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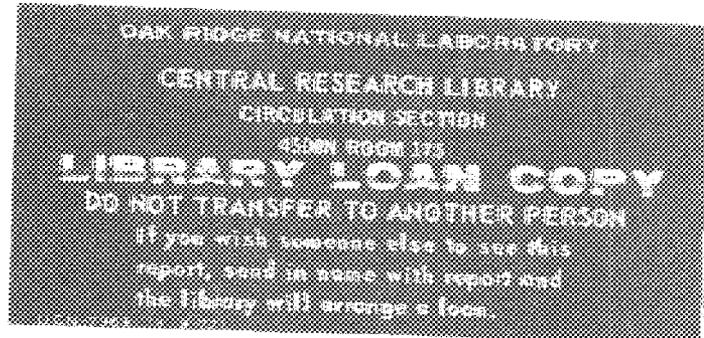
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Correlating Microemulsion Fuel Composition, Structure, and Combustion Properties

W. L. Griffith
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Prepared by the Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
operated by
Martin Marietta Energy Systems, Inc.
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Abstract

Microemulsion fuels provide a method for increasing the use of byproduct and biomass materials, including alcohols, in diesel fuels. The ability to replace 50% of diesel fuel with byproduct and biomass-derived materials microemulsion fuels could significantly decrease petroleum consumption. However, it is likely that the low particulate and NO_x emissions characteristic of these fuels will drive the adoption of this technology. This report is concerned with the development of a series of short experiments to determine the fuel composition changes required to support development of microemulsion fuels which have combustion properties acceptable to the public and adequate to support widespread use in current diesel engines. The goal is delineation of microemulsion diesel fuel compositions which have acceptable compression ignition and emissions properties and which permit the replacement of one-third to one-half of current diesel fuel petroleum. A review of the literature on cetane enhancers for conventional and alternative diesel fuels was performed and a small number of enhancers likely to be effective with high-alcohol fuels selected. Based on linear regression analysis of emissions from a passenger diesel engine using alcohol and aqueous microemulsion fuels, correlation between microemulsion solution structure as determined by small-angle neutron scattering and actual NO_x and particulate emissions was determined. The analysis indicates that solution structure and microemulsion composition play major roles in emissions modification.

1. Introduction

During the period of reflection surrounding the petroleum import interruptions of the early 1970's, short, reasonably manageable crises in petroleum supply were thought likely to continue into the next century due to both supply management difficulties and to political problems. Gasoline supplementation with small alcohols was promoted as a method for replacing petroleum and did not, as such, find a market. However, emissions controls are gradually creating a market for methanol and ethanol as both emissions control additives and octane enhancers. Unfortunately, a similar solution has not occurred with diesel fuels, primarily due to the poor blending and compression ignition properties of methanol and ethanol. This is particularly troubling in that diesel fuel use is largely for transportation, industrial applications, and electric power generation. The ability to modify physical and chemical properties of alcohol and byproduct materials so that they can be used both to extend diesel fuel and to decrease emissions from its combustion is the subject of this report.

Combustion Studies on Alcohols as Diesel Fuel

Although the original reason for supplementing gasoline with alcohols was energy conservation, the current driving forces are emissions controls and improved vehicle performance. Although the course of adoption has been somewhat unsteady, it presently looks as if emissions controls and conservation will mandate increasing amounts of methanol and ethanol in gasoline. It is not unlikely that, with federal subsidies and mandates, methanol or ethanol blends with a small fraction of gasoline will become a standard fuel for fleets in the next few years. Some states (*e.g.*, Hawaii) are presently planning for complete conversion of present spark-ignition vehicles to methanol (Neill 1989).

However, to date the story has been different for use of small alcohols in compression-ignition fuels simply because these materials do not ignite at compression values and temperatures appropriate to conventional diesel vehicles. The contribution of alcohols toward decreased diesel particulates has been long recognized (Sapienza *et al.* 1985, Kobyashi *et al.* 1986, and Yamamoto and Matsumoto 1983). However, the decrease in cetane rating as a result of addition of small alcohols to diesel fuel is also well known (Kobyashi *et al.* 1986, Yamamoto and Matsumoto 1983, Holmer *et al.* 1980, and Holmer 1977). This is due to the combustion properties of ethanol and methanol. In a detailed study of ethanol and methanol combustion under diesel engine conditions, Siebers and Edwards (1987) found that a cylinder temperature of 1100 K is required to produce ignition delays and pressure rise rates appropriate to current diesel engines. Taking reported research into account, it

appears that use of methanol and ethanol in diesel fuel results in a proportional decrease in cetane rating.

Fuels for Existing vs. Altered or New Engine Designs

Several methods for improving the performance of diesel engines on fuels with small alcohols are available: basic modifications of the engine itself, changes in fuel blends to take advantage of alcohol chemical properties, and development of effective cetane enhancers. There are basic advantages and disadvantages inherent in each of these. Engine modifications which have been tested include dual fuel systems (Holmer 1977, Holmer *et al.* 1980, Berg *et al.* 1979, and Kobyashi *et al.* 1986), spark ignition (Kobyashi *et al.* 1986), and electronic control systems (Henein 1985). The advantage of engine modification is the possibility of tailoring an engine which will produce acceptable performance on practically any defined fuel. Often, it is possible to take advantage of the change in design to introduce new features which substantially improve engine efficiency or performance but which would be difficult to incorporate into existing engines. Disadvantages to this approach have historically included substantial retooling costs and a relatively slow impact on fuel use, due to the gradual turnover of the domestic vehicle fleet.

Conversely, because fuels are bulk commodities produced and marketed by a reasonably small number of commercial entities, a technologically feasible change in fuel composition is somewhat simpler to implement, as seen from the adjustments to alcohol-supplemented and unleaded fuels across the last decade. Primary problems with alcohol addition to gasoline have included unexpected materials incompatibilities and safety concerns due to lowered flash point. However, the amount of alcohol which can be substituted for conventional fuel without changes in engine design is limited: it is reasonably easy to add small amounts of methanol or ethanol to gasoline in a crisis, but use of 100% ethanol or methanol is a different matter. At a minimum, the energy content, viscosity, and lubricity of the fuel have been substantially changed. For conventional diesel fuels with a cetane range of 42 to 50, expected increases in ignition delay, which are roughly proportional to the amount of alcohol added, imply an upper limit of 10 to 25% methanol or ethanol. A cetane of 40 is necessary for adequate starting at typical winter temperatures (Clerc 1986). This implies the need for cetane enhancing additives or for inexpensive, high-cetane fuel components.

Byproduct Use, Fuel Flexibility, and Conservation

Several materials have been reported to meet these requirements. These include ethers (Brook and *et al.* 1984) made from small alcohols and monoesters made by reacting alcohols and vegetable oil triglycerides in the presence of an acid or base catalyst. Klopfenstein (1985) reported that esters of fatty acids with chain lengths higher than 10 generally had cetane ratings exceeding 50. Cetane increases with increasing fatty acid chain length. It is also likely, based on chemical structure, that some aromatic alcohols presently available as high-volume chemical byproducts will also be effective cetane enhancers. If it is possible to recognize the conservation benefits and decreased emissions likely to be inherent in alcohol-supplemented diesel fuels, they would contribute substantially to energy security by both

decreasing imports and increasing the ability to provide diesel fuel during supply disruptions. Thus, even if their use is not mandated, the nation would derive additional security from the availability of methods for incorporating alcohols into diesel fuels in a fuel supply interruption.

Role of Microemulsions

Microemulsions and micelles provide an additional method for changing fuel compositions to accommodate the addition of alcohols, industrial byproducts, and vegetable or tree oil free fatty acids. Because of the small amount of water or methanol normally included as a dispersed phase in diesel fuel, it is possible to include inorganic salts, such as ammonium nitrate, which are good, inexpensive cetane enhancers. These materials are also sparingly soluble in micellar fuels in which a polar alcohol forms the continuous phase.

Microemulsion fuels containing water and a fully neutralized fatty acid soap have been evaluated extensively for military applications in engines ranging from conventional diesels (Naegeli and Moses 1982 and 1983; Owens and Wright 1976; Weatherford 1985; and Weatherford *et al.* 1979, 1983, and 1984). The focus of these efforts has largely been directed toward evaluation of fire resistant diesel and turbine aircraft fuels. Additionally, there has been considerable effort devoted toward producing stable fuels containing vegetable or tree triglycerides and alcohols, often with diesel fuel (Faletti *et al.* 1982 and 1984, Goering and Fry 1984, Goering *et al.* 1982 and 1983, Pryde 1984, Schwab *et al.* 1982, Schwab and Pryde 1985, Ziejewski 1987, and Ziejewski *et al.* 1984 and 1986a,b). In most of these investigations, vegetable triglycerides, sometimes mixed with diesel fuel, formed the continuous fuel phase. These fuels generally were capable of sustaining diesel combustion. However, vegetable oil fuels were reported to cause excessive engine wear and a heavy buildup on injectors. A limited amount of effort has been devoted to the production of microemulsions which contain a substantial amount of methanol and which are likely to provide effective fuels for diesel engines (Gilberg and Friberg 1976, Johnson and Stoffer 1983), although these fuels have often relied on relatively expensive commercial surfactant formulations.

This report is concerned with developing a plan for rationally evaluating the use of microemulsion and micellar diesel fuels which maximizes their potential use in sparing petroleum. This requires assessing the best use of agricultural and industrial byproducts as well as small alcohols in diesel fuels as a function of the physical, chemical, and combustion properties of the fuels. Because of the probable low cetane rating of the materials, particular effort will be devoted toward assessment of additives and bulk constituents which decrease ignition delay.

