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Milestone Report

Advanced Petroleum Based Fuels Program and Renewable Diesel Program

Milestone Report: Technical Barriers to the Use of Ethanol in Diesel Fuel

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Summary

Ethanol-diesel blends (or e-diesel) contain up to 15 volume percent ethanol and an additive known as an emulsifier. The fuel mixture is known as a micro-emulsion and is prepared by splash blending, a process that requires no special equipment or temperature control. Ethanol-diesel blends have a number of potential advantages including:

- Displacement of imported petroleum with a domestic and renewable resource.
- Significant lowering of diesel particulate matter emissions.
- Possible improvement in cold flow properties imparted by the ethanol.
- Possible improvement in fuel lubricity imparted by the emulsifier additives.

The main technical barriers to commercializing e-diesel are:

- *Low flashpoint of this fuel.* E-diesel cannot be safely handled like conventional diesel but must be handled like gasoline. This may necessitate some modifications to storage and handling equipment, as well as vehicle fuel systems. Some stakeholders believe that this fact limits the market for e-diesel to centrally refueled fleets, estimated to represent some 5 billion gallons of diesel fuel annually. If the market is limited to fleets, E-diesel represents a potential market for fuel-grade ethanol of several hundred million gallons.
- *Obtaining OEM warranty acceptance*. Currently engine manufacturers will not warrantee their engines for use with e-diesel because of concerns about safety and liability, as well as materials and component compatibility. A large body of test data acquired in close cooperation with the OEM's will be necessary to address this issue.
- *EPA fuel registration requirements*. As a non-baseline diesel fuel, e-diesel will be required to undergo Tier 1 and Tier 2 emission and health effects testing, a time consuming and expensive process.

In addition to these major concerns there are issues related to quantifying the stability, water tolerance, and other fuel properties of e-diesel. There are also currently little or no data on e-diesel produced using the ultra-low sulfur diesel that will be required in 2006. These issues are discussed in detail in this report.

1 Introduction

The objectives of this study are a) to examine the status of ethanol-diesel blends and b) to identify barriers and technical gaps that hinder rapid introduction of these fuels into the market. The results of this assessment and planning process will allow the Department of Energy (DOE) to understand the issues facing the industry and to determine if and how DOE involvement might assist in overcoming the identified technical barriers. This document includes a brief description of ethanol production, distribution, and storage as background information. This is followed by a description of ethanol-diesel blends (e-diesel) and the properties of these fuels. Engine performance and regulatory requirements are also described. Potential technical barriers are noted in each of these areas and summarized at the end.

This report is the deliverable for the National Renewable Energy Laboratory (NREL) FY 2001 AOP milestones 2.9.1 (Summary Report on Technical Barriers to Use of Ethanol in Diesel Fuels). Work on this milestone was completed in September 2001.

2 Production of Ethanol/Diesel Blends

2.1 Ethanol Production/Supply Potential

Ethanol production for use as a gasoline-blending component began in the U.S. in the late 1970s when it was used as a product extender (gasohol) during the OPEC oil embargoes. Fuel grade ethanol production, primarily corn-based, has grown from approximately 175 million gallons in 1980 to over 1.63 billion gallons in 2000. There are currently 62 ethanol production facilities in the United States, located in twenty different states, although the majority of production (roughly 90%) occurs in the Midwest and north-central states of Indiana, Illinois, Iowa, Minnesota, and Nebraska. Total U.S. ethanol nameplate production capacity is over two billion gallons per year (as of late 2000), and 2001 annual production is expected to be near 2 billion gallons. The majority of ethanol is produced from corn, and the National Corn Growers Association expects production capacity for corn-based ethanol to double in the next five years (Watkins, 2001).

Research continues on the development of efficient, cost-effective processes for producing ethanol from other feedstocks such as waste from agricultural crops, food and beverage processing, wood and paper processing, and municipal refuse. The goal of the DOE National Bioethanol Program (Ferrel, 2000) is to establish an economically viable and environmentally sound supply of bioethanol with the potential to produce 8 billion gallons per year by 2025 and as much as 50 billion gallons by 2050. The DOE National Bioethanol Program focuses on the production of ethanol from cellulosic feedstocks found in all plant matter. These "biopolymers" are like starch (used in the ethanol production process from corn), but with three important differences: 1) hemicellulose and cellulose represent the most abundant form of stored carbon in nature; 2) the chains of sugars are more difficult to hydrolyze; and 3) hemicellulose contains unique sugars that are not as readily fermented. These differences represent the key technical challenges the Program faces. (Ferrell, 2000)

The Program supports a portfolio of activities that is balanced across the spectrum of technology development. DOE is helping to initiate pioneer production facilities using new ethanol production processes. In partnership with biotechnology companies, they are developing better enzymes that will replace sulfuric acid hydrolysis with biological hydrolysis resulting in higher yields and lower production costs. By reducing the cost and technical risk, DOE intends to achieve the Program production metric of 8 billion gallons per year of ethanol in the marketplace by 2025. Thus DOE anticipates ethanol for fuel use to be widely available for the foreseeable future.

2.2 Distribution and Storage of Ethanol

Ethanol is shipped to destination markets by barge/ship, rail, and truck, with roughly one-third of production being transported by each mode (Reynolds, 2000). Among existing ethanol plants, five are located on navigable waters enabling them to ship via barge. Two additional plants have initiated programs to transport their product overland to navigable waters. Collectively these plants can ship 928 mgy (million gallons per year), or 50% of current industry capacity, by barge. Most of the remaining plants ship by a combination of rail and transport truck although some of the smaller plants (i.e. under 20 mgy) ship exclusively by transport truck. These shipping capabilities enable the ethanol industry to access any market in the contiguous forty-eight states in a reasonably efficient manner. Transportation costs can be as low as a few cents per gallon in markets close to the plants or as much as 14-15 cents per gallon in the case of shipping from the Midwest to the west coast.

