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IEA AMF

Annex XVIII

Future Greener Diesel Fuels

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Battelle
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Acronyms

AMF	Advanced Motor Fuels committee
ASTM	American Society for Testing and Materials
C	degrees Celsius
CAS	Chemical Abstracts Service
CO	carbon dioxide
DBM	dibutyl maleate
DBXM	dibutoxymethane
DEM	diethyl maleate
DPE	dipentyl ether
EXEE	2-ethoxyethyl ether
F-T	Fischer Tropsch
GTB	glycerol tributrate
IEA	International Energy Agency
NO_x	oxides of nitrogen
OS	oil sands diesel
PM	particulate matter
R	a hydrocarbon group (in chemical structure)
TPGE	tripropylene glycol methyl ether
ULS	ultra-low-sulfur diesel
vp	vapor pressure

1 Introduction

1.1 Rationale

1.1.1 Use of Diesel Engines Is Increasing

Vehicles with diesel engines are more fuel efficient than vehicles with spark-ignited gasoline engines. For this reason, vehicles with diesel engines are becoming more popular in several IEA member nations. Nearly all heavy multi-ton trucks have used diesel engines for some time; and the use of diesel engines has spread to smaller trucks and also to personal transportation vehicles. Continued design improvements in small diesel engines make it likely that the number of vehicles with diesel engines will continue to increase.

1.1.2 Reducing Diesel Engine Emissions is a Challenge

Compared to gasoline engines, diesel engines have relatively low hydrocarbon and carbon monoxide emissions. The greater fuel efficiency of diesel engines can also lead to a reduction in carbon dioxide emissions. Moreover, compared to gasoline engines, diesel engines tend to have relatively high emissions of oxides of nitrogen (NO_x) and particulate matter (PM). Through reactions with hydrocarbons and sunlight, NO_x emissions contribute to the formation of photochemical smog. In particular, the growing concern over the health effects of fine particles has led to a search for ways to decrease PM emissions from diesel engines.

Although the development of aftertreatment devices to address NO_x and PM emissions from diesel engines is under way, the feasibility of these devices can be enhanced by lowering the engine-out emissions.

1.1.3 Oxygenates Can Reduce Diesel Engine Emissions

Laboratory tests have shown that the addition of oxygenates to diesel fuel can lead to substantial reductions in engine-out emissions of PM and NO_x.

Particulate Matter Emissions Reduction

Because a high proportion of PM emissions consists of unburned carbon and carbon compounds, increasing the supply of oxygen during the combustion process can reduce the formation of particulate matter. This is especially true if the sulfur content of the diesel fuel has already been reduced, thus limiting the formation of solid sulfate in the exhaust. While mechanical design changes to improve the mixing of fuel and air in the engine cylinder can improve combustion and reduce emissions, tests have shown that blending an oxygen-containing compound with the fuel can be especially effective in reducing PM emissions.

For example, in the United States, the Coordinating Research Council (CRC) VE-10 study found that increasing the oxygen content of diesel fuel from 0 to 2 percent by adding the oxygenates 1,2-dimethoxyethane (monoglyme) or 2-methoxyethyl ether (diglyme), decreased PM emissions by 10 to 15 percent,[1] These and other results have heightened interest in the use of oxygen-containing compounds that can be blended with diesel fuel for reducing PM emissions.

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NO_x Emissions Reduction

Other tests have shown that using diesel fuels of increased cetane number can reduce NO_x emissions. Fuels of high cetane number ignite more readily, and reducing the ignition delay is thought to reduce the time available for the formation of NO_x. Many oxygenates under consideration for blending with diesel fuel have high cetane numbers and so would be expected to contribute to this effect. Laboratory tests with neat dipentyl ether, 2-methoxyethyl ether, and other oxygenates have shown that the use of these oxygenates can reduce NO_x emissions by 30 to 50 percent over a Fischer-Tropsch-type diesel fuel.[2]

In addition, the combination of the use of diesel fuel oxygenates with the use other emissions control strategies has been shown to be beneficial. For example, in 1995 Murayama et al.[3] showed that simultaneous reductions of NO_x and PM could be achieved though the use of an oxygenate with EGR.

1.2 Need for Property Data for Diesel Fuel Oxygenate Blends

Oxygenates that are blended with diesel fuel must meet operational constraints necessary for a successful motor fuel. In particular,

- The oxygenate must be miscible with various types of diesel fuels over the range of environmental temperatures seen in vehicle service.
- The oxygenate blend must not produce excessive volatility when mixed with various diesel fuel base stocks. The flammability of fuel in tanks depends on its volatility, so this can be an important safety issue.
- The oxygenate-diesel fuel blend must have an adequate cetane number and preferably show an increased cetane number.