2. Physical and Chemical Properties

Microemulsions and micellar fluids are thermodynamically stable liquid systems in which aggregates of one phase are distributed throughout a second continuous and immiscible phase. They may appear transparent because the aggregates are smaller than the wavelength of visible light. At the extremely small sizes of the aggregates – 1 to 100 nanometers – Brownian motion is sufficient to make the aggregates stable in solution. Both micelles and microemulsions are stable within definable ranges of chemical composition, temperature, and pressure, although current theory suggests that the dispersed phase aggregates may transition through a variety of shapes and sizes. Polar heads turned outward into a polar continuous phase generally characterize micelles. If hydrocarbon is solubilized by incorporation into the micelles, the micelles are sometimes called “swollen micelles” and the system, an oil-in-water, or O/W microemulsion, to distinguish it from a W/O microemulsion, in which the hydrocarbon phase is continuous.

Commercial microemulsion applications include flavoring extracts, liquid shoe polish, shampoos, dry cleaning fluid, and the emulsions in which many commercial plastics are polymerized. Some of the formulations have been defined sufficiently as to permit field preparation using a concentrate containing the surfactant and any coagents. Generally water and hydrocarbon are added to the concentrate, and the microemulsion forms on simple stirring. Microemulsion technology has generally been used in systems with well defined components intended for storage and used within a specified temperature range. However, many microemulsions will reform spontaneously after freezing.

Although microemulsion technology was in limited use before World War II, commercial use has substantially increased. Formulation has been primarily empirical, as reported by Prince (1977). The petroleum supply interruptions of the early 1970s provided a reason for fundamental investigation of microemulsion properties in support of enhanced oil recovery. The effective use of micellar flooding required the development of micelle systems capable of holding crude oil in brines during a year-long passage through the pores of rock formations. Systems capable of remaining effective in formations in spite of substantial variations in temperature, pressure, salt concentration, and pH were developed. New techniques including NMR were used to elucidate micelle and microemulsion internal structure (Shah *et al.* 1971). Correlations of phase behavior with favorable properties for oil displacement (interfacial tensions, for example) were found (Healey and Reed 1974, Cayias *et al.* 1976).

In some cases, microemulsions can remain a single phase even though the continuous and discontinuous phases have been reversed. As shown in Fig. 2.1, the phase diagram for a typical alcohol : fatty acid : diesel fuel is dominated by the single-phase region (Grey *et al.* 1988). This encompasses both alcohol and diesel fuel continuous regions, as well as the expected surfactant-continuous region. Temperature, pressure, and additional components

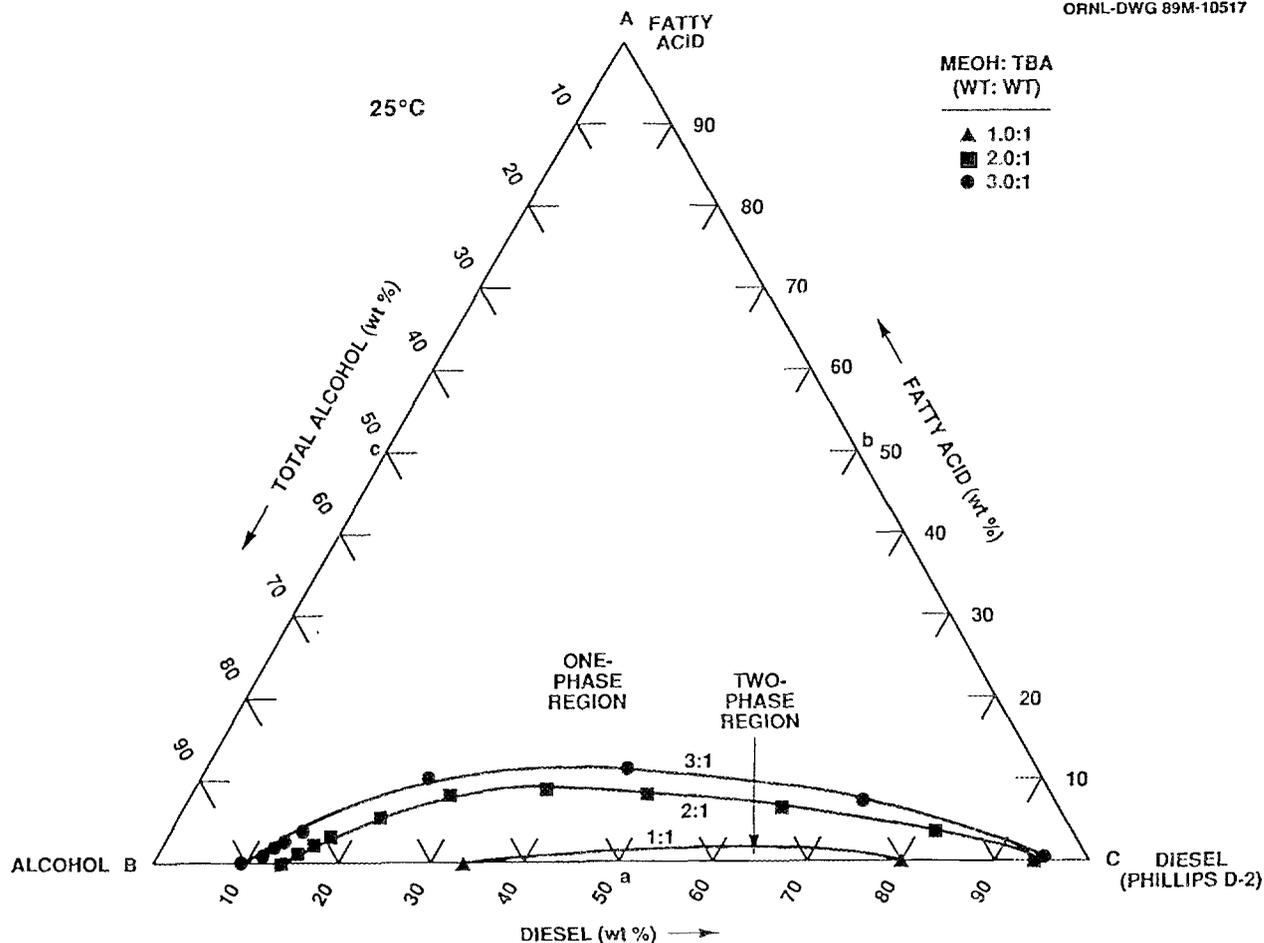


Fig. 2.1. Phase diagram for alcohol : fatty acid : diesel fuel system at 25 C.
(Source: Grey *et al.* 1988.)

(*e.g.*, salts, water) can substantially affect the single-phase boundary. Changes in the two-phase boundary region at 0 C are shown in Fig. 2.2.

Although much of the theory on microemulsion structure and behavior is applicable to microemulsion fuels, the need for the fuels to be combustible has generally constrained interest to a relatively small composition region in which water does not exceed 30% and free fatty acids do not exceed 25%. This limitation does not apply to micellar fuels in which a polar small alcohol forms the continuous phase and water is limited or absent, because such fuels are likely to be combustible throughout their composition range. Table 2.1 gives an indication of the range of microemulsion fuel composition which has been investigated. Although the research is reasonably limited, base fuels include vegetable oil triglycerides and middle distillate fuels.

