OXYGENATED MICROEMULSION DIESEL FUEL

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ABSTRACT

New low emission fuel technology is needed to meet stricter world-wide particulate and NO_X emission standards for both "on-road" and "off-road" fuel applications. The **Energy Policy Act of 1992** and the **1993 Executive Order 12844** establish clear national goals for the year 2000 and beyond which will reduce petroleum derived fuel use and provide greater utilization of alternate fuel vehicles. Technologies under evaluation include M85, E85, CNG/LPG, biodiesel esters, and electric vehicles. Microemulsion diesel fuel technology, which utilizes oxygenates to help compatibilize a biomass derived or hydrocarbon petroleum phase and water phase, offers strong potential as an alternate fuel option. Oxygenate selection criterion, microemulsion fuel formulation, and performance issues are discussed. Fuel formulations based on alcohol, glycol, ether, and glycol ether microemulsifying agents, which are readily available from world-scale propylene oxide / oxygenated coproduct technology, are described. Evaluation results suggest oxygenated microemulsion fuels are viable alternate fuel candidates.

INTRODUCTION

The trend toward low emission diesel fuels is growing worldwide. In the United States, **Clean Air Act** legislation will mandate reduced diesel particulates in 1994 and lower diesel NO_X emissions in 1998 (1). A combination of new engine technology, additives, and new low emission fuels will be required to achieve these targets. The **National Energy Policy Act of 1992** and **Executive Order 12844** of 1993 establish clear national goals for the year 2000 and beyond which will both reduce petroleum derived fuel use and ozone forming emissions. The **Clean Cities** program provides the framework for implementation which includes greater utilization of alternate fuel vehicles. In addition to "on-road" applications, there is considerable recent focus on "off-road" applications as a major source of particulate and NO_X emissions. A comprehensive E.P.A. report (2) describes our national problem. A NO_X emission inventory shows the magnitude of this problem in ozone nonattainment areas. Emissions from construction, agriculture, railroads, mining, marine, industrial stationary powerplants, airport services, and lawn and garden services all contribute to the global NO_X problem. New altemative fuel technologies under evaluation include: M85, E85, CNG, LPG, and biodiesel esters (3). Microemulsion diesel fuel technology also offers great potential for reducing emissions and dependency on oil (4).

DISCUSSION

Oxygenate Selection

Microemulsions are clear, stable, two-phase nanodispersions which readily form upon mixing water with an oil phase. Water-in-oil (w/o) microemulsions are comprised of a continuous non-polar hydrocarbon phase and a discontinuous aqueous phase. Because of the small droplet size (2 to 200 nanometers) of the discontinuous phase, these microemulsions appear to be clear, one-phase systems. Microemulsion diesel fuel technology uses a microemulsifier to compatibilize a diesel or biodiesel fuel and a water phase. The microemulsifier typically contains a surfactant and a compatibilizing agent (an oxygenate). The resulting microemulsion fuel, when utilized in conventional diesel engines, is "clean-burning", gives no power loss or increase in fuel consumption, and is thermal and shear stable in the fuel handling system.

The purpose of the oxygenate is to help solubilize the surfactant in the fuel, adjust the properties (i.e. viscosity) of the fuel, and possibly contribute to improving the ignition properties of the water-containing microemulsion fuel. Oxygenates in the microemulsifiers are also required to achieve inorganic salt tolerance, thermal and shear stability, and good shelf life. Oxygenates used as microemulsifying agents include C_{1-6} alcohols (5), benzyl alcohols (6), and glycols (7). Key issues are oxygenate cost, flammability, and impact on stability of the microemulsion fuel.

The oxygenates must be inexpensive to achieve economics which are competitive with specialty diesel fuels. Alcohols, such as methanol, ethanol, and t-butyl alcohol, are inexpensive and readily available. Although they all are effective in microemulsion fuel preparation, these alcohol microemulsifiers are flammable. Less volatile alcohols, such as 1-phenyl alcohol (MBA), eliminate the flash point issue, but the resulting microemulsions are more difficult to prepare and have narrower stability windows. Clearly, new candidates, which provide stability and less flammable microemulsion fuels, are desirable.