However, the consideration of oxygenates for use with diesel fuels is relatively recent. Thus, although some basic physical and chemical property data exist for neat oxygenates, there is a lack of data related to their ability to be blended successfully with various diesel fuels and the ability of such oxygenate-diesel fuel blends to have the properties that are required of motor fuels.

In this regard, if key fuel properties are unsuitable, certain oxygenates may be eliminated from further consideration.

1.3 Scope of Project

In this project seven oxygenates and three diesel fuels were selected for testing. The oxygenate blend levels were 0, 5, 10, 30, and 100 percent by volume. Thus, data were obtained for the neat fuels and neat oxygenates, as well as for three intermediate blend levels.

Separate series of tests were conducted to study miscibility, cloud point, water tolerance, flash point, and vapor pressure at temperatures ranging from –30 to 30 C. In addition, AET Ltd. conducted ignition quality testing on behalf of Natural Resources Canada.

1.4 Organization of Project Report

The organization of this project report is as follows:

1. Discussion of the selection of the oxygenates and base diesel fuels and preparation of the oxygenate-diesel fuel blends. (Section 2)
2. Discussion of the individual series of tests for miscibility (Section 3), water tolerance (Section 4), cloud point (Section 5), flash point (Section 6), vapor pressure (Section 7), and ignition quality (Section 8).
3. Available information on health effects is referenced (Section 9).
4. Implications for possible future Phase II and Phase III activities (Section 10).

2 Selection of Oxygenates and Diesel Fuels

2.1 Oxygenates

2.1.1 Types of Candidate Oxygenates

Proposed diesel fuel oxygenates fall under the categories of

- simple ethers
- complex ethers (acetals)
- esters.

Ethers

Simple ethers have an oxygen atom connecting two hydrocarbon groups, where O is an oxygen atom and R is a hydrocarbon group:

$$R - O - R$$

Figure 1 shows the structure of a simple ether, dipentyl ether.

Acetals and Complex Ethers

Acetals have two (or more) oxygen-atom linkages attached to a single carbon atom, as in:

$$R - O - C - O - R$$

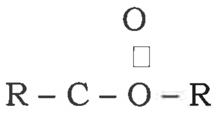
Figure 2 shows an example of an acetel. More complex ethers may have multiple carbon atoms with oxygen-atom linkages, as in:

$$R - O - R - O - R$$

Figure 3 shows the structure of 2-methoxyethyl ether, an example of a complex ether.

Esters

Esters have the following type of structure:



$$R - C - \overset{\overset{O}{\square}}{O} - R$$

Figure 4 shows the structure of dibutyl maleate, which is a di-ester.

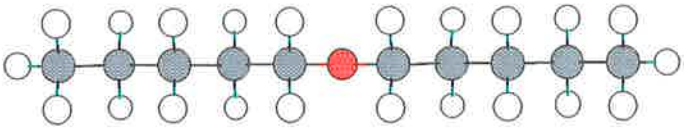


Figure 1. Pentyl Ether, a Simple Ether

[Gray shading indicates carbon atoms, red pattern indicates oxygen atoms, open circles indicate hydrogen atoms.]

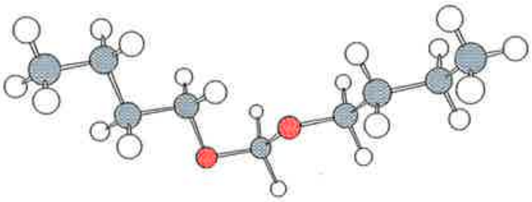


Figure 2. Dibutoxymethane, an Acetal

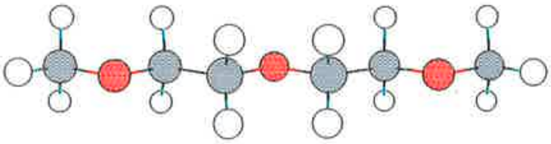


Figure 3. 2-Methoxyethyl Ether, a Complex Ether

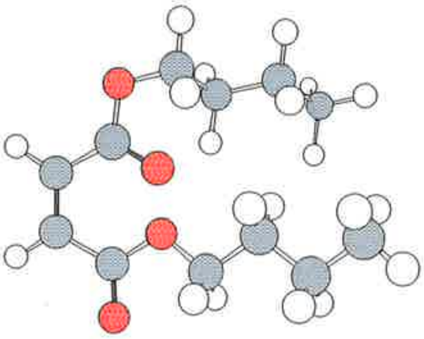


Figure 4. Dibutyl Maleate, a Di-ester

2.1.2 Selection of Oxygenates

The selection of oxygenates was guided by several considerations:

- **Boiling point and Flash Point in Diesel Fuel Range**. Because this was a study of *diesel fuel* oxygenates, the oxygenate boiling point was required to be in the range of temperatures commonly observed for diesel fuel components and the flash point of the oxygenate was required to be greater than 52 C, to meet commonly adopted diesel fuel fire safety requirements.

- **Variety of Chemical Types**. Oxygenates were selected to represent a variety of chemical structures, including simple and complex ethers, and esters. Different numbers of carbon atoms in the – O – R – O – linkage are represented.
- **Existing Reviews and Experimental Data**. Some oxygenates have been the subject of previous investigations, including the generation of engine emissions data.[4, 5, 6] For example Bertola et al.[7] recently considered 27 oxygenates as diesel fuel additives.
- **Results of an ad hoc Study Committee**. In the U.S. an ad hoc committee on the use of oxygenates in diesel fuels contracted with Southwest Research Institute (SwRI) to survey potential oxygenates and develop a short list of candidates. The results of this evaluation[8] were used in the selection of oxygenates for this work.
- **Consultations**. Discussions were held with several interested people.

2.1.3 Names, Structures and Basic Properties of Oxygenates

The names, Chemical Abstracts Service (CAS) numbers, chemical formulas oxygen contents, boiling points, and chemical structures are shown in Table 1 for the seven oxygenates studied in this Annex.

Table 1 also shows oxygenate name abbreviations used elsewhere in this report. A photo showing the appearance of samples of all the oxygenates examined in this study is shown in Figure 5.

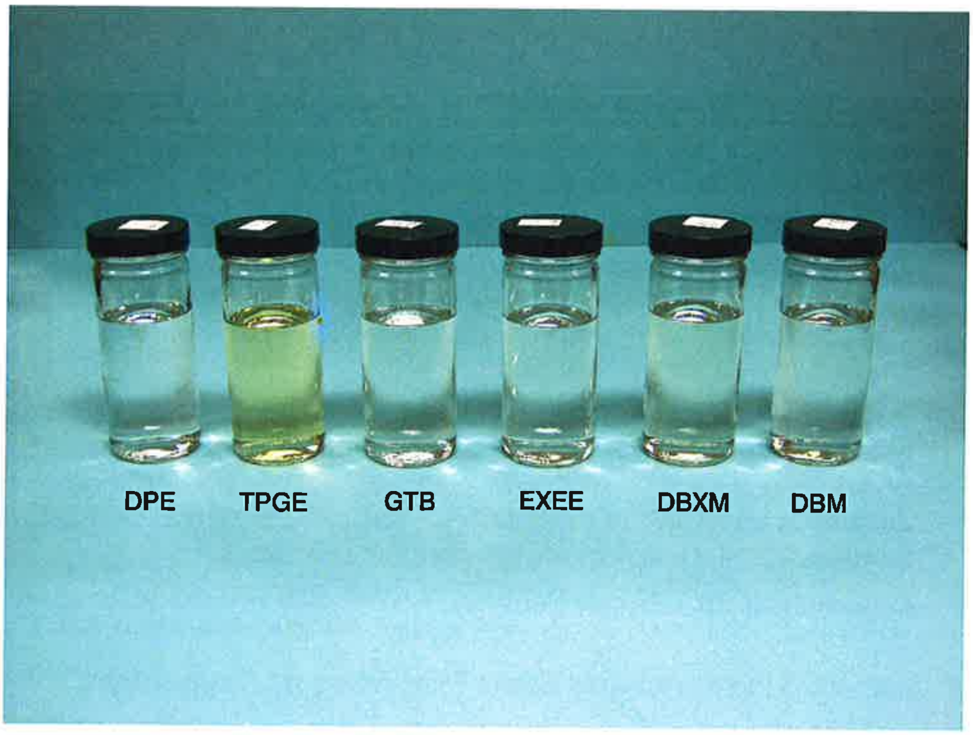


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Figure 5. Appearance of Oxygenate Samples