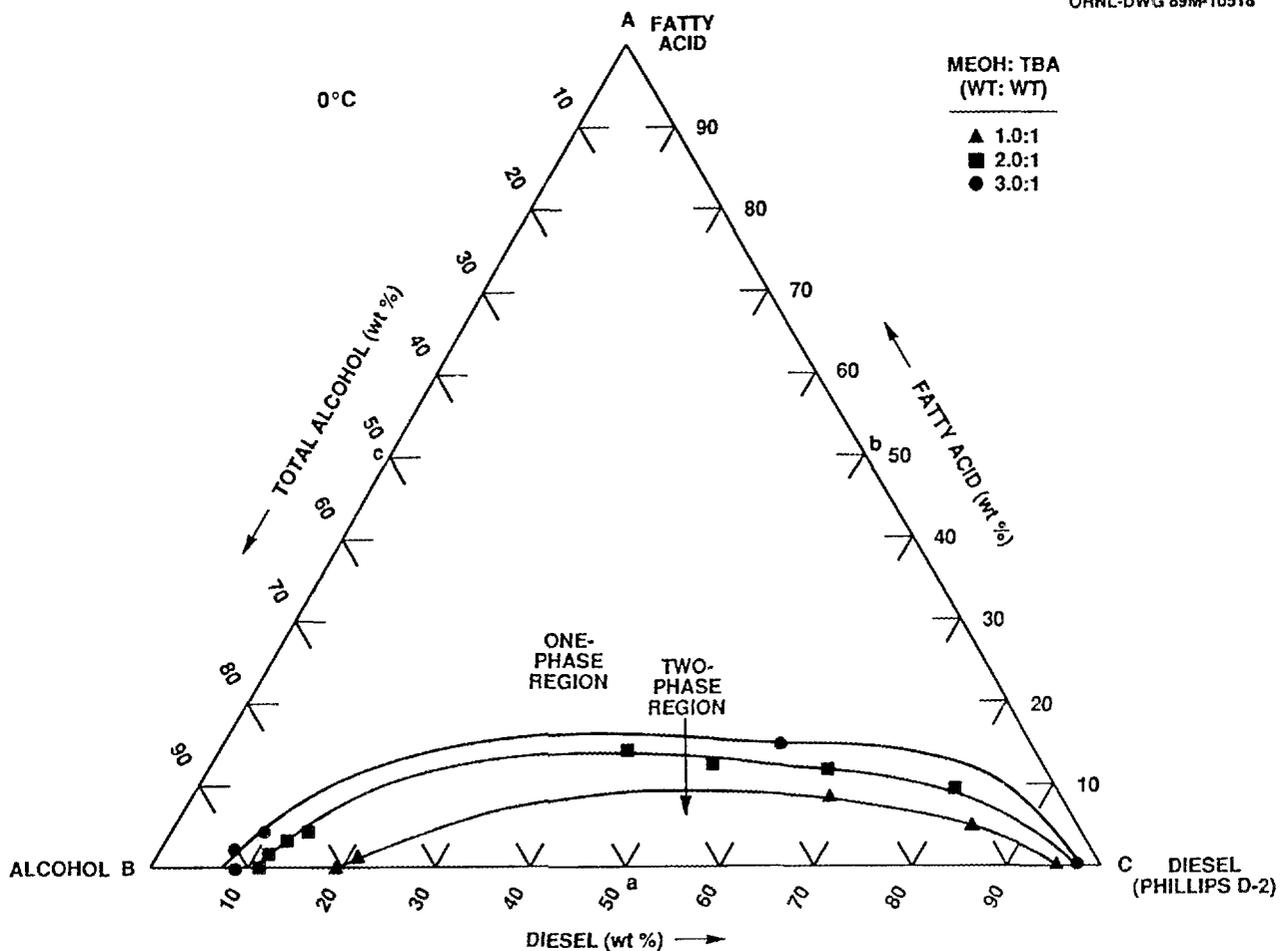


Fig. 2.2. Phase diagram for alcohol : fatty acid : diesel fuel system at 0 C.
(Source: Grey *et al.* 1988.)

Physical Properties: Viscosity and Density

Microemulsion fuels generally have viscosities reasonably close to those of conventional fuels. Table 2.1 shows the measured viscosities and densities of selected microemulsion fuels. Although microemulsions in conventional fuels have a slightly higher viscosity than the neat base fuels, microemulsions in high viscosity materials, such as vegetable oil triglycerides, have substantially decreased viscosity.

Density of micellar and microemulsion fuels can be calculated by summing the contributions of individual structural groups to obtain partial molar volumes for microemulsion constituents. These partial molar volumes are then summed and the density of the liquid calculated. Generally, hydrocarbon group, alcoholic -OH, and -COOH volumes are estimated from incremental volumes of homologous series. Ionic volumes are as reported by Millero

Table 2.1. Viscosities and densities of selected microemulsion and micellar diesel fuels

Composition							Viscosity, 38 - 40 C, mPa·s	Density, g/cm ³	Reference
Nonpolar ^a	Polar ^b	Coagent ^c	Surfactant ^d	Basis ^e					
1.0	DF						4.4 ^f	0.83	Googin <i>et al.</i> 1983
0.736	DF	0.050 H ₂ O	0.104 NBA	0.110 SFA	W		5.4 ^f	0.84	Googin <i>et al.</i> 1983
0.680	DF	0.107 H ₂ O	0.103 NBA	0.110 SFA	W		6.0 ^f	0.85	Googin <i>et al.</i> 1983
0.84	MDF	0.10 H ₂ O		0.06 EOA	V		8.6 ^f	0.86	Weatherford <i>et al.</i> 1981
1.0	MDF				V		4.4		Weatherford <i>et al.</i> 1981
0.500	SO	0.25 ME		0.25 2OCT	V		4.6		Schwab and Pryde 1985
0.667	DF	0.167 ET95		0.166 SFA	W		3.1		Boruff <i>et al.</i> 1982
0.80	DF	0.10 ME98		0.10 HEX	W		1.7	0.84	Johnson and Stoffer 1983a
0.775	DF	0.15 ET95		0.075 HEX	W		1.7	0.84	Johnson and Stoffer 1983a
0.66	DF	0.12 H ₂ O		0.22 15S5	W		5.8	0.89	Johnson and Stoffer 1983a
0.533	SFO	0.133 ET95		0.334 NBA	V		5.5	0.87	Ziejewski <i>et al.</i> 1984
0.50	DF	0.05 ET	0.25 SO	0.20 NBA			3.1		Faletti <i>et al.</i> 1984
0.648	DF	0.112 H ₂ O	0.09 ME	0.15 MSF	W				Wenzel and Steinmann 1976

^aDF, diesel fuel; MDF, military diesel fuel with aromatic carbon content adjusted to 15 to 20%; SO, soybean oil; SFO, sunflower oil. ^bET95, 95% ethanol; ME98, 98% methanol. ^cNBA, 1-butyl alcohol; SO, soybean oil. ^dSFA, soy fatty acids partially neutralized with ethanolamine; EOA, ethanolamine oleamide; 2OCT, 2-octanol; HEX, hexanol; 15S5, Turgitol 15-S-5; MSF, 5.5 Lipcal-9-OL, 4.3 oleic acid, 5.2 ammonium oleate. ^eComposition basis: V, volume; W, weight. ^f25 C.

(1972) or are estimated from values of similar compounds. Calculated densities agree closely with measured densities. Microemulsion fuel densities will generally be higher than those of the neat base fuel due to addition of water.

Energy Content

Energy content of fuels can be readily estimated using the heating values of and partial molar volumes of individual constituents. Fig. 2.3 shows the diagram for methanol-supplemented microemulsion and micellar diesel fuels with superimposed lines of constant heat value. Generally, water-containing fuels will be useful only in the range below 30% water due to energy content. It is important to consider the phase behavior of these fuels as a function of water content in that water contamination of storage and fuel tanks is a likely problem. It is also likely that any highly polar cetane enhancers (*e.g.* NH₄NO₃) will concentrate primarily in an alcohol or aqueous phase.

Solution Structure of Hydrocarbon-Continuous Microemulsions

A body of domestic and foreign research has established that microemulsion fuels have promise as a method for modifying diesel fuel composition, combustion properties, and physical properties. However, when laboratory microemulsion fuel systems have been scaled up

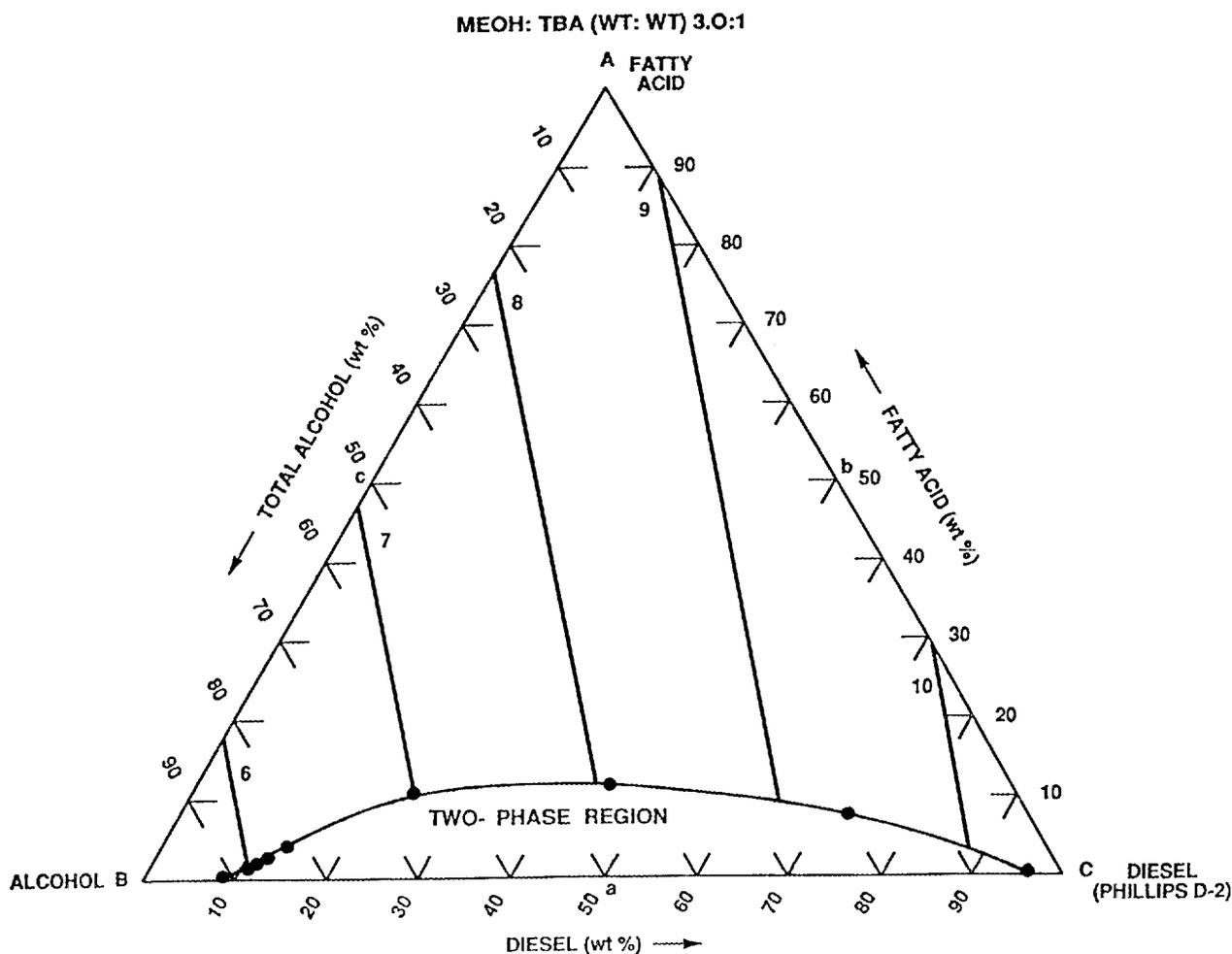


Fig. 2.3. Isocal diagram for the system alcohol : oleic acid : diesel fuel. (Diesel fuel calculated as hexadecane.)

to practical levels, intermittent problems in reproducing laboratory results have occurred. These problems have generally concerned stability of the microemulsion (Weatherford *et al.* 1979). Additionally, although there have been trends in emissions data, the work of individual investigators does not always agree. In contrast, the commercial microemulsions with which we are all familiar, *e.g.*, flavoring extracts and self-polishing waxes, have been formulated to be stable during years of storage and provide consistently high performance in a consumer market (Prince 1977). Our major research question has been delineating those factors that can make microemulsion fuel performance as consistent as that of conventional hydrocarbon fuels. What underlying physical and chemical factors cause unexpected phase separations or poor emissions in systems that have previously evinced satisfactory performance? What can be done to improve fuel performance to the levels needed to meet present emissions and conservation goals?