World-scale propylene oxide technology as practiced by ARCO Chemical Company produces t-butyl alcohol (TBA) and 1-phenylethanol (MBA) as primary coproducts. TBA is the precursor to isobutylene, MTBE, and ETBE and MBA is a styrene monomer precursor. Using these coproducts as building-blocks, several new oxygenates were developed which have application as microemulsifying agents.

Preparation

The microemulsions which have been formulated are water-in-oil microemulsions made up of four basic components: diesel fuel, surfactant, oxygenates, and water. The diesel fuel is a D-2 low sulfur fuel (< 0.5 wt% sulfur, 31% aromatics, 43 cetane number) which is commercially available. The surfactant for these formulations is the anionic long chain fatty acid Emersol 315. This linoleic/oleic/linolenic acid mixture has been neutralized (40% unless noted otherwise in Table I) with monoethanol amine (MEA). Oxygenates may be used alone or as combinations of several oxygenated compatibilizing agents. The microemulsifiers are formed by mixing the Emersol 315, MEA, and oxygenates.

The microemulsion fuels are mixed in the following order: diesel fuel, microemulsifier, water. After mixing the three components, the fuel mixture is shaken and allowed to settle. Any sign of phase separation, solid formation, or cloudy appearance over several weeks is a negative result. If a clear, single phase system is observed, the microemulsion is considered to have formed. Some of the microemulsion fuels prepared are listed in Table I.

Performance

As shown in Table I, the choice of oxygenate in the microemulsifier has a major influence on the stable formation of a microemulsion diesel fuel. Combinations of oxygenates can also improve the ability of the fuel to form stable microemulsions. Optimization of the fuels for surfactant concentration will also improve the formation potential. Although not specifically shown in these examples, it is expected that the character of the different oxygenated compatibilizing agents will change the surfactant requirement of the overall microemulsion fuel. This will allow optimization of the fuels for cost, water loading and performance. Among the performance issues of importance to microemulsion fuels are thermal stability, shear stability, flash point, storage stability, engine performance, and emissions.

TABLE I

Microemulsion Fuel Formulations†

Fuel #	ME‡	Wt% Oxygenate	Wt% Surfactant*	Stable Formation
1	A	34.1	65.9	+
2	B	34.1	65.9	+
3	C	34.1	65.9	+
4a	D1	34.1	65.9	+
4b	D2	34.1	65.9 (100%)	-
4c	D3	10.0	90.0 (27%)	-
5	E	34.1	65.9	+
6	F	33.9	66.1	-
7	G	33.9	66.1	+
10	J	34.0	66.0	+
11	K	33.8	66.2	-
12	L	34.2	65.8	-
13	M1	34.0	66.0	-
14	M2	33.8	66.2	+
15	N	34.0	66.0	-
16	O1	34.1	65.9	-
17	O2	34.6	65.4	+
18	P	34.6	65.4	-
19	R	34.4	65.6	+
20	E	34.1	65.9	+

† 71 / 19 / 10 vol% D-2 / ME / H_2O formulation except: Fuel 2: 75.5 / 14.5 / 10 vol% D-2 / ME / H_2O and Fuel 20: D-2 phase is 95% D-2, 5% of a 80/20 wt% mixture of biodiesel / Di-*t*-butyl glycerol (DTBG).

‡ ME is microemulsifier used in the particular formulation. Each letter designates a different oxygenate composition. Components of the various microemulsifiers will be discussed in the presentation.

*surfactant weight is total of fatty acid and MEA. MEA is added at 40 mol% (40% neutralization) unless noted differently by the number in parentheses

A microemulsion diesel fuel is generally expected to remain stable for several weeks in a temperature range between -10°C and 70°C. This range covers most extremes a fuel would face either in storage and delivery or in the heat of a modern diesel engine fuel delivery system. The fuel must also be stable to the shear forces present in the fuel delivery system within a diesel engine. Preliminary results show microemulsion diesel fuels containing oxygenates in the microemulsifier phase are thermally and shear stable. If the fuel can withstand these conditions in the engine and fuel system, the fuels can be used in current engine technology without major modifications. This makes microemulsion diesel fuel an immediate possibility as an alternative fuel.

