or butyl rubbers not be allowed to come in contact with pure biodiesel. Biodiesel can be stored in the same stored tanks as petroleum based diesel, but it has a shorter shelf life, which makes it less suitable for use in emergency generators or engines that operate in frequently.
Emission data comparing biodiesel to CARB diesel are limited, but data comparing biodiesel to conventional diesel fuel are more redily available. Compared to CARB diesel or conventional diesel fuel, the use of B100 significantly reduces diesel PM, CO, and HC, but significantly increases NO_x. Also, based on Ames studies, B100 may provide a 90 percent reduction in cancer risk compared to conventional diesel fuel. In comparing B20 to conventional diesel fuel, the changes in emissions are directionally the same, but smaller.

The table provides a summary of emission test results from the use of B100 and B20 compared to conventional diesel fuel.

Table 4. Potential Emission Benefits of Biodiesel and a 20-Percent Biodiesel Blend

Pollutant	B100 (%)	B20 (%)
NO_x	+13	+2
Carbon Monoxide	-50	-20
Hydrocarbons	-93	-30
Particulate Matter	-30	-22
Sulfates	-100	-20
Polycyclic Aromatic Hydrocarbons	-80	-13
Nitro-PAH's	-90	-50

Source: Biodiesel Emissions, Fact Sheet, National Biodiesel Board, USA

Biodiesel reduces the health risks associated with conventional diesel fuel. Biodiesel emissions showed decreased levels of PAH and nitrited-PAH (n PAH) compounds, which have been identified as potential cancer causing compounds. In recent tests, PAH compounds were reduced by 75 to 85 percent, while the exception of benzo(a)anthracene, while was reduced by roughly 50 percent. Also n PAH compounds were reduced significantly.

The 2-nitrofluorene and 1-nitropyrene emissions were reduced by 90 percent, and the rest of the n PAH compounds were reduced to only trace levels. These toxic emission differences are likely to be smaller when compared to CARB Diesel fuel, but may still be significant. More data comparing CARB Diesel to biodiesel are needed.

Table 5. Biodiesel's specifications:

Property	ASTM Method	Limits	Units
Flash Point	D93	130 min.	Degrees C
Water & Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40 C	D445	1.9 - 6.0	mm^2/sec.
Sulfated Ash	D874	0.020 max.	% mass
Sulfur	D5453		
S 15 Grade		15 max.	ppm
S 500 Grade		500 max.	
Copper Strip Corrosion	D130	No. 3 max.	
Cetane	D613	47 min.	
Cloud Point	D2500	Report	Degrees C
Carbon Residue 100% sample	D4530**	0.050 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/gm
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus Content	D 4951	0.001 max.	% mass
Distillation Temp, Atmospheric Equivalent Temperature, 90% Recovered	D 1160	360 max.	Degrees C

Biodiesel can be produced from biomass, in a two-stage technology involving the gas synthesis and the Fischer-Tropsch process. In this way, kerosene and methanol are also obtained.
The cost per tonne is very high - €700-800. Unfortunately, this technology is still being developed.

In Freiberg, Germany, a pilot plant has been producing biodiesel and methanol from vegetable and organic waste since 2002, having a budget of €11 million.

A laboratory preparation method of biodiesel involves little work and very few materials. This method is based on trans-estherification, which substiutes alcohol for the glycerine in a chemical reaction, using lye as catalyst. The following are needed:

- 1 l of vegetable oil, new, cooking or used;
- 200 ml methanol, 99 % pure;
- lye catalyst – potassium hydroxide (4.9 g 99 % or 5.8 g 85 %) or sodium hydroxide (3.5 g 96 %);
- blender or mini-processor;
- scales accurate to 0.1 g or less;
- measuring beakers for methanol and oil;
- 500 ml Erlenmayer flask with bung and srew-on cap;
- 2 funnels to fit the flask;
- 2 l cylinder for settling;
- 2 l flask for washing;
- duct tape;
- thermometer.

All equipment should be clean and dry.
The lye must be measured very rapidly, because it absorbs water from the atmosphere and water interferes with the biodiesel reaction. The lid of the container must be firmly and quickly closed, winding up so there's not much air in it with the lye and no more air can get in.

200 ml methanol are poured into the 500 ml flask via the funnel. Methanol also absorbs water from atmosphere so it must be done quickly and the lid of the methanol container in to be replaced tightly.

The lye is carefully added to the container via the second funnel. The bung and the screw on the cap are replaced.

The container is being shaken for a few minutes, swirling around rather than up and down. The mixture gets hot from the reaction.

The lye must be completely dissolved in the methanol, forming sodium methoxid or potassium methoxid. As soon as the liquid is clear with no undissolved particles, the process can begin. Mixing KOH is better as it dissolves in the methanol more easily than NaOH. Pre-heat the oil to 55^{o}C and pour it into the blender. Then carefully pour the prepared methoxide from the flask into the oil.

Secure the blender lid tightly and switch on. Lower speed is enough. The blending time is at least 20 minutes. As soon as the process is completed, pour the mixture from the blender into the 2 l cylinder for settling and screw on the lid tightly. The time settling is 12-24 hours.

The by-product (dark glycerine) will collect in a distinct layer at the bottom of the recipe, with a clear line of separation from the pale liquid above, which is the biodiesel (yellow-coloured).

Carefully decant the top layer of biodiesel into a clean recipe. For washing, a 2 l cylinder and a 500 ml of water flask are needed. The biodiesel is poured into a recipe and washed with 500 ml of fresh water, using an air-pump for bubble-washing or a variable-speed drill for stirring. For drying, the clear, translucent biodiesel can be heated gently up to 48^{o}C. emissions, but they are still under a R&D stage.

4. CONCLUSION

The fuels discussed in this paper contain oxygenated compounds. They have all demonstrated great promise for reducing

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