The least expensive mode of transportation to many markets would be via pipeline. Ethanol-gasoline blends are not currently shipped by pipeline primarily because of ethanol's affinity for water, which might lead to phase separation, and the same would be true of ethanol-diesel blends. The inability to ship gasoline ethanol blends by pipeline has resulted in the current industry practice of blending ethanol into gasoline at the finished products terminal just before it is to be delivered to the retail facility or end user. This practice would likely be followed for ethanol-diesel blends. However shipment of fuel-grade ethanol via pipeline is feasible. Williams Bioenergy, an ethanol producer and pipeline company, claims to routinely ship fuel grade ethanol by pipeline in the Midwest (Smith, 2001). Pipeline transport of large batches (25,000 to 50,000 barrels) minimizes the potential for contamination by water, petroleum products, or pipeline deposits. However, to date pipeline operators do not consider pipeline shipment of ethanol to be economical. Another consideration is the fact that most pipelines originate in the Gulf Coast running north, northeast, and northwest. With most ethanol plants located in the Midwest it would still be necessary to transport product south by barge to access many pipeline markets.

2.3 Fuel-Ethanol Standard

In the United States a number of organizations set fuel ethanol quality standards and specifications. The U.S. Bureau of Alcohol, Tobacco, and Firearms sets minimum standards for denaturing fuel grade ethanol. High taxes of $13.50 U.S./proof gallon are imposed on ethanol that is not properly denatured. The most common denaturant is natural gasoline, an inexpensive and low quality by-product of natural gas production. The minimum denaturant required is two gallons per 100 gallons of ethanol. However, because natural gasoline is less expensive than ethanol, the standard practice in the United States is five gallons of natural gasoline per 100 gallons of ethanol. The American Society for Testing and Materials (ASTM) has developed a standard for denatured ethanol for blending with gasoline; ASTM D4806-9. The relevant properties of this standard are shown in Table 1. Currently fuel-ethanol used in diesel will have been produced for use in gasoline and will thus meet the same standard.

Table 1. ASTM D4806-9 Fuel Ethanol Specifications

Property	Limit
Ethanol, vol. %	92.1
Water, vol. %	1.0 max
Methanol, mg/L	0.5 max
Acetic Acid, wt %	0.007
Chlorine, mg/L	40 max
Copper, mg/l	0.1 max
Denaturants, vol. %	1.96 –4.76

2.4 Ethanol-Diesel Blend Production

As noted, blending of ethanol and diesel occurs at the finished product terminal. Each is stored in its respective tank until drawn from inventory. The terminal must have a tank(s), of sufficient size to meet projected e-diesel demand. Blending systems must be installed (or existing blending systems modified) to accommodate ethanol-diesel blending. Additionally, piping modifications and modifications to the loading rack may, in some cases, be necessary. The estimated cost of installing a 25,000 barrel tank is $450,000 while costs for blending systems and modifications to receive ethanol at the terminal could push the cost to a total of $1.0 million. However if one assumes 24 inventory turns per year, this equates to a cost of only $0.007 per gallon of ethanol (29.4 cents per barrel) after amortizing the initial capital investment (Reynolds, 2000). Once blended at the terminal, the ethanol-containing blend is transported via truck to the retail outlet or fleet fueling facility.

Facilities already producing ethanol-gasoline blends may not require additional ethanol storage but may require new storage capacity for e-diesel and for the emulsifier additive package that is also required (see below). E-diesel can be prepared by splash blending the components so no special blending equipment is required. However, as noted below, the flashpoint of e-diesel is much lower than that of conventional diesel so that in storage and transportation e-diesel must be handled like gasoline.

2.4.1 Solubility of Ethanol in Diesel

A number of different terms are used when discussing ethanol-diesel blends, and it is important to properly understand the definitions to avoid confusion. These are described below.

> *Solution*. A solution is a single-phase liquid system, homogeneous at the molecular level. Some e-diesel formulations may be a solution of ethanol, plus additives, in diesel fuel.
> *Solvent*. A solvent is a liquid substance capable of dissolving one or more other substances. A *cosolvent* is a solution component that imparts solvent behavior to a system where solubility does not exist or is limited otherwise.
> *Miscible*. The term miscible or miscibility means that two or more components are capable of being mixed in any ratio without separation into two phases. Two liquids that are *immiscible* cannot be blended to make a solution (like oil and water). Ethanol and diesel fuel are not accurately described as either miscible or as immiscible. Some ethanol can be dissolved in diesel fuel at room temperature, but as the temperature is lowered the solution will separate into two phases.
> *Emulsion.* A system consisting of a liquid dispersed with or without an emulsifier in an immiscible liquid as very small droplets (as fat in milk). Emulsions tend to look cloudy or milky. E-diesel is not an emulsion. Stability of emulsions is always a concern, and emulsions may separate into two phases during storage.
> *Micro-emulsion.* A chemically and thermodynamically stable ultra-fine (or colloidal) dispersion of a dispersed liquid phase in an immiscible host phase. A micro-emulsion is clear, like a solution, but actually consists of droplets or micelles dispersed in the host phase. The micelle size is roughly one micron. A surfactant additive called an *emulsifier* and a small amount of water are typically required for formation of a micro-emulsion. E-diesel formulations are most likely micro-emulsions.

Ethanol-diesel micro-emulsions appear to have been first described by Boruff and coworkers in 1982. They used a mixture of unsaturated fatty acids and N,N-dimethylethanolamine as the emulsifier at a concentration well in excess of 10 volume percent. Since that time, emulsifier technology has advanced and today less than 1 volume percent is required in some cases. Stability is much less of a concern for micro-emulsions as these have proven stable for extended periods. However, stability of e-diesel micro-emulsions under a range of storage conditions will need to be demonstrated.

Gerdes and Suppes (2001) presented a detailed study of the solubility of ethanol in various diesel fuels as a function of temperature and ethanol blending level (with no emulsifier). Their results show that the phase separation temperature for up to 5% ethanol in conventional No. 1 and No. 2 diesel is identical to the cloud point of the pure fuel. Thus blending of up to 5% ethanol places no additional temperature restrictions on these fuels (if no water is present). Lowering diesel aromatic content reduces the solubility of ethanol. For example, blending ethanol with a zero aromatic Fischer-Tropsch diesel increased cloud point by nearly 25°C at 5% ethanol. Thus, diesel fuel chemical properties can have a large effect on ethanol solubility. Gerdes and Suppes also demonstrate that ethanol-diesel blends are even less tolerant of water than ethanol-gasoline blends, in the absence of emulsifier.