Particulate emissions have long been thought to be strongly affected by the size and structure of the dispersed phase aggregates (Dryer and Glassman 1977). Small angle neutron scattering (SANS) provides the opportunity to examine the size and shape of dispersed phase aggregates as well as to target the location of individual components, such as alcohols, within the aggregate. The localization of individual components is determined by changing the scattering contrast, largely a function of isotopic content, of selected solution constituents. Use of a scattering standard to obtain values for absolute intensity permits systematic evaluation of the adequacy of models.

There have been, and remain, fundamental questions about structure. W/O microemulsions comprised of potassium oleate, water, 1-pentanol, and hexadecane, chemically similar to some in Table 2.1, were believed on the basis of conductivity, NMR, and other conventional measurements to be molecularly dispersed (Shah *et al.* 1977), in contrast to compositions in which 1-hexanol was cosurfactant (Shah *et al.* 1971). SANS measurements by some of our group clearly demonstrated that aggregates having water cores of dimensions of several nanometers were present in both cases (Caponetti *et al.* 1986). Not so certain is whether or not in three-phase systems, in which the middle microemulsion phase contains approximately equal amounts of water and oil, the arrangement is sheets of water and oil separated by a layer of surfactant, rather than closed particles. SANS measurements have been claimed to indicate such a bicontinuous structure in water, toluene, sodium dodecyl sulfate, 1-butanol systems (Auvray 1984). However, most of the compositions so far of interest as fuels are in regions in which (when water is the polar component) there seems now to be a consensus that closed aggregates exist in a continuous phase of the major component.

Because of the frequent use of natural fatty-acid surfactants in fuel compositions, SANS measurements on oleate-stabilized W/O microemulsions are of particular interest. Several reports agree that patterns cannot be adequately represented by monodisperse spheres (Caponetti *et al.* 1986; Cebula *et al.* 1980 and 1982). Cebula *et al.* suggested a polydisperse distribution of spheres; Caponetti *et al.* obtained substantially better fits by oblate ellipsoids having permeable shells of surfactant and alcohol hydrocarbon than with either prolate ellipsoids or polydisperse spheres.

No substantial difference between microemulsions containing pentanol and hexanol could be determined. The assumption that discontinuous phase aggregate alcohols largely resided in a soft, permeable shell was subsequently tested by simultaneously fitting scattering results with different contrasts (Caponetti *et al.* 1988). The best fits were obtained for partition coefficients of about 1:1. In connection with these SANS studies, we developed an exact method for computing patterns for polydisperse spheres (Griffith *et al.* 1986 and 1987).

Another major question has been explanation of the difference in stability between commercial microemulsions and conventional microemulsion fuels. It appeared that the reason for the stability might be neutralization of the fatty acid soaps used as surfactants. Although military microemulsion fuels have used full to excess neutralization (Weatherford 1979), commercial microemulsion formulations are often partially neutralized. Early tests on the phase stability of vegetable oil fatty acid microemulsions indicated that neutralization played a major role in fuel phase stability (Compere *et al.* 1986). Comparison of microemulsions stabilized by potassium oleate and by ethanolamine oleate indicated that

the nature of the counterion had little effect (Caponetti *et al.* 1988). The SANS results in that study (Table 2.2), combined with dependence of aggregate dimension on water/surfactant ratio (Kotlarchyk *et al.* 1982), further showed that only neutralized surfactant was active. This conclusion was confirmed in a survey over a wider range of compositions (Caponetti *et al.* 1989). Comparison with fuel compositions (soy fatty acids as surfactant and diesel fuel as hydrocarbon) demonstrated that, as shown in Fig. 2.4, oleate-stabilized compositions were a good model for fuel compositions.

By merely varying the degree of neutralization from fully neutralized to half-neutralized at half-concentration, it was possible to change the particle size of the microemulsion as shown in Table 2.2. Although the ratios of number of moles of water, alcohol, and hydrocarbon to the moles of oleate salt were varied by a factor of four, the composition of the microemulsion based on oleic acid, water, hydrocarbon, and alcohol varied only a few percent. Thus, formulation of microemulsion fuels with different aggregate sizes but with essentially the same overall composition became possible.

Table 2.2. Guinier radii of diesel fuel microemulsions^a

Fraction neutralized	D ₂ O	1-Butanol	Diesel fuel	κ -range	R _g , Å
0.20	69.5	18.8	28.4	0.025 - 0.05	54
0.42	33.5	9.2	13.2	0.08 - 0.11	26
0.51	54.0	7.2	14.8	0.03 - 0.06	41
0.54	25.8	6.9	11.3	0.075 - 0.10	25
0.56	24.1	6.6	47.8	0.075 - 0.10	23
0.73	19.3	5.4	8.0	0.08 - 0.11	21
0.82	17.3	4.7	6.9	0.08 - 0.11	17
0.99	13.7	3.7	5.9	0.08 - 0.11	14

^a In computing stoichiometries, molecular weight of soy fatty acid was taken to be the same as that of oleic acid, and the molecular weight of diesel fuel, as that of hexadecane. Composition is given as moles/mole neutralized soy fatty acid. (Source: Caponetti *et al.* 1989.)

Non-Aqueous Microemulsion and Micellar Fuels

As discussed earlier, microemulsion diesel fuels have generally been limited to the combustible region of the phase diagram, generally less than 30% water. As shown by Fig. 2.1 (p. 8), substitution of a combustible polar alcohol for water implies that the bulk of the phase diagram becomes a stable, single-phase combustible fuel. It is likely that, as aqueous microemulsion structure translates readily to alcohol microemulsion structure, aqueous

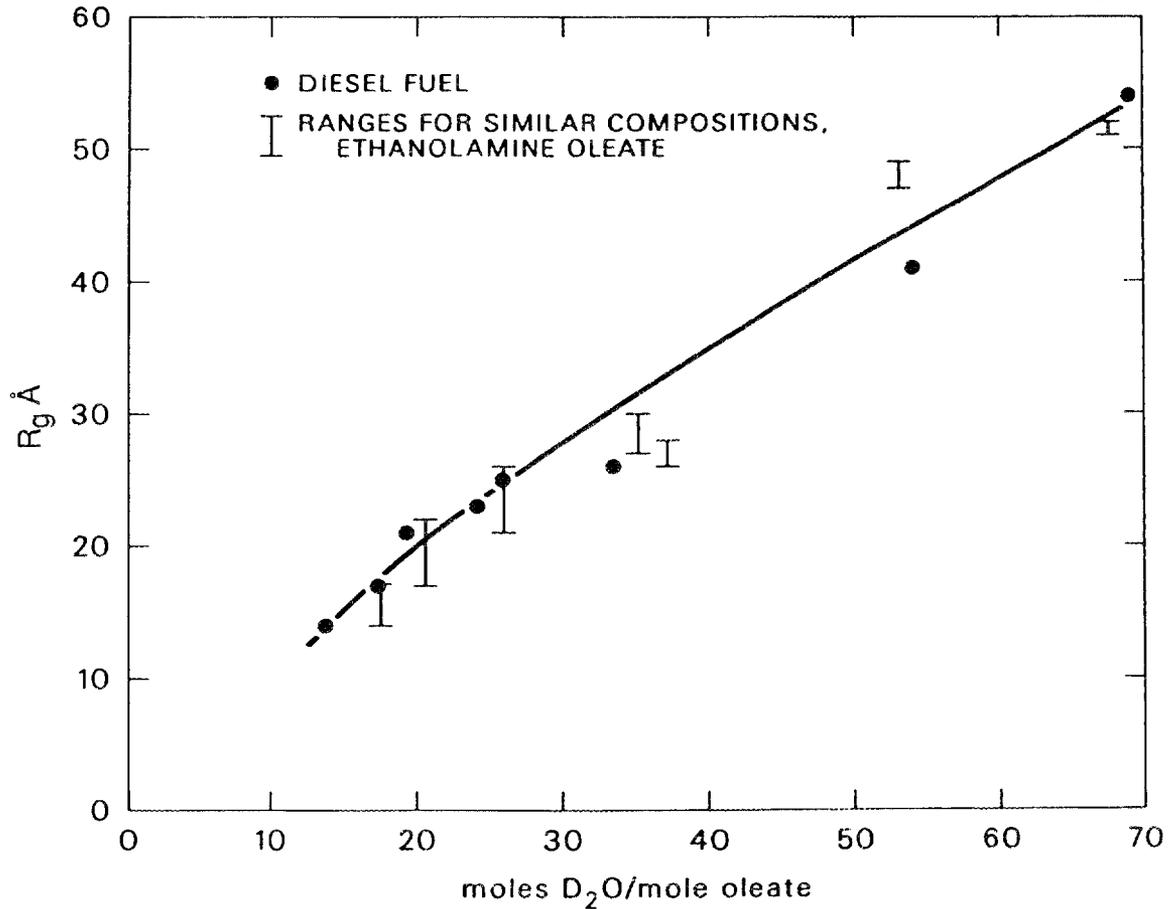


Fig. 2.4. Comparison of Guinier radii of hexadecane : ethanolamine : oleic acid and diesel fuel : ethanolamine : soy fatty acid microemulsions. (Source: Caponetti *et al.* 1989.)

micelle structure will provide a basis for understanding alcohol-continuous fuels with hydrocarbon and fatty acid micelles. This technique could permit modification of the combustion properties of, for example, methanol diesel fuels to decrease ignition delay and increase lubricity.