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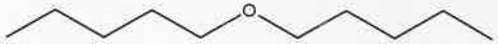
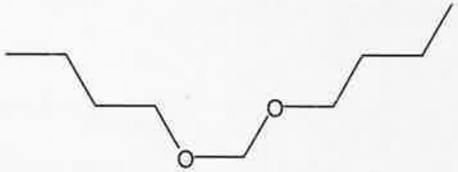
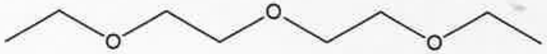
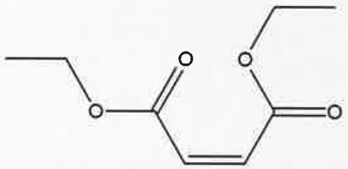
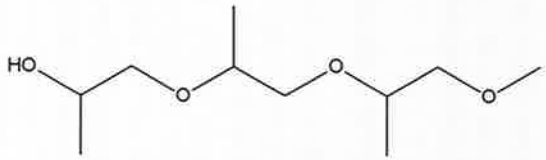
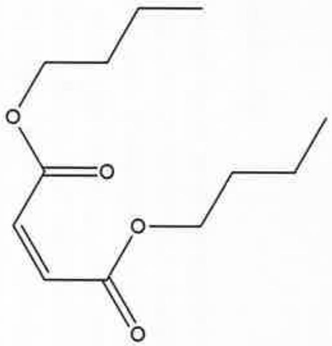
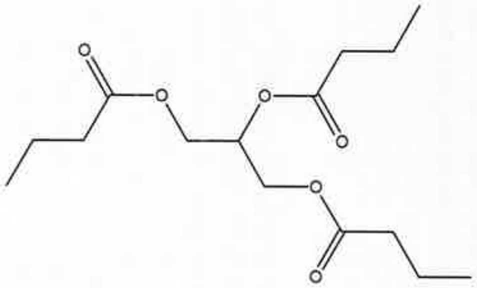
Table 1. Names, Formulas, and Structures of Oxygenates

Oxygenate		CAS Number	Formula	Oxygen, %	Boiling Point, C	Density, kg/m³	Chemical Structure
DPE	Dipentyl ether	693-65-2	$C_{10}H_{22}O$	10.11	187	783	
DBXM	dibutoxymethane (butylal)	2568-90-3	$C_9H_{20}O_2$	19.97	179	834	
EXEE	2-Ethoxyethyl ether (diethylene glycol diethyl ether)	112-36-7	$C_8H_{18}O_3$	25.59	188	906	
DEM	diethyl maleate	141-05-9	$C_8H_{12}O_4$	37.17	223	1066	

Oxygenate		CAS Number	Formula	Oxygen, %	Boiling Point, C	Density, kg/m^3	Chemical Structure
TPGE	Triproplylene glycol monomethyl ether	25498-49-1	$C_{10}H_{22}O_4$	31.02	242	968	
DBM	Dibutyl maleate	105-76-0	$C_{12}H_{20}O_4$	28.03	281	987	
GTB	Glycerol tributrate (tributyrin)	60-01-5	$C_{15}H_{26}O_6$	31.75	307	1035	

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2.2 Diesel Fuels

Three diesel fuels were selected to represent a range of fuel compositions and properties. These three fuels were used as the base for the preparation of the diesel fuel-oxygenate blends.

2.2.1 Selection of Diesel Fuels

The first fuel was a diesel fuel that was formulated by Chevron Phillips Specialty Chemicals to have physical properties and cetane number typical of U.S. diesel fuels. The fuel formulation was developed with extensive inputs from energy companies, diesel engine manufacturers, and the U.S. Department of Energy to represent a typical U.S. diesel fuel, but with very low sulfur (ULS). This fuel saw extensive use in the recent diesel emissions control sulfur effects (DECSE) study and is currently being used in the $35 million Advanced Petroleum-Based Fuels – Diesel Emissions Control (APBF-DEC) study, as well as by several other research programs. This fuel offers the advantages of being exceptionally well-characterized, having a being a consistent formulation, and being readily available to other researchers. A description of this fuel may be found in reference [9].