2.4.2 Emulsifiers/Additives

Emulsifiers are known to extend the stability of ethanol-diesel blends to lower temperatures at ethanol blending levels as high as 15% or even 20% in conventional No. 2 diesel. Different additive packages are presently available from several different suppliers, and the known emulsifiers or emulsifier manufacturers are listed in Table 2. For a 15% ethanol blend the emulsifier blending level ranges from 0.75% to 5%, depending upon the base fuel properties and additive supplier. Conventional No. 2 diesel has a nominal aromatic content of 30%. Detailed data on the efficacy of emulsifiers as a function of temperature and fuel aromatic content do not appear to be publicly available. However, some manufacturers have successfully tested their product with nominally 10% aromatic fuels and Swedish Class 1 diesel. Most manufacturers have not optimized emulsifier and ethanol blending levels and thus the numbers in Table 2 should be regarded as current practice only.

Table 2. Emulsifier manufacturers and blending levels (percent by volume)

Emulsifier Producer	Preferred Ethanol Level	Emulsifier Level
AAE Technologies, Inc./Octel Starreon, LLC	7.7 or 10	0.5[a]
Akzo-Nobel	10 to 15	1 to 4
Betz-Dearborn, Inc.	5, 10 or15	0.25, 0.35-0.75, or 1
Pure Energy Corporation	5 to 15	1 to 5
Biodiesel	10	10

[a]AAE05/Octimax 4930

Emulsifiers are also known to improve the water tolerance of ethanol-diesel blends. A emulsifier is required, even at 5% ethanol, for the fuel to remain a single phase in the presence of water and providing water tolerance is a main function of emulsifiers. In addition to emulsifier effects, a number of other benefits are claimed for the emulsifiers. These include improved lubricity, detergency, and low temperature properties.

Because of the low cetane number of ethanol (on the order of 8) the additive package (i.e. the emulsifier plus other additives) must also include a cetane-enhancing additive such as ethylhexylnitrate or ditertbutyl peroxide. Depending upon the cetane additive blending level, the e-diesel cetane number can be increased relative to that of the blending diesel.

Additionally, biodiesel is known to act as an emulsifier for ethanol. Reported work to date involved blending 50:50 or 65:45 (biodiesel:ethanol by volume) mixtures into a conventional diesel at 20 volume percent. Solubility of ethanol was dramatically improved over a wide temperature range. Results for water tolerance were not reported, which may be an issue with this emulsifier approach. Substituting ethanol for some of the biodiesel in B20 (a blend of 20 volume percent biodiesel in petroleum diesel) may also improve cold flow properties relative to those of B20 (Hanna, et al, 1996).

3.1 Ethanol/Diesel Blend Properties and Issues

Required properties for No. 2 diesel fuel are defined by the ASTM D975 specification. For e-diesel to be utilized in existing No. 2 diesel distribution and storage infrastructure it is likely that all of the requirements of ASTM D975 must be met. Furthermore, state retail fuel quality laws usually require that this specification be met. The list of properties included in this specification, testing methods, and specified property ranges or values, are shown in Table 3. Also included in Table 3 are a number of other fuel properties that, while not included in ASTM D975, may be important for e-diesel utilization. Many of the results included in Table 3 were supplied by Growmark (2001) where emulsifiers supplied by different manufacturers (additives A, C, and D) were used to prepare e-diesel from the same No. 2 diesel and fuel ethanol blending stocks. The properties of the No. 2 blending diesel before adding ethanol are also included in the table. Additive B was blended with Swedish MK-1 diesel. Data on additive B and e-diesel produced using biodiesel are not truly comparable to those for the other fuels as they are from different studies using different base diesel fuels.

Examination of Table 3 indicates that e-diesel does not meet the requirements of ASTM D975. The low flash point of e-diesel is the most significant property difference with conventional diesel. Because e-diesel cannot meet the requirements of ASTM D975, it is unlikely that it could be legally sold at the retail level. However, this does not preclude fleet customers (i.e. wholesale customers) from buying and using this fuel. Because there are important properties not covered in ASTM D975 such as water tolerance and stability (see below), it may be necessary to develop an e-diesel specification providing minimum requirements for these blends.

Another important issue for fuel property performance research is the fact that diesel fuel specifications will be changing in the relatively near future. Beginning in 2006 ultra-low sulfur diesel (ULSD) fuel will be required for on-highway use in the United States. In addition to very low sulfur content (less than 15 ppm), the nature of the sulfur removal processes are such that this fuel may have other property differences compared to conventional diesel fuel of today (such as lower aromatic content). While the exact nature of 2006 ULSD is unknown, e-diesel research performed today needs to include testing with surrogate ULSD to insure that e-diesel is a viable fuel beyond 2006. The following sections examine important fuel properties in more detail.

Table 3. Properties of conventional diesel fuels and various e-diesel products. Additives A, C, and D are blended with listed blending diesel

Property	ASTM Method	Units	No. 2 Diesel Spec: On-Road	Blending Diesel	Additive A E-Diesel	Additive B E-Diesel[d]	Additive C E-Diesel	Additive C E-Diesel	Additive D E-Diesel	Additive D E-Diesel	Biodiesel E-Diesel[e]
Ethanol Content	Nominal	vol%	--	--	10	10	10	15	10	15	7
ASTM D975											
Flash Point	D93	°C, min	52	58	13	<24	13	13	14	13	27
Water and Sediment	D2709	vol%, max	0.05								
Distillation T90	D86	°C, min	282[a]	318	314		314	314	313	313	
		°C, max	338								
Kinematic Viscosity 40°C	D445	mm^2/s, min	1.9			1.73					1.98
		mm^2/s, max	4.1								
Ash Content	D482	wt%, max	0.01								<0.01
Sulfur	D2622	wt%, max	0.05	<0.05		<3 ppm					
Corrosion, Copper strip	D130	max	No. 3			1A					1A
Cetane Number	D613	min	40	42	52	52.6	51	47	51	44	
Cloud Point	D2500	°C, max	[b]	-19	13	-37	20	18	27	16	-8
Carbon Residue[c]	D524	wt%, max	0.35								0.13
One of the following											
Cetane Index	D975	min	40								50.4
Aromaticity	D1319	% vol, max	35								
Other Properties											
Acid No.	D3242	MgKOH/g	--	0.004	0.009		0.010	0.010	0.010	0.010	
Pour Point	D97	°C	--	-29	-54		-32	-46	-46	-54	-15
Specific Gravity	D4052		--	0.8628	0.8565	0.81	0.8519	0.8519	0.8565	0.8519	0.8392
Electrical Conductivity		pS/m	--	280	450		450	450	450	450	
Distillation IBP	D86	°C		176	76		76	76	76	76	