We have begun investigation of the solution structure of methanol/oil microemulsions. An example is shown in Fig. 2.5. Expressed in volume fractions, it is approximately 0.06 methanol, 0.19 *t*-butyl alcohol, 0.66 diesel fuel, and 0.09 surfactant. Clearly there is structure characterized by dimensions experimentally accessible in this kappa range, but we have not yet carried analysis to a point allowing inferences about models or sizes.

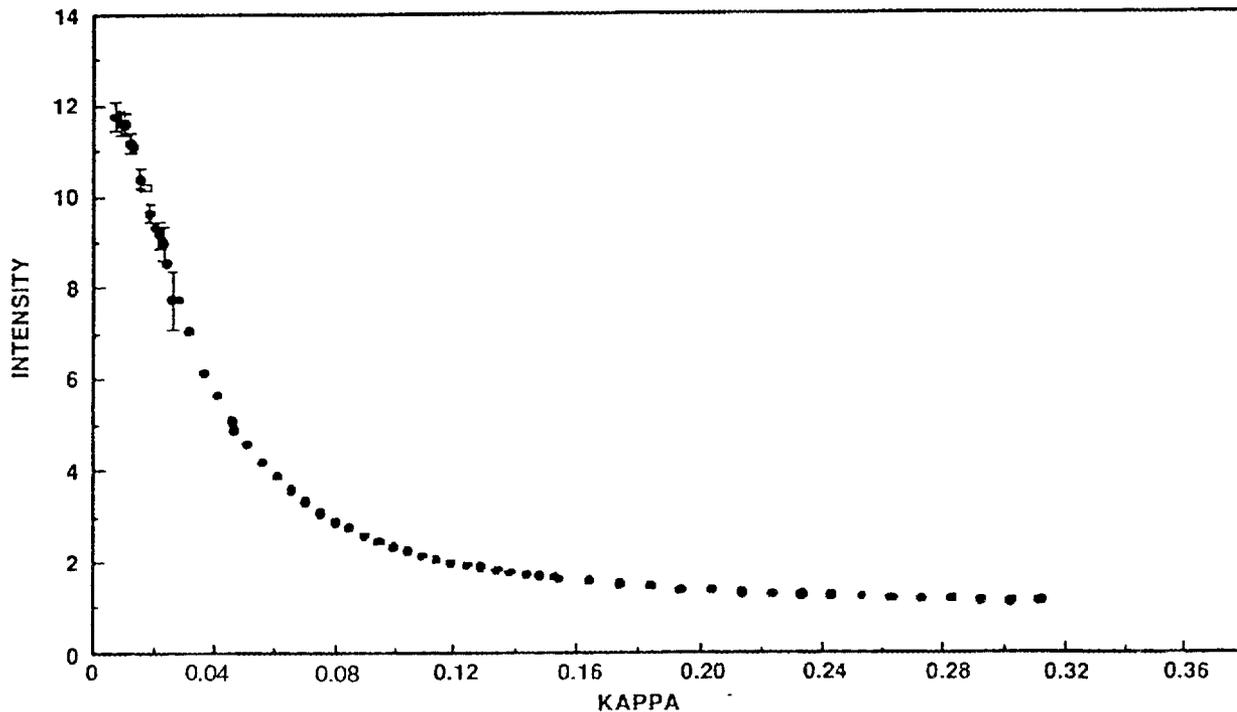


Fig. 2.5. Scattered intensity pattern from a methanol containing microemulsion. (Table 2.3, fuel 4, methanol-d8).

Emissions Modification

In 1986, Arco Chemical Company performed engine tests on microemulsion diesel fuels to determine emissions and best operating conditions. As a part of our informal collaboration, these results were available to us and are shown, with their permission, in Table 2.3. The tests were performed using a Volkswagen diesel engine operated under steady state conditions (DeJovine 1986). The results indicate that it is possible to significantly alter the emissions from compression ignition engines using microemulsion fuels. Although some improvement in particulate emissions occurs with addition of small amounts of alcohols or surfactants, the use of microemulsions containing surfactant, coagent alcohol, and a polar liquid (methanol or water) provide the most substantial decrease in particulate emissions. Substantial decreases in particulate emissions were obtained with both diesel fuel and kerosene base fuels. NO_x emissions were decreased by oxygenates (alcohols and water) but increased by surfactant.

Although the data were limited, we fitted the values for diesel fuel emissions using the SAS General Linear Models procedure, GLM (Spector *et al.* 1987). Because of the limited amount of data for fuels containing additives and kerosene, these data were excluded from the analysis in order to permit data analysis using a mixture model without block variables

Table 2.3. ARCO Steady-State Microemulsion Fuel Tests in VW-Diesel

Test	Fuel Composition ^a						Particulates ^b				Avg. NO _x , ppm	Fuel use mean chg., ^d ± %
	H ₂ O, v%	TBA, v%	EMUL, v%	MEOH, v%	KER, v%	D2, v%	4.16 hp, g/gal	7.24 hp, g/gal	17.7 hp, g/gal	mean chg., ^c ± %		
12	0	0	0	0	0	100	0.473	0.374	0.233	0.0	185	0.0
1	5	10	9	0	0	76	0.328	0.243	0.239	---25.0		8.9
2	10	10	18	0	0	62	0.190	0.176	0.165	-50.8	258	23.3
3	0	10	10	10	0	70	0.269	0.198	0.170	-41.1	234	11.4
4	0	6	18	14	0	62	0.240	0.174	0.166	---46.4	278	14.8
5	0	0	18	0	0	82	0.437	0.323	0.249	-6.7	286	2.9
6	0	0	10	0	0	90	0.512	0.404	0.257	8.6	245	3.7
7	0	0	10	0	90	0	0.450	0.352	0.259	-1.7	237	7.2
8	0	0	18	0	82	0	0.404	0.365	0.207	-9.7	278	6.9
9	0	25	0	0	0	75	0.464	0.397	0.276	3.1	156	3.1
10	0	10	0	0	0	90	0.350	0.322	0.204	---18.9	150	6.5
11	0	0	0	0	100	0	0.359	0.298	0.196	-21.1	208	3.6
13 ^e	10	10	18	0	0	62	0.309	0.242	0.254	---25.6	220	17.5
14	0	14	10	10	0	66	0.215	0.208	0.171	-45.0	202	13.9
15	0	14	0	10	0	76	0.217	0.224	0.170	-43.3	160	12.0
16 ^f	0	6	18	14	0	62	0.368	0.215	0.165	---30.8	247	15.8
17 ^g	0	6	18	14	0	62	0.262	0.221	0.169	-39.7	245	14.2
18 ^f	0	0	0	0	0	100	0.429	0.338	0.168	---13.3	176	3.7
19	0	0	0	0	0	100	0.468	0.410	0.205	0.3	183	3.3
20 ^g	0	0	0	0	0	100	0.441	0.356	0.218	-6.1	198	2.3

^a TBA = t-Butyl Alcohol; MEOH = Methanol; EMUL = Emulsifier; D2 = No. 2 diesel fuel; and KER = Kerosene; ^b VW best operation: 2nd gear, 4.164 hp; 3rd gear 7.237 hp; 4th gear (cruise) 17.74 hp. ^c Average of three conditions: ± percent change for test fuel relative to 100% D2, Test 12. ^d Average of three conditions: gph change for test fuel relative to 100% D2, Test 12. ^e Combustion improver CV-100 (iron derivative of 2,4,6 trinitrophenol) added 1/8 oz/gal. ^f Cerium octoate, 0.5 g/gal, added. ^g Rare-earth octoates, 0.5 g/gal, added.

or an intercept. Using a linear mixture model, we obtained the following equations for particulates for best operation in 2nd, 3rd or 4th gear:

$$P_{2nd} = 0.00620E + 0.00450H + 0.00294B - 0.01464M - 0.02241W, \quad R^2 = 0.989,$$

$$P_{3rd} = 0.00237E + 0.00378H + 0.00317B - 0.01030M - 0.01453W, \quad R^2 = 0.992,$$

$$P_{4th} = 0.00434E + 0.00218H + 0.00402B - 0.00589M - 0.07351W, \quad R^2 = 0.993,$$

$$P_{avg} = 0.00430E + 0.00349H + 0.00338B - 0.01027M - 0.01477W, \quad R^2 = 0.993,$$

where P is particulates in g/gal of fuel, E is the surfactant concentration, H is the hydrocarbon concentration, B is the t-butyl alcohol concentration, M is the methanol concentration, and W is the water concentration. All values are in volume percent.