Fuel flammability is a major concern. The flash point of the fuel must be above 52°C (126°F) in order to be transported via pipeline in the U.S. As well, the international flammability standard is 140°F. Depending on the oxygenates chosen, the flash point of the microemulsion fuel may be widely adjusted. This is best represented by the data shown in Table II. By using combinations of oxygenates, it is possible to optimize the microemulsion fuel for stability while providing a fuel that meets flammability standards. As an example, fuels 4a and 5 contain the same oxygenate, except in fuel 5 the oxygenate is in combination with another oxygenate. Fuel 5 is a more stable microemulsion fuel formulation compared to fuel 4a, yet still shows an acceptable flash point. Another benefit of microemulsion fuels containing a dispersed water phase is fire resistance. Studies have shown that a microemulsion diesel fuel can be self-extinguishing or will not burn in the presence of an open flame (6). The choice of oxygenate will have an influence of this property of a microemulsion diesel fuel.

TABLE II
MICROEMULSION FUEL FLASH POINTS

Fuel #	ME	Seta Flash Point (°F)
2	B	116
4a	D1	204
5	E	128
7	G	126
10	J	58
20	E	138

Long term stability is necessary to allow for tank storage of the fuel for extended periods of time, especially in some stationary applications. Several of the formulations have shown excellent long term stability, including some which are stable for over one year. Some of the stability data is shown in Table III.

TABLE III
LONG TERM STORAGE STABILITY
OF MICROEMULSION DIESEL FUELS

Fuel #	ME	Storage Stability
1	A	> 1 year
2	B	> 1 year
3	C	> 1 year
4a	D1	> 1 year
5	E	> 1 year
7	G	> 3 months
10	J	> 1 month
20	E	> 1 month

As previously mentioned, microemulsion diesel fuels can be used in current engine technology without major modifications to the engine. However, because of the water and surfactant concentrations in a microemulsion diesel fuel, some loss of ignition properties may be possible (4). The proper choice of oxygenate can reduce or eliminate this problem. As well, the aqueous phase of a microemulsion diesel fuel offers a way for the ignition properties of the fuel to be augmented with inexpensive cetane enhancers.

Regardless of these other performance issues, microemulsion fuels must reduce engine emissions to be a viable option as an alternative fuel. Microemulsion diesel fuels are known to reduce both NO_x and particulates significantly over standard diesel fuels (5). The NO_x reduction is believed to occur through the lowering of combustion temperatures. This is a result of the higher specific heat of the water and oxygenates in the microemulsion fuel. The microexplosion of the water in the discontinuous phase, more effectively vaporizing the fuel in the combustion chamber, is believed to lower the particulate emissions. Surfactant and oxygenate choice and concentrations have an effect on the size of the water micelles in the microemulsion fuel. Therefore, the selection of the proper oxygenated compatibilizer can improve the performance of the engine toward particulate emissions.

With these lower emissions, several new options are available as a result of the use of microemulsion fuels. First, in stationary applications, the lower NO_x emissions from microemulsion fueled sources may help offset other more costly and difficult NO_x emission reduction options. This will be especially beneficial when regional attainment targets are enforced in the near future. Second, a decrease in NO_x and particulate emissions from a microemulsion fueled engine may allow flexibility to tune the engine to reduce other emissions as well.

CONCLUSIONS

With new emissions goals mandated by the Clean Air Act and other legislative mandates, alternatives to petroleum based fuels must be sought. Microemulsion diesel fuels are a cost-effective alternative fuel for both "on-road" and "off-road" applications. These fuels offer significantly reduced NO_x and particulate emissions compared to normal diesel fuel. Microemulsion fuels which contain low cost oxygenated compatibilizing agents offer a range of possible formulations for these fuels. These new formulations have widely tunable stabilities, flash points, and engine performance, depending on the oxygenates chosen. Microemulsion diesel fuels also work with the existing engine technology and do not require any changes to the engines or the fuel infrastructure.

Microemulsifier E offers strong possibilities as a component for microemulsion diesel fuels. This microemulsifier phase contains a combination of oxygenates that gives a fuel which meets many of the requirements for an acceptable alternative microemulsion diesel fuel.

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