[a]When a cloud point less than -12°C is specified, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.7 mm^2/s, and the minimum T90 shall be waived. [b]Local specification. [c]On 10% distillation residue. [d]Blended with Swedish MK-1 diesel, properties unknown. [e]A blend of 80% No. 2 diesel (properties unknown), 13% methyl tallowate, and 7% ethanol, data from Ali and Hanna, 1996.

3.1.1 Flash Point and Vapor Pressure

Flash point is the lowest temperature at which the vapor pressure of a liquid is sufficient to produce a flammable mixture in the air above the liquid surface in a vessel. Vapor pressure is a related property (not a part of the ASTM D975 diesel specification), which is defined as the pressure exerted by a vapor over a liquid in a container at a specified temperature. Vapor pressure and flash point are important from both a fire safety standpoint and from the standpoint of evaporative hydrocarbon emissions. Typical combustion safety metrics for diesel, ethanol (neat), and gasoline are listed in Table 4. Based on the results shown in Table 3, the flash point for ethanol-diesel blends is very similar to the flashpoint of pure ethanol, which is as much as 50°C lower than that of typical diesel.

Additionally, in a report prepared for Growmark, Inc. (1998), Battelle demonstrated that blends of 10%, 15%, and 20% ethanol in conventional diesel exhibit combustion safety characteristics essentially identical to those listed in Table 4 for pure ethanol. These data were acquired using diesel ethanol blends that contained no emulsifier. However based on the data in Table 3 the presence of emulsifiers has no effect on flashpoint. There is some possibility that flashpoint could increase for ethanol blending levels below 10%. Thus additional data are required to quantitatively understand the flash point issue. It is also notable that the ethanol denaturant used in the Growmark study was most probably natural gasoline. The use of a higher boiling (lower vapor pressure) denaturant such as kerosene may have an impact on flash point.

Table 4. Approximate combustion safety characteristics of neat fuels (taken from Growmark, Inc., 1998 and other sources).

	Typical Diesel	Ethanol	Typical Gasoline
Vapor pressure@38°C, psi	0.04	2.5	7-9
Flash point, °C	55-65	13	-40
Boiling point (or range), °C	170-340	78	33-213
Autoignition temperature, °C	230	366	300
Flammability limits, vol%	0.6-5.6	3.3-19.0	1.4-7.6
Flammability limits, °C	64-150	13-42	(-40)-(-18)

The National Fire Protection Association (NFPA) has established guidelines for the safe storage and handling of flammable liquids (NFPA 30, 1996). This code uses flash point to distinguish between different liquid fuels. A Class I liquid has a flash point below 38°C (100°F) and a Class II liquid has a flashpoint above this level. Ethanol and gasoline are Class I liquids while diesel is a Class II liquid. Adding ethanol to diesel fuel changes its NFPA classification to Class I. This means that e-diesel has more stringent storage requirements than conventional diesel, including more distant location of storage tanks from property lines, buildings, other tanks, and vent terminals, as well as the requirement of flame arrestors on all vents. Essentially e-diesel must be stored and handled like gasoline. This places a considerable end user education burden on the industry to insure that the product is properly transported, stored, dispensed, and used. The need for distributors and end users to make modifications to storage tanks and fuel handling equipment will also have significant cost. Some stakeholders in the e-diesel industry believe that low-flashpoint limits the market to centrally refueled fleets, where there can be considerable control over fuel handling. This market is believed to represent about 5 billion gallons per year of fuel.

In addition to storage requirements, there may be additional safety requirements for transporting e-diesel by truck or for on-board vehicle fuel tanks. In particular, neat ethanol can produce a flammable mixture in a vehicle fuel tank under a wide range of temperatures. This contrasts with the situation for gasoline where the vapor is too rich to be flammable at all but the lowest ambient temperatures, and for diesel where the vapor is too lean to be flammable. Because e-diesel appears to have vapor pressure properties identical to those of neat ethanol, the flammability of the tank vapor space may also be an issue here. An examination of regulations affecting fuel transport, on-board tanks (CFR 49.393.67 and 49.571.301), and refueling equipment (NFPA 30A, 1996) is required to begin to understand the safety implications of e-diesel use. Fire safety experts and insurance underwriters should be consulted to determine if new fire safety standards need to be developed for this fuel, or if the existing regulations are adequate.

Furthermore, the low flashpoint may create safety issues with the engine fuel system design. Equipment manufacturers that permit use of e-diesel may be exposing themselves to liability. original equipment manufacturers (OEMs) view the low flashpoint as a major hurdle, especially in the existing fleet.

3.1.2 Solubility, Water Tolerance, and Stability

While ethanol is reasonably soluble in diesel fuel at room temperature, as discussed above (Gerdes and Suppes, 2001), the presence of water can lead to phase separation. Conventional diesel fuel can carry very little water, on the order of 0.1%. Emulsifier manufacturers claim that their products make ethanol-diesel blends tolerant of reasonable water content without phase separation. For example, recent presentations and product literature from Pure Energy Corporation (PEC) and Betz Dearborn indicate tolerances of up to 3% water under some conditions. It would be desirable for emulsifier manufacturers to publish more detailed data quantifying the water tolerance of their products in diesel fuel of varying properties. For both ethanol solubility and water tolerance, a minimum requirement for e-diesel needs to be specified. No data on the water tolerance of diesel/biodiesel/ethanol blends appear to be available.