In a similar fashion, exhaust emission NO_x in ppm is given by:

$$\text{NO}_x = 7.759E + 1.811H + 0.410B + 1.500M + 0.197W, \quad R^2 = 0.998.$$

Over the limited composition region tested, surprisingly good fits were obtained using the simple linear composition-mixture model.

Based on our SANS data (Caponetti *et al.* 1988 and 1989) on the effect of different microemulsion constituents, we felt that the effects on microemulsion size and structure could be rationally divided into effects of particle core (H_2O , methanol), particle shell (surfactant and butanol), and hydrocarbon (diesel fuel). We tried a regression analysis in which we treated particulate decrease as a function of the size of discontinuous phase aggregates as measured by the volume of total material in the core or the shell. We obtained the following equations for particulates for best operation in 2nd, 3rd or 4th gear:

$$P_{2nd} = 0.00333S + 0.00457H - 0.01393C, \quad R^2 = 0.984,$$

$$P_{3rd} = 0.00231S + 0.00382H - 0.02229C, \quad R^2 = 0.990,$$

$$P_{4th} = 0.00397S + 0.00220H - 0.00583C, \quad R^2 = 0.993,$$

$$P_{avg} = 0.00353S + 0.00321H - 0.01009C, \quad R^2 = 0.991,$$

where P is particulates in g/gal of fuel; S is the shell comprised of butyl alcohol and surfactant; C is the highly polar core comprised of methanol and H_2O ; H is the fuel hydrocarbon; and R is the multiple correlation coefficient. It should be noted that the different engine loads were not weighted to approximate normal driving patterns, but were given equal weight in both regression analyses.

In a similar fashion, exhaust emission NO_x in ppm is given by:

$$\text{NO}_x = 0.727O + 7.878E + 1.800H, \quad R^2 = 0.998,$$

where O is the oxygenated fuel components (butanol, methanol, and water) and E is the surfactant, or emulsifier.

Within the range of testing performed, our model had good fit to the data obtained. However, if the literature on emissions modification is viewed as a whole, reproducibility is often poor. This is most probably due to the significant variation in fuel quality and in engine design and operation. Diesel fuel is presently specified as a distillation cut which meets some physical-chemical performance standards, *e.g.* cetane, pour point, color, or residual gum. Although the performance is specified, the composition is not. If the predictions from even a conceptually simple model like Wade's EACN are used as a model for phase behavior, it becomes clear that it is possible to substantially change the phase behavior of a

fuel without changing many of its performance specifications. This concept has been successfully used by Southwest Research Institute to stabilize military diesel fuel by adding an aromatic concentrate which substantially reduces the fuel's EACN. It is possible that similar types of modifications will be required to provide stable fuels.

3. Improving Ignition Delay

Using microemulsion technology, it is possible to make thermally stable, clear mixtures which have appropriate physical and chemical properties. At present it appears that the ignition delay of microemulsion fuels which are predominantly diesel fuel with relatively small amounts of water and surfactant are adequate for use (Owens and Wright 1976, Weatherford *et al.* 1979, and Callahan *et al.*). However, it is likely that microemulsion fuels which contain substantial amounts of low cetane materials, such as methanol, will require addition of cetane enhancers. An appropriate enhancer could also enhance desired fuel characteristics, such as lubricity. Characteristics of selected cetane enhancers, predominantly nitrogen compounds, are summarized below.

Cetane Enhancement by Nitro-Compounds

Although the simplest (and least expensive) nitrogen compound used for cetane enhancement is NH_4NO_3 (Tsenev 1983 and De Beer 1984), both organic and inorganic nitrates have been used as cetane enhancers. Small amounts of enhancers – a few hundred parts per million to 5% – are typically used to improve the combustion properties of conventional diesel fuels. The materials used include inorganic nitrates (*e. g.* NH_4NO_3) and organic nitrates (polynitrate esters, alkyl nitrates). With the exception of a small number of fundamental research studies (Tingman and Simmons 1988), the bulk of work on cetane enhancement by nitro-compounds has been industrial development directed toward patent coverage of materials directly usable in diesel fuel. As indicated in Table 3.1, nitrogen compounds have been particularly favored because of ease of preparation. For example, Knapp, Baylerian, Marguerite, and Seemuth claimed a process for rapidly nitrating aliphatic compounds by reaction with a mixture of H_2O , HNO_3 , and H_2SO_4 (1984). Purcell and Hallock (1985) reported on synthesis methods for the preparation of nitroalkyl and nitroalkoxy nitrates by esterification nitroalkanols with nitric acid in the presence of sulfuric acid.

Although effective in increasing the cetane rating of petroleum distillate fuels, the concentrations of additives reported by various investigators (*e.g.* Stiff 1983, 1984) for alcohol fuels are substantially higher than the concentrations of similar materials used in diesel fuel.

Several investigators have reported work on the production of cetane enhancers from nitration of industrial byproducts or diesel fuel. Chibber, Anand, and Malik reported that addition of 0.6% of the alkyl nitrates prepared from sugar processing fusel oils increased the cetane rating of diesel fuel by 9 (1986). This value is comparable to results achieved with commercial cetane enhancers. Fusel oils are also a byproduct of industrial alcohol fermentations (Prescott and Dunn 1959). Gorman (1986) claimed the use of dewatered, nitrated

Table 3.1. Improvement of fuel ignition properties by nitrogen-containing additives

Additive	Δ Cetane/ % additive	Base fuel ^a	Amount, %	Reference	Remarks ^b
Nitrates					
Alkyl nitrates		CGO	0.05	Minkov <i>et al.</i> 1985	
Alkyl nitrates		DF		Knapp <i>et al.</i> 1984	
Amyl, cyclohexyl, or 2-ethylhexyl nitrates		LSL	0.5-2.0	Cornils and Lipps 1984	
Butoxyethyl nitrate		DF		Li and Simmons 1988	
2-Ethoxyethyl nitrate		DF	0.3	Desikan <i>et al.</i> 1979	SS
		HSL	0.1-0.5		FC = 45
Isopropyl nitrate		DF		Li and Simmons 1988	
1-Methyl-3 or 4-piperidyl nitrate		DF	0.05-1.5	Seemuth 1983b	
N-morpholinylethanol nitrate				Seemuth 1983d	
Tetrahydro-2,5-furandimethanol dinitrate		DF	0.05-0.5	Seemuth 1985b	
Tetrahydrofurfuryl nitrate		MA,EA	6	Stiff 1983	+ 1% CO
Tetrahydro-3,4-furandiol dinitrate		DF	0.05-0.5	Seemuth 1983c	
3-Tetrahydrofuranlyl nitrate		DF	0.05-0.15	Filbey 1983	PM
Tetrahydro-2H-pyran-3-ol nitrate		DF	0.05-0.5	Seemuth 1983a	
Nitrated diesel fuel	0.1-0.3	DF	15	Zarrineghbal <i>et al.</i> 1987	
Ethyl nitrate	6	DF	2	Krishnamurthy 1980	25% FS
Azo-isopropane	7	DF	1	Jessup <i>et al.</i> 1988	
C ₅₋₁₆ B-Nitroalkenes	10.9	DF		Dory 1985	
Alkyl nitrates	15	DF		Chibber <i>et al.</i> 1986	BP
1,3 Dioxolane-4-methanol nitrate	31	DF	0.15	Seemuth 1984	
m-Dioxan-5-ol nitrate	31	DF	0.15	Seemuth 1984	
Isooctyl nitrate + 2-ethoxyethyl nitrate	39	DF	0.11	Hinkamp and Hanlon 1984	
Cyclododecyl nitrate	50	DF	0.05	Thomas 1983	PM
Nitrated fusel oil	59	DF	0.09	Gorman 1986	62.8% as FN
3-Methyl-3-nitro-2-butyl nitrate	62.7	DF	0.15	Purcell and Hallock 1985	PM
2-Methyl-2-nitropropyl nitrate	75	DF	0.05	Hinkamp 1983	
Esters					
Polynitrate esters		CDF	0.05-1	Yan 1987	DE
Bi- and tricyclic nitrate esters		DF		Seemuth 1985a	DE
Azoles					
Many tetrazoles and triazoles		DF	0.05	Martella 1986	
Nitroxides					
di-tert-butyl nitroxide	9	DF	0.3-2.0	Standard Oil Co. 1983	
Azides					
2,6-dimethyl-1,4-benzoquinoline diazide	43	DF	0.2	Hartle and Singerman 1981	
Ethers					
Nitrated polyoxyalkylene ethers		DF		Born <i>et al.</i> 1985	PM
Poly(ethylene oxide)dinitrate	9	MA,EA	5	Stiff 1984	DE

^a CDF = coal derived middle distillate; CGO = catalytic gas oil; DF = diesel fuel; HSL = high severity coal liquefaction middle distillate; EA = ethanol; LSL = low severity coal liquefaction middle distillate; MA = methanol. ^bBP = byproduct; CO = castor oil; DE = decreased explosivity; FC = fuel cetane; FN = fusel nitrate; FS = fuel savings; PM = preparation method; SS = storage stable.

fusel oil at 3.5 cc per gal to increase diesel fuel cetane by more than 10%. The major compounds in the nitrated fusel oil were ethyl nitrate (5-28%), *iso*-butyl nitrate (16-33%), and *iso*-amyl nitrate (30-77%). This material was one of the most effective cetane enhancers. Zerrineghbal and Quinlan (1987) claimed a method for increasing diesel fuel cetane by treating a small portion of neat diesel fuel with nitric acid, separating the acid, neutralizing the fuel, and blending the treated fuel with neat diesel fuel. They recommended blends having 100 to 450 ppm N and indicated that the blend samples had good storage stability and color. In a related patent, Zerrineghbal, Kittrell, and Darien (1987) claimed a cetane increase of 1 to 4 from adding 15% of a fuel treated to have 0.2 to 0.4% nitrogen to neat diesel fuel of cetane 40. As a function of the amount required, it appears that 2-methyl-2-nitropropyl nitrate (Hinkamp 1983) was the most effective of the nitrogen-containing cetane enhancers.