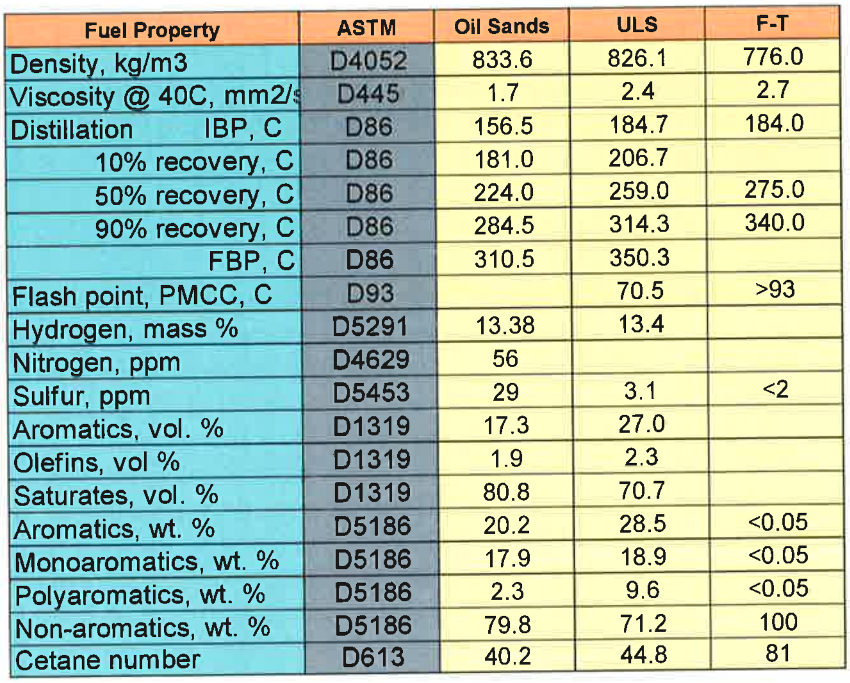
The second fuel was a Fischer-Tropsch (F-T) diesel fuel. This fuel was intended to not only represent synthetic diesel fuels that are made by the Fischer Tropsch process, but also to represent the extreme of petroleum fuels, such as "City diesel" and "Swedish diesel" that are manufactured to have essentially no low sulfur, very low aromatics, relatively low density and a relatively high cetane number. Properties of the Fischer Tropsch fuel may be found in reference [10].

A third fuel was an oil-sands-derived diesel. This fuel was more dense, but somewhat more volatile than the DECSE diesel. It was intended to be representative of oil sands-derived fuels. This fuel was also intended to be representative of lower cetane number fuels. A description of this fuel may be found in reference [11].

2.2.2 Properties of Diesel Fuels

Properties of the three diesel fuels are shown in Table 2. A photos samples of the three diesel fuels used in this study is shown in Figure 6.

Table 2. Diesel Fuel Properties



Fuel Property	ASTM	Oil Sands	ULS	F-T
Density, kg/m3	D4052	833.6	826.1	776.0
Viscosity @ 40C, mm2/	D445	1.7	2.4	2.7
Distillation IBP, C	D86	156.5	184.7	184.0
10% recovery, C	D86	181.0	206.7	
50% recovery, C	D86	224.0	259.0	275.0
90% recovery, C	D86	284.5	314.3	340.0
FBP, C	D86	310.5	350.3	
Flash point, PMCC, C	D93		70.5	>93
Hydrogen, mass %	D5291	13.38	13.4	
Nitrogen, ppm	D4629	56		
Sulfur, ppm	D5453	29	3.1	<2
Aromatics, vol. %	D1319	17.3	27.0	
Olefins, vol %	D1319	1.9	2.3	
Saturates, vol. %	D1319	80.8	70.7	
Aromatics, wt. %	D5186	20.2	28.5	<0.05
Monoaromatics, wt. %	D5186	17.9	18.9	<0.05
Polyaromatics, wt. %	D5186	2.3	9.6	<0.05
Non-aromatics, wt. %	D5186	79.8	71.2	100
Cetane number	D613	40.2	44.8	81

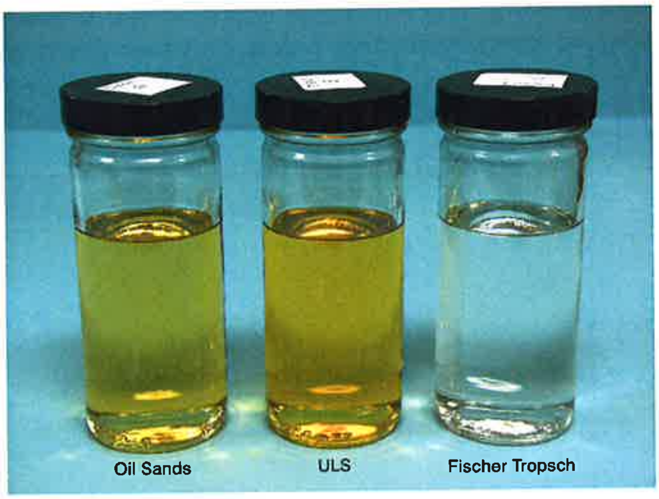


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Figure 6. Diesel Fuels

2.3 Preparation of Diesel Fuel-Oxygenate Blends

There were a total of 73 samples included in the study: 10 were single components (seven neat oxygenates and three diesel fuels) and 63 were oxygenate-diesel fuel blends at 5, 10, and 30 percent oxygenate by volume. All the oxygenate-diesel fuel blends were prepared gravimetrically; the required masses were calculated from the density values of the different components. Each blend was shaken well to promote mixing.