A related issue is the stability of e-diesel blends. While PEC claims their e-diesel formulation is stable to -30°C (-22°F), stability in a range of diesel fuels over a range of normal temperatures and water content needs to be proven. Stability when e-diesel is blended with conventional diesel already present in a tank (comingling) is also an issue. Maintenance of a stable micro-emulsion for a period of several months would seem to be required at a minimum, although discussions with users and stakeholders will be required to quantify the storage time requirements. In addition to stability with respect to phase separation, oxidative and biological stability also need to be examined. Finally, the stability of the emulsifier additives during storage must also be proven.

3.1.3 Cold Flow Properties

Cold flow properties are quantified in the United States by cloud point and pour point. Cloud point is the temperature at which initial crystallization or phase separation (i.e. freezing) of the fuel begins (because diesel fuel is a mixture of many components it does not have a well defined freezing point but solidifies over a wide temperature range). Pour point is the temperature below which the fuel will not pour, using a definition specific to the ASTM D97 procedure. During winter in the northern states many conventional diesel fuels must be modified by blending with No. 1 diesel or kerosene, or low temperature flow improving additives, to avoid phase separation or fuel gelling.

Because of the very low freezing point of ethanol relative to diesel fuel it might be expected that e-diesel would have improved low temperature flow properties, as long as the ethanol remains soluble. All emulsifier manufacturers claim that their products make ethanol soluble to very low temperatures. In fact, most additive manufacturers claim improved low temperature performance. In support of this claim, the data in Table 3 indicate a very significant pour point depression for most e-diesel formulations. However, the cloud point data indicate a significant increase. The cloud point data (thought to be indicative of phase separation) are difficult to interpret in this regard because cloud point appears to increase significantly, and to levels that seem unrealistic for a practical fuel. Engineers in the e-diesel industry believe that upon cooling of e-diesel micro-emulsions the micelles grow to near micron size causing a clouding of the fuel. These ethanol micelles are liquid and will apparently flow through a fuel filter. This is in contrast to the cloud point of a conventional diesel, which indicates the onset of formation of solid wax crystals that can plug a fuel filter. Including the cold filter plugging point (CFPP) test may therefore be desirable in future e-diesel property measurements. Because of the relatively high cost and limited availability of No. 1 diesel and kerosene in some markets, the ability to use e-diesel during the winter months may have an economic advantage should the claims regarding cold flow properties be substantiated.

Additionally, there are reports suggesting that B20 (a blend of 20% biodiesel in conventional diesel) prepared from a 50:50 mixture of biodiesel and ethanol (rather than 100% biodiesel) has low temperature flow properties as good or better than those of the blending diesel (Aulich, 2001). Biodiesel has poor cold flow properties, with B20 blends encountering difficulties at temperatures as high as 20°F (7°C).

3.1.4 Cetane number

The blending cetane number of ethanol is 8 and ASTM D975 requires a minimum cetane number of 40 for a diesel fuel. There is considerable evidence that cetane numbers below 40 cause poor engine operation and increasing cetane number can improve engine performance and reduce emissions. Adding a cetane-enhancing component is required for e-diesel to retain the performance level of the blending diesel fuel. Because cetane-enhancing additives are expensive, the lowest cost approach is to use only enough cetane additive to bring the cetane number of the e-diesel up to the level of the blending diesel fuel. However use of additional cetane additive may be desirable to reduce NO_x emissions and to allow marketing as a premium diesel fuel.

3.1.5 Lubricity

Lubricity is the ability of the fuel to lubricate metal surfaces and is relevant to wear in fuel pumps and other engine components that are lubricated by the fuel. Severely hydrotreated, ultra-low sulfur diesel fuels as well as Fischer-Tropsch diesel fuels tend to have low lubricity. This can be remedied through the use of a lubricity additive or by blending with higher lubricity components. There is at present no ASTM specification for diesel fuel lubricity, although several engine manufacturers specify a minimum lubricity level for fuel used in their engines. Ethanol is not expected to impart increased lubricity to diesel fuel. However, most emulsifier manufacturers claim that the emulsifier itself can impart improved lubricity. This would seem to be substantiated by data made public by PEC that shows premium lubricity properties (i.e. HFRR of less than 300 micron and SLBOCLE of more than 5200 g[jht1]).[1] Demonstration of good lubricity properties will be important for obtaining warranty acceptance for e-diesel by engine and fuel pump/injector manufacturers. Additionally, as the sulfur content of conventional diesel is lowered to 15 ppm in the coming years it is expected that fuel lubricity will decrease. Better quantification of the effect of e-diesel on fuel lubricity for both conventional and ultra-low sulfur fuels is needed. Because this may be an area where e-diesel has premium properties relative to conventional diesel the inclusion of lubricity in an e-diesel standard may be desirable.

3.1.6 Energy content

The lower heating value of ethanol is 42% lower than that of a typical diesel fuel on a volume basis, as shown in Table 5. Blending ethanol with diesel lowers the volumetric energy density in proportion to the ethanol content of the fuel as shown in the calculated heating values in Table 5. The lower fuel energy content will translate directly into a lower miles per gallon fuel economy, and a lower maximum horsepower. At some blending level modification to the fuel injection system to allow injection of larger quantities of fuel is likely to be required for engine performance and for fuel injector/pump durability.

Table 5. Lower heating value of ethanol, diesel, and theoretical ethanol-diesel blends.

Fuel	LHV, btu/gal (MJ/L)	% Decrease from Diesel
Typical Diesel	132,000 (36.6)	--
5% Ethanol/Diesel	129,222 (35.8)	2.1
10% Ethanol/Diesel	126,443 (35.1)	4.2
15% Ethanol/Diesel	123,665 (34.3)	6.3
Ethanol	76,431 (21.3)	42

3.2 Engine Performance of Ethanol/Diesel Blends

There are a number of concerns regarding engine performance. These include the idea that the solvency effect of ethanol might loosen deposits in older vehicles causing breakdowns. Another concern is that because of e-diesel's higher volatility there may be a greater incidence of pump and injector cavitation, leading to increased wear and hot restart problems. The lower energy content may require changes to governing strategy to prevent stalling under certain conditions such as steep grades, high temperature, and altitude. While some of these concerns may prove to be unfounded, they will likely require investigation. The following sections examine what is known regarding engine performance with this fuel.