Another major problem with organic nitrogen compounds, particularly nitrates, has been instability. Several investigators have been interested in the development of cetane enhancers with low explosivity. Desikan *et al.* (1979) investigated the use of 2-ethoxyethyl nitrate and found that, in spite of its effectiveness as a cetane enhancer, it had low explosivity. Yan (1987) found polynitrate glycol esters whose solubility with oil is stabilized with diphenyl amine or urea compounds to be effective cetane enhancers for coal derived diesel fuels at concentrations of 0.05 to 1%. He also reported low explosivity for these materials. His findings were similar to those of Stiff (1984), who claimed decreased explosivity for poly(ethylene oxide) dinitrate esters. Seemuth (1985a) claimed the addition of a bi- or tri-cyclic ring nitrate ester to an explosive organic nitrate cetane enhancer could decrease the explosive hazard to permit safe handling and transportation. Concurrently (1985b) he claimed the use of 50 to 500 ppm of tetrahydro-2,5-furandimethanol dinitrate as a cetane enhancer. Hanlon and Hinkamp (1984) claimed a method for decreasing the explosion hazards characteristic of highly effective cetane improvers by blending these materials with C₅-C₁₂ alkyl nitrates. The resultant mixtures provide cetane enhancement with limited sensitivity to shock. Born and coworkers (1985) reported synthesis of dinitrate esters of polyoxyalkylene ethers by reaction with nitric acid. The dinitrate esters could be used as surfactants, cetane improvers, and emission-reducing agents. These materials can also, as reported by Stiff (1984), increase the cetane of methanol and ethanol fuels, although the level of addition reported was 5%, somewhat high for economic use. Polyoxyalkylene ethers with a wide variety of endcaps are presently used as detergent and lubricity additives in conventional fuels.

Cetane Enhancement by Hydrocarbons

As shown in Table 3.2, a number of organic compounds have been shown to increase cetane rating of fuels. These materials fall into two primary classes, peroxides and compounds having double bonds. The most promising materials are a group of polymers, reported by Puchin and coworkers (1970), which have both peroxide endcaps and repeating groups with double bonds. At concentrations of 100 ppm, these materials increased diesel fuel cetane rating by 10. Monomers were one or two orders of magnitude less effective than the polymerized material. Of the remaining hydrocarbon materials, only cumene hydroperoxide was comparable to the bulk of the organic nitrogen cetane enhancers.

Table 3.2. Effect of hydrocarbon additives on fuel ignition properties

Additive	Δ Cetane/ % additive	Base fuel ^a	Amount, %	Reference
di-Butyl oxalate	0.2	DF	1	Dillon and Jessup 1988a
1-Phenyl-1-propanol	0.2	DF	20	Taylor 1988
Tetralin hydroperoxide	0.4	GO/LCO	10	Date, Tamanochi, and Kawate 1988 ^b
2,2,6-Trimethyl-1,3-dioxen-4-one	3.6	DF	3	Dillon and Jessup 1988b
Cumene hydroperoxide	14	LO	0.5	Date and Akasaka 1986
Tert-butyl permethacrylate	10-100	DF	0.1-2.0	Puchin <i>et al.</i> 1970
Poly(tert-butyl peracrylate)	1000	DF	0.01	Puchin <i>et al.</i> 1970
Poly(dimethyl(vinylethynyl)methyl hydroperoxide	1000	DF	0.01	Puchin <i>et al.</i> 1970
Poly(dimethyl(vinylethynyl) methyl tert-butyl peroxide	1000	DF	0.01	Puchin <i>et al.</i> 1970

^a DF = diesel fuel; and GO/LCO = gas oil (60%) with light cycle oil (40%); LO = light oil. ^b Preparation method.

Sulfur Compounds

Some sulfur compounds have been shown to increase cetane rating of diesel fuels. Bowden and Frame (1986) found that supplementation of diesel fuel with sulfur compounds to a level of 1% sulfur with tert-butyl disulfide significantly increased cetane number. Similarly, Smith *et al.* found that addition of 0.22 to 0.61% dithiocarbamate increased the cetane rating of diesel fuel by up to 7.6 (1984). However, it should be noted that addition of substantial amounts of sulfur compounds to fuels is likely to contribute to the emission of sulfur oxides.

Other Additives

Guibet and coworkers have been interested in the development of cetane enhancers for high-oxygenate diesel fuels. These have included cetals (1984) amyl nitrate (1982a) and fatty acid monoesters (1982b). Long chain fatty acid monoesters are particularly interesting because of their high cetane rating and because they are readily produced by reacting small alcohols with vegetable oil in the presence of an acid or base catalyst (Reid and coworkers 1943). A number of investigators have reported use of vegetable oil fatty acid esters as diesel fuel substitutes (Chancellor and Raubach 1981, Pischinger *et al.* 1982, and Hawkins and Fuls 1982). They have limited biotoxicity and are effective extractants for fermentation alcohols (Compere *et al.* 1984a and b; Googin *et al.* 1983; and Griffith *et al.* 1983, 1984a and b, 1987). Small monoesters are readily incorporated into aqueous micelles (Friberg and Gan-Zuo 1983), and it is likely that vegetable oil monoesters in a predominantly alcohol system will be capable of forming stable liquid systems. Fatty acid monoesters are reasonably stable, low in viscosity, and free of nitrogen and sulfur.

Klopfenstein (1985) has reviewed the cetane ratings of a variety of fatty acid monoesters. He found that cetane rating is largely a function of the chain length of the fatty acid, and is approximated by:

$$y = 24.28 + 8.431 x - 0.1299 x^2,$$

where y is the fitted cetane number and x is the fatty acid chain length. The highest cetane rating reported was 87 for methyl stearate. Because of the melting point of methyl stearate (37-39 C), its cetane was estimated based on ignition delay of a 30:70 mixture in petroleum ether.

Klopfenstein's observations are closely paralleled by those of Guibet and coworkers (1982b) if it is assumed that cetane rating is a function of the cetane rating of components in the fuel blend.

Similarly, Brook and coworkers (1984) found that supplementation of methanol with approximately 1 to 2% dimethyl ether was able to improve compression ignition performance sufficiently to permit performance comparable to neat diesel fuel. These investigators reasoned that dimethyl ether could be produced from methanol using the process heat from methanol synthesis. As with vegetable oil esters, dimethyl ether is free of nitrogen and sulfur. However, it has a high vapor pressure. Although the behavior of ethers in low concentrations may differ, peroxide formation during extended storage has been a problem with pure compounds. However, assuming that a fuel equivalent to diesel fuel in performance has a similar performance rating, the cetane increase per percentage dimethyl ether is between 20 and 40, comparable to the better nitrogen-containing organic cetane enhancers.

4. Correlating Microemulsion Composition, Structure, and Combustion Performance

As discussed earlier, microemulsion fuel diesel emissions appear to be correlated to discontinuous phase aggregate size (particulates) and to the presence of materials which lower combustion temperature (NO_x). Because microemulsions are complex multicomponent systems, it is difficult to design small, simple experiments which permit separation of the effects of variables. Current understanding of some microemulsion fuel systems indicates that it may be possible to design paired experiments in which fuel composition, aggregate structure, and combustion patterns are compared. Best separation of variables can be obtained by using samples distributed throughout the phase region investigated. This is likely to result in a need for combustion bomb studies on fuel compositions throughout a phase region. Some compositions are likely to be unacceptable for practical use in a conventional engine.

Correlation between Solution Structure and Particulate Emissions

Decreased particulate emissions have been credited to both macro- and microemulsions. The regression analysis in the previous chapter indicates that it is likely that the size of discontinuous phase aggregates has the strongest effect on diesel particulate emissions. Microexplosion – the explosion of individual aggregates due to vaporization of low-boiling constituents – has been thought to account for at least part of the decrease in particulate emissions. However, it has been difficult to design combustion experiments with sufficient control to permit determination of this effect. Based on previous SANS experiments, it is possible to substantially change the diameter of microemulsion aggregates by simply changing the degree of oleic acid neutralization. To the extent that experimental results can be estimated in advance of performance, it appears likely that an experimental matrix with several levels of particle diameter will be required to provide an estimate of the effect of solution structure on particulate emissions. As shown in Table 4.1, it is possible to provide a wide range of aggregate sizes within a composition range of 2% in bulk microemulsion fuel composition. Variation of microemulsion water content also provides a method for changing aggregate diameter. Cetane tests performed by Weatherford's group on military diesel fuels have shown that variations of water within the levels indicated in Table 4.2 do not have a substantial effect on fuel cetane rating (Weatherford *et al.* 1979).