[1] HFRR (high frequency reciprocating rig) and SLBOCLE (scuffing load ball-on-cylinder lubricity evaluator) are lubricity testing methods

3.2.1 Pollutant Emissions

Regulated pollutant emissions for e-diesel fuels produced by three manufacturers have been reported (Spreen, 1999; Kass, et al., 2001; Peeples, 2001). As shown in Figure 1, studies at three different laboratories show comparable PM emissions benefits for all three forms of e-diesel examined, with the observed particulate matter (PM) reduction a linear function of fuel oxygen content. However closer examinations of the data indicates significant variation in PM emissions with e-diesel formulation, and in some cases PM emissions reductions in excess of 30% have been obtained at 7.7% ethanol. E-diesel developers claim large reductions in smoke opacity as well. Studies of nitrogen oxide ($NO_{x)}$ emissions are not conclusive, with some reporting significant benefit in terms of NO_x and others showing no effect. Results for both AAE and PEC e-diesel showed a 15% to 20% decrease in emissions of carbon monoxide (CO) (at 10% ethanol content). CO emissions increased in the study of Betz Dearborn e-diesel but were still one order of magnitude below the emission standard for heavy-duty engines. Total hydrocarbon emissions increased by as much as 100% in all three studies, but were still an order of magnitude below the hydrocarbon emissions standard for heavy-duty engines. It is unknown to what extent emissions can be effected by the emulsifier. A diesel oxidation catalyst or other advanced catalytic aftertreatment technology could easily reduce the hydrocarbon emissions to very low levels.

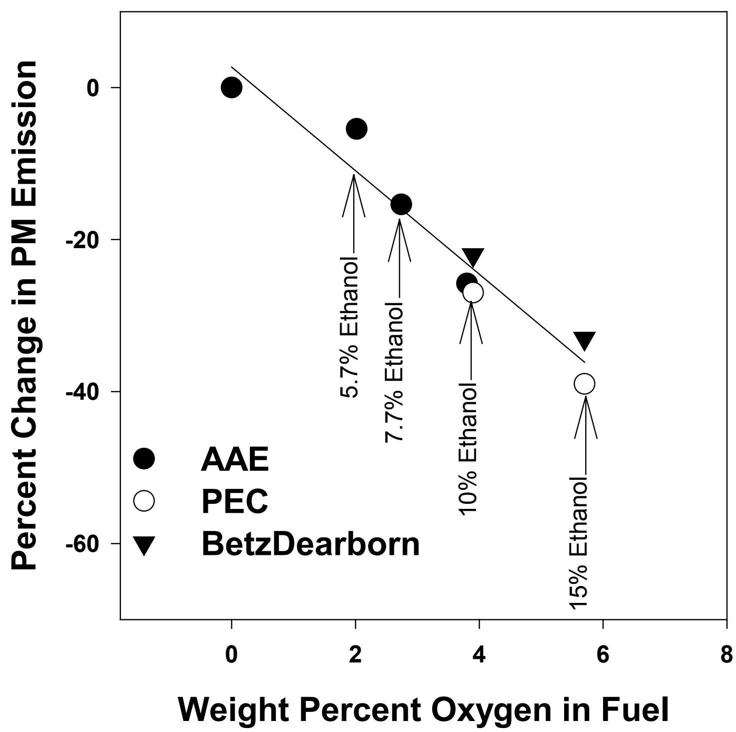

Figure 1. Change in PM emissions for e-diesel blends relative to blending diesel. AAE and PEC data utilized a 1991 DDC Series 60 engine and the heavy-duty transient test (AAE at CSM and PEC at SwRI). Betz Dearborn utilized a 1999 Cummins ISB engine and the AVL 8-mode test (performed at ORNL).

The three studies cited above show clear and consistent PM emissions benefits. However other studies have shown a PM increase over the AVL 8-mode tests (Sluder, et al., 2001) or a PM decrease over only a fraction of the engine map (Cole, et al., 2001). Additional studies will be required to understand potential emissions benefits for all engine models and driving cycles. The situation for CO emissions is less clear, but given observed correlations between CO and PM (Yanowitz, et al., 1999) it seems likely that CO emissions are decreasing in concert with PM emissions on a cycle average basis. It is likely that adding ethanol will have no effect on cycle average NO_x emissions as long as the cetane number of the e-diesel is matched to that of the blending diesel. If the emulsifier package is formulated to increase the cetane number relative to the base fuel by 5 or more cetane numbers it may be possible to realize NO_x benefits. Because of the cost of cetane improving additives there may be significant economic barriers to this approach, and the same NO_x benefit could be obtained by adding cetane improver to a conventional diesel.

The increase in hydrocarbon emissions is likely to be all ethanol, but this must be confirmed. It is also possible that the emulsifier could be contributing to hydrocarbon emissions. Additionally, using ethanol might be expected to increase emissions of certain carbonyl compounds such as acetaldehyde and acetic acid. Thus a detailed study of speciated hydrocarbon and carbonyl emissions is needed. Including ethanol in diesel fuel might also be expected to reduce emissions of polyaromatic hydrocarbons (PAH) by both the dilution of fuel aromatic and PAH content and by the oxygenate effect on PM. These effects, should they exist, need to be quantified. All of these data will be required for EPA registration of these fuels, as discussed below.

AAE has made available some data on testing ethanol-biodiesel-diesel blends (Peeples, 2001), which is shown in Table 6. The results show a significant reduction in PM and CO, while NO_x is unchanged and HC increases.

Table 6. Emissions testing results for ethanol-biodiesel-diesel blend. Data acquired at CSM using a 1991 DDC Series 60 engine and heavy-duty FTP (hot start), average of three runs.

	Cert Fuel Average	Cert+8.7%AAE E-diesel +11.3%Biodiesel+1000 ppm EHN Average	p-value	Significance
HC	0.0452	0.0980	0.0007	yes
NO_x	4.657	4.630	0.062	no
CO	4.867	3.789	0.0002	yes
PM	0.255	0.161	<0.0001	yes

Finally, there are no data available on emissions durability. Acquisition of such data should be an important part of engine durability testing using e-diesel, as discussed below.

3.2.2 Materials Compatibility

Ethanol is chemically very different from diesel fuel components and will interact differently with elastomers and metal surfaces. This may also be true for emulsifier chemicals. Demonstrating a similarity between e-diesel and conventional diesel fuel in terms of materials compatibility is a necessary prerequisite to expensive engine durability testing. If similarity cannot be demonstrated, an understanding of what materials must be replaced and of suitable replacements must be obtained. Engine durability testing and fleet studies are, in a sense, the ultimate test of materials compatibility. However, if certain materials need to be replaced on engines using e-diesel this should be known before initiating durability or fleet studies.

3.2.3 Field Demonstrations and Durability Testing

A number of field demonstrations of e-diesel are ongoing or have recently been completed. Only a few of these studies are described here. Marek (2001) recently described several studies and this description is briefly summarized here. In 1999 Archer-Daniels-Midland (ADM) began a test using three new 1999 Mack trucks equipped with Mack E7 engines. Two of the trucks were operated on PEC e-diesel with 15% ethanol (E-15) while the third was operated on diesel as a control. As of this writing these trucks have each accumulated 270,000 miles with no fuel related problems. Fuel economy (mpg) for the e-diesel vehicles was 11% lower than for the diesel truck. A second field test of PEC E-15 was initiated at the Chicago Transit Authority, also in 1999. Fifteen e-diesel buses and fifteen controls were operated for roughly 20,000 miles each. No fuel related problems were encountered, and fuel economy for the two fifteen vehicle fleets was identical. A number of farm equipment tests have also been reported with no fuel-associated problems. One difficulty with studies of this type is the lack of statistical analysis, a particularly important requirement for field demonstrations because of the relatively high uncertainty associated with real-world data. There are several other ongoing field demonstrations, but those described above are illustrative.

While the field demonstrations strongly suggest that e-diesel will not cause engine durability problems, they do not eliminate the need for more carefully controlled laboratory durability studies of engines and engine components. A 500-hour durability test using PEC 15% e-diesel was recently completed by the University of Illinois (Hansen, et al., 2000) using a Cummins B5.9 engine. Because the expense of running a controlled study was too great (i.e. running two 500-hour durability tests in parallel) the study relied on examination of engine components for abnormal wear and analysis of the lubricant for abnormal levels of wear metals. The study found that e-diesel promotes abnormal wear and corrosion on certain parts of the Bosch fuel pump and fuel injectors. There was also a materials incompatibility problem with an electronic sensor on the fuel pump. The excessive fuel pump wear was thought to be caused by excessive backlash in the timing device because of high fueling rates, and thus may have been caused by the lower energy content of the e-diesel. On the positive side there was no increase in metal contaminants in the lubricant and use of e-diesel appeared to reduce the amount of injector nozzle coking relative to petroleum diesel.

To facilitate large-scale commercialization of e-diesel, major vehicle and parts manufacturers must warrantee their products for use with this fuel. Engine manufacturers warrantee the materials and workmanship of their engines, and are able to void the warranty if certain fuels are used in an engine that was not designed for them. The same is true for individual engine parts, such as fuel injectors. Therefore, it is important to gain acceptance of e-diesel by engine manufacturers for warranty coverage. It seems likely that a fuel will have to have a significant number of users before engine manufacturers will become interested in considering warranty issues. The materials compatibility and durability testing requirements suggested above are required so that the ethanol and e-diesel community can provide potential customers with assurance that e-diesel will not harm their engines, and as the initial data for convincing the engine manufacturers that the fuel should not void a warranty.

4 Regulatory and Deployment Issues

In addition to fuel property and engine performance issues, there are a number of regulatory compliance issues that will need to be addressed.

4.1 EPA Registration Requirements

Since 1975, under Section 211 (b) of the Clean Air Act (CAA), it has been unlawful to introduce into commerce any gasoline, diesel fuel, or fuel additives unless they are registered with EPA. The Code of Federal Regulations, Title 40, Part 79 identifies the process for registering fuels and additives in response to the CAA. To complete registration, products must be subjected to at least a two- and possibly three-tier toxicological testing programs. Tier 1 requires manufacturers to provide combustion and evaporative emissions characteristics and a literature search of existing scientific information on public health and welfare effects of the emissions. If inadequate data exists, manufacturers are required, under Tier 2, to conduct specified toxicology tests to screen for potential adverse health effects of the fuel's emissions. These include 90-day subchronic toxicity test on rodents with additional health effects testing for carcinogenicity, mutagenicity, teratogenicity, reproductive toxicity, toxicity, and neurotoxicity. Tier 3 testing, which entails additional toxicological tests, may be required at EPA's discretion after reviewing the Tier 1 and Tier 2 results, although this is highly unlikely.

The regulations include provisions to reduce information collection and testing burdens by allowing a voluntary grouping and cost-sharing program. This allows manufacturers of similar fuels and fuel additives to pool their resources and efforts in complying with the requirements. Under section 40 CFR 79.56, fuel and fuel additives are broken down into their respective groups. As identified under subsection (e)(3)(ii)(B), non-baseline diesel fuels (i.e., diesel fuel which contains 1.0% or more of oxygen by weight in the form of alcohol(s) and/or ether(s)) must have a separate group for each individual alcohol or ether listed as a component in the registration application. For each group, the testing formulation should consist of the diesel base fuel (No. 2 diesel) blended with the relevant alcohol or ether in an amount equivalent to the highest recommended concentration.

Special provisions and waivers for small manufacturers are also included, and manufacturers of baseline and non-baseline fuels with total annual sales of less than $50 million are not required to meet the requirements of Tier 1 and Tier 2 until sales reach this threshold (40 CFR 79.58(d)(2)).

E-diesel clearly qualifies as a non-baseline group based on ethanol content, and will likely need to undergo Tier 1 and Tier 2 testing should the market reach sufficient size. The composition of emulsifier formulations is unknown. At this time it is not clear if each emulsifier will have to undergo Tier 1 and Tier 2 testing individually.

The 40 CFR 79 document and EPA (Jim Caldwell at 202-564-9303) should be referenced for more detailed information on the testing requirements for unique e-diesel blends. Discussions need to be initiated with EPA regarding the need for testing all emulsifiers individually versus testing one e-diesel formulation.