Table 4.1. Compositions and dimensions of selected microemulsions

Oleic acid neutralization, %	H ₂ O, % w/w	Oleic acid, %w/w	1-Pentanol, % w/w	Ethanolamine, % w/w	Hexadecane, % w/w	R _{core} , nm
100	13.4	12.0	22.1	2.59	50.0	1.7
84	13.4	12.0	22.2	2.19	50.2	1.8
67	13.5	12.1	22.3	1.75	50.4	2.2
50	13.6	12.1	22.4	1.31	50.6	3.0
33	13.6	12.2	22.5	0.87	50.9	5.4

Table 4.2. Compositions and dimensions of microemulsions with varying water content

H ₂ O, % w/w	Oleic acid, % w/w	Alcohol, % w/w	Ethanolamine, % w/w	Hexadecane, % w/w	R _g , nm
8.1	12.9	23.8	1.40	53.8	1.7
13.6	12.1	22.4	1.31	50.6	3.0
19.1	11.4	20.9	1.23	47.4	4.3
23.9	10.7	19.7	1.16	44.6	5.4

Combustion bomb technology can permit an evaluation of the combustion properties of such fuels without requiring individual fuels to meet the varied requirements of a conventional engine. Some caveats should be mentioned. Pure component model fuel systems which are not practical in application are likely to provide the best experimental control. To get the widest variation in aggregate diameter, fuels which are near the limits of phase stability may be used.

Evaluation of Ignition Initiators for Micellar and Microemulsion Fuels

Conventional ignition initiators were developed primarily to improve the performance of conventional diesel fuels. They may be appropriate for use with microemulsion fuels which have diesel fuel as a continuous phase, although the presence of a polar phase can permit use of a number of inexpensive cetane enhancers which are too polar to dissolve in conventional diesel fuel. However, an alcohol-continuous diesel fuel is likely to require a new type of ignition initiator because its initial ignition delay is long and because alcohol fuels tend to be dispersed as vapors, rather than mists. A short series of matrix experiments would provide information on the cetane enhancers most suitable for use in microemulsion and micellar fuels.

As discussed earlier, a number of distinct chemical classes of diesel ignition initiators have been reported. The most successful include alkyl nitrates, polynitrate esters, nitrated polyoxyalkylene ethers, peroxides, ethers, and esters. The utility of at least one member of each of these classes in microemulsion and micellar fuels should be investigated to provide information on ignition enhancement of fuels with extremely low cetane ratings. For purposes of discussion, a typical set of fuel compositions for test is shown in Table 4.3. Cetane ratings for these fuels have been estimated by summing the cetane ratings of their constituents with the exception of Emersol 315. Fatty acid surfactant and water were not considered because they did not appear to have a discernible effect on the cetane rating of military fire-safe diesel fuels at concentrations which permit compression ignition (Weatherford *et al.* 1979).

The selection of cetane enhancers for microemulsion and micellar fuels is likely to be required if significant amounts of petroleum are to be replaced with alcohols in conventional

Table 4.3. Compositions, cetane rating, and energy content of selected microemulsions

Composition, % w/w								
Methanol	Emersol 315	<i>t</i> -Butyl alcohol	Diesel fuel	Methyl oleate	Diethyl ether	Propyl nitrate	Estimated cetane	Energy, kcal/g
10	10	5	75				38.4	9.6
20	10	10	60				31.8	8.9
30	10	15	45				25.2	8.2
40	10	20	30				18.6	7.5
50	10	25	15				11.9	6.8
10	10	5	65	10			43.1	9.5
20	10	10	50	10			36.4	8.8
30	10	15	35	10			29.8	8.0
30	10	15	25	20			34.5	7.9
40	10	20	10	20			27.9	7.2
40	10	20	0	30			32.6	7.0
10	10	5	74		1.0		60.1	9.6
20	10	10	59		1.0		53.5	8.9
30	10	15	43.5		1.5		57.8	8.2
40	10	20	28.5		1.5		51.1	7.5
50	10	25	13		2.0		55.4	6.7
10	10	5	64	10		1.0	53.7	9.4
20	10	10	49	10		1.0	47.1	8.7
30	10	15	34	10		1.0	40.4	8.0
30	10	15	24	20		1.0	45.1	7.8
40	10	20	9	20		1.0	38.5	7.1
40	10	20	0	29		1.0	42.7	7.0

diesel engines. The relatively polar nature of these fuels can permit the use of a variety of polar ignition initiators. However, the properties of cetane enhancers for these alternative fuels are likely to be substantially different from those used with conventional diesel fuels because of the high volatility of small alcohols. In normal diesel fuel combustion, the bulk of the fuel is atomized as droplets. The combustion pattern in the cylinder is also likely to be different. The development of microemulsion and micellar fuel ignition initiators may require significant effort. However, this research area presents opportunities commensurate with its likely difficulties.

A promising alternative for future evaluation is the aromatic alcohols which have been investigated by ARCO Chemical Company as coagents for fire-safe fuels (Hazbun and Schon 1988). These industrial byproducts have high flash points, high energy density, and produce microemulsion fuels with very low cloud and pour points. An interesting feature of the compounds is that they, like monoesters, are reportedly cetane enhancers.

Combustion Properties of Model Fuel Systems

As earlier noted, a reasonably simple linear model provided a good fit to a small amount of emissions data whose composition was restricted to a very limited range. From these fits it is clear that a linear model is unlikely to adequately describe the combustion of microemulsion and micellar fuels over a wide range of fuel compositions. As envisioned, fuel compositions spanning the range of application would be tested; however, the region of interest would be limited to a small part of the possible fuel compositions because of phase boundaries, energy content, or other factors that preclude fuel use. If one represents the feasible subregion as a polyhedron within the phase diagram, one normally selects the compositions corresponding to the vertices of the feasible polyhedron as the basic set of compositions needed. To obtain information about nonlinearity, additional compositions comprising the midpoint of each side of the polyhedron and its centroid are generally also required. This design of such mixture experiments has been developed in some detail by Cornell (1981 and 1983). Application to solvent systems with limited single phase regions has been discussed in some detail by Bayne and Ma (1987 and 1989).

The first proposed experiment with aqueous fuel microemulsions was developed to better understand the role of particle size on combustion properties. As can be seen from the engine test correlations discussed earlier, the effect of volume of water contained in the dispersed phase is very important in reducing particulate and NO_x emissions. Since the feasible subregions for these systems are limited to compositions with $< 30\%$ water and to reasonable amounts of surfactant and alcohol from practical as well as phase considerations, a mixture experiment can probably be constructed with limited ignition improver data as proposed above. Such a test could be run in conjunction with the fuels described in Tables 4.1 and 4.2. The additional points required for analysis of the feasible subregion are described in Table 4.4. Phase boundaries constrain the system to a region where the surfactant, alcohol, and water mix to form single-phase, clear solutions (without the addition of hydrocarbon) as a first approximation.

Table 4.4. Compositions and dimensions of selected microemulsions

H ₂ O, % w/w	Oleic acid, % w/w	Alcohol, % w/w	Ethanolamine, % w/w	Hexadecane, % w/w
5.7	5.1	NPA, 9.4	1.11	78.7
10.2	9.1	NPA, 16.8	1.97	62.0
13.9	12.5	NPA, 23.0	2.70	48.0
12.2	10.9		2.36	74.5
9.9	8.9	NHA, 18.9	1.92	60.4
10.4	9.4	NBA, 14.5	2.02	63.7

As discussed earlier, there is a good correlation between the volume of methanol-containing discontinuous phase droplets and decreased particulate and NO_x emissions. The question is whether fuel composition ranges in which particulate emissions are minimized can be defined. The feasible subregion of the phase diagram for this system is constrained not only by phase boundary considerations but also by compositions that have reasonable ignition delays and practical limits on individual fuel components.

5. Summary and Recommendations

Microemulsion fuels present an opportunity to replace up to 50% of the petroleum in diesel fuels with biomass and byproduct materials, including alcohols, vegetable oil fatty acids, and aromatic alcohols. The technology is expected to be driven by lowered NO_x and particulate emissions, although petroleum sparing and energy security are major energy-related objectives. Major factors in the adoption of this and other market fuel technologies include cetane rating, emissions decreases, and appropriate physical chemical properties, *e.g.* cloud point, vaporization.

A literature review indicates that ignition initiation, as measured by cetane rating, is not substantially affected by the fatty acid soaps or water used in aqueous microemulsion fuels, although the reasons for this have not been elucidated. The use of alcohols in these fuels is, however, expected to affect ignition delay. High alcohol fuels are expected to need ignition initiators to permit use in conventional engines. An analytical review of compression ignition initiators indicates that several classes of materials, including peroxides, alkyl nitrates, monoesters, ethers, and aromatic alcohols, are likely to be effective in fuels which have a high alcohol content. Because alcohols can decrease cetane rating substantially below that normally expected in diesel fuels and because of the high volatility of alcohols, it is likely that a mixture of cetane enhancers will be more effective than a single enhancer.

The reasons for the modification of particulate and NO_x emissions found with microemulsion fuels have to date been elusive. Linear regression analysis to correlate solution structure, determined by small-angle neutron scattering, and passenger diesel engine emissions was performed on program data. There is close correlation between the size of fuel solution aggregates and particulate emissions, and between the amount of methanol or water in a fuel and particulate emissions. There is also good correlation between NO_x reduction and methanol or water concentration.

Because microemulsions have a large number of classes of chemical constituents, experiments to separate the effects of composition and structure require the use of carefully controlled conditions combined with an experimental design capable of permitting separation of the effects of variables. A series of small mixture experiments to permit composition variable separation were presented. Experimental design was tailored to minimize the data needed for adequate analysis.

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