4.2 CARB Certification

For a diesel fuel to be sold for use in California, a fuel certification emissions test must be completed successfully. In this test the candidate fuel emissions are compared to the emissions of a so-called California reference diesel. The procedures and related issues are described in California Code of Regulations Title 13, Sections 2281 and 2282. Should the e-diesel community see significant market opportunities in California, an Executive Order from the California Air Resources Board (CARB) granting certification will be required. At the present time it is unclear if all emulsifiers will require CARB certification individually or if there is a pathway for joint certification of all e-diesel formulations.

4.3 EPAct Legislation

The Energy Policy Act of 1992 (EPAct) has the goal of increasing U.S. energy security by establishing national goals for energy efficiency and fossil fuel use reduction. EPAct requires the purchase and use of alternative fueled vehicles for certain types of vehicle fleets, or the use of alternative fuels in conventional vehicles. Alternative fuels approved for EPAct compliance include neat ethanol and E85 for gasoline engines, but not gasoline containing 10% ethanol (the typical level). E-diesel is not specifically listed as an EPAct fuel, and the industry may want to examine the implications of obtaining EPAct listing, if possible.

5 Summary of Technical Barriers and Other Research Issues

Based on the technical and regulatory issues described in the previous chapters it is apparent that the e-diesel industry faces a significant R&D burden to overcome the barriers to commercialization. The technical barriers involve fuel property issues such as low flashpoint and poor quantification of possible fuel property benefits, durability issues such as materials compatibility and engine warranty, and regulatory issues such as EPA fuel registration requirements. The issues identified in this analysis are listed below.

1. Detailed data on the efficacy of emulsifiers as a function of temperature and fuel chemical properties do not appear to be available. Additionally, no information is available on the performance of emulsifiers in ULSD that will be required in 2006. More definitive data on the effect of emulsifiers on ethanol solubility and water tolerance in diesel are needed, and in diesel fuel of varying properties.
2. Because e-diesel cannot meet the requirements of ASTM D975, and because there are other important properties not covered in ASTM D975, it may be necessary to develop an e-diesel specification providing minimum requirements for these blends. For both ethanol solubility and water tolerance a minimum requirement for e-diesel needs to be specified.
3. Essentially e-diesel must be stored and handled like gasoline because of its low flashpoint, and has different fire safety code requirements than diesel. This places a considerable end user education burden on the industry to insure that the product is properly transported, stored, dispensed, and used. The need for distributors and end users to make modifications to storage tanks and fuel handling equipment will also have significant cost. Fire safety experts and insurance underwriters should be consulted to determine if new fire safety standards need to be developed for this fuel, or if existing regulations are adequate. There may also be safety issues with vehicle fuel system design that need to be addressed.

4. The safety issues noted above are likely to limit the potential market for this fuel. Some stakeholders believe the market is limited to captive, centrally refueled fleets and that this market is roughly 5 billion gallons annually. A study of the diesel market, the size of the centrally refueled fleet market, potential e-diesel market penetration and the impact of e-diesel on this market need to be examined.
5. Additional data are required to quantitatively understand a number of fuel property issues, but in general the impact of ethanol blending level on all relevant fuel properties for each of the various emulsifier formulations needs to be quantified.
   a. Flash point. The impact of ethanol blending level (down to 5%), denaturant, and emulsifier on flashpoint needs to be quantified.
   b. Lubricity. Better quantification of e-diesel lubricity for both conventional and ultra-low sulfur base fuels is needed. Because this may be an area where e-diesel has premium properties relative to conventional diesel, the inclusion of lubricity in any e-diesel standard may be desirable.
   c. Cold flow properties. Ethanol may significantly improve cold flow properties. Because of the relatively high cost and limited availability of No. 1 diesel and kerosene in some markets, the ability to use e-diesel during the winter months may have an economic advantage should the claims regarding cold flow properties be substantiated.
6. At some blending level modification to the engine fuel injection system to allow injection of larger quantities of fuel is likely to be required for engine performance and for fuel injector/pump durability. An understanding of this issue and at what blending level modifications may be required is needed.
7. Additional emissions studies will be required to show that potential emissions benefits translate to all engine models and driving cycles. The impact of ethanol blending level and of the various emulsifiers on emissions must be better understood. Data on emissions durability are also needed.
8. EPA Fuel Registration Requirements. Under 40 CFR Part 79 e-diesel clearly qualifies as a non-baseline group based on ethanol content, and will likely need to undergo Tier 1 and Tier 2 testing. At this time it is not clear if each emulsifier will have to undergo Tier 1 and Tier 2 testing individually. This is a very time consuming and expensive process. The industry needs to evaluate the most cost effective way to move forward.
9. Ethanol is chemically very different from diesel fuel and will interact differently with elastomers and metal surfaces. This may also be true for emulsifier chemicals. An understanding of materials compatibility is a necessary prerequisite to expensive engine durability testing.
10. To facilitate large-scale commercialization of e-diesel, major vehicle and parts manufacturers must warrantee their products for use with this fuel. This typically requires long term durability testing, as well as other activities.

In addition to the technical barriers to commercialization, other research issues that may be important to the e-diesel community were identified. These include:

1. Biodiesel/ethanol/diesel blends. Including ethanol in biodiesel/diesel blends may improve cold flow properties. However, no data on the water tolerance of

diesel/biodiesel/ethanol blends appear to be available and there is a general lack of quantitative information on fuel properties and engine performance.
2. The relatively high carrying capacity of e-diesel for water, and the success of diesel-water emulsions at emissions reduction, suggests the idea of examining diesel-ethanol-water blends as a potential low emissions fuel.

6 Conclusions

This document has reviewed information available to NREL regarding technical barriers to commercialization of e-diesel. This topic will also be the subject of a stakeholder workshop sponsored by DOE and others. One important outcome of the workshop will be additional information on the technical barriers noted here, and possibly other barriers not recognized at this time. The input will be used to update this document, and to formulate a research plan for addressing the identified technical issues. Notably the research plan will indicate the priority of each of the issues and lead to a time line for performing the research necessary for commercialization of e-diesel.

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I have added a footnotePage: 11
[jht1]should these acronyms be defined or will your audience understand??