3 Miscibility

3.1 Background

Miscibility is the ability of two liquids to mix freely with one another. Substances that are miscible form a single phase, while those that are not miscible form two or more phases. (The presence of more than one phase is indicated by discontinuous changes in density, enthalpy, entropy and/or other physical properties as the transition between the two phases is traversed.) Miscibility is often a function of temperature; substances that are miscible at one temperature may not be miscible at a lower or higher temperature.

While a variety of physical properties may be used to indicate miscibility, generally the refractive index changes across the phase boundary. The result is that the existence of separate phases may simply be observed visually.

In order for an fuel-oxygenate blend to be commercially feasible, the fuel and oxygenate must be miscible.

3.2 Need for Miscibility Data

The available data on the miscibility of several oxygenates with diesel fuel were summarized in a recent report on motor fuel properties.[12] However, many of the sources cited in this report provide incomplete data or only anecdotal evidence. For the purposes of evaluating diesel fuel oxygenates, miscibility data are incomplete if the diesel fuel component of the mixture is not well-described, and/or if miscibility and solubility data are only available at one temperature. And, anecdotal comments, such as that a particular oxygenate showed "good solubility with diesel fuel," need quantification.

Data on low-temperature miscibility of oxygenate-diesel fuel blends are especially sparse, despite the importance of all-weather operation of motor vehicles in regions with cold climates.

3.3 Miscibility Test Procedures

For the miscibility tests, 150 mL samples of each oxygenate-diesel fuel blend were measured with a graduated cylinder and poured into a 240 mL jar and capped tightly. These jars were then placed into a bath maintained at temperatures of –30, -15, 0, 15, or 30 C. The bath temperature was monitored with a thermocouple readout. This readout was calibrated by a mercury thermometer for each target temperature. A batch of nine samples could be put in the bath at one time; for each batch the temperature in one of the samples was monitored with a small type K thermocouple to assure that the samples had reached the bath temperature.

Once the sample had reached the temperature of interest, it was removed from the bath briefly and visually studied for any changes in appearance. The color and clarity of the sample was recorded. The number and type of any phases present were also recorded, and the estimated size of each phase was noted.

For reference, each of the neat oxygenates and diesel fuels were subjected to the same procedure and miscibility observations were recorded for these as well.

3.4 Results of Miscibility Tests

3.4.1 Neat Oxygenates

All the neat oxygenates were liquids at all the test temperatures and, as expected, all showed only a single phase.

Table 3. Neat Oxygenate Results

Oxygenate	Test Temperatures, C	Results
DPE	-30, -15, 0, 15, 30	colorless (slightly hazy at –30) liquid
DBXM	-30, -15, 0, 15, 30	colorless liquid
EXEE	-30, -15, 0, 15, 30	colorless liquid
DEM	-30, -15, 0, 15, 30	colorless liquid
TPGE	-30, -15, 0, 15, 30	slightly yellow liquid
DBM	-30, -15, 0, 15, 30	colorless liquid
GTB	-30, -15, 0, 15, 30	colorless liquid

3.4.2 Diesel Fuels

The results of the diesel fuel tests are shown in Table 4. Although some of the samples solidified at low temperatures, there was no evidence of phase separation prior to solidification.

Table 4. Diesel Fuel Results

Diesel Fuel	Test Temperatures., C	Results
Oil sands	-30, -15, 0, 15, 30	Clear, golden color liquid
Ultra-low sulfur	-30	Yellow color solid
	-15, 0, 15, 30	Clear, golden color liquid
Fischer-Tropsch	-30, -15	White solid
	0, 15, 30	Colorless liquid

3.4.3 Diesel Fuel-Oxygenate Blends

Miscibility results for the fuel oxygenate blends are shown below. The legend is as follows:

Number and Appearance of Phases

🟢 – one phase, clear
▲ – one phase, hazy
🟩 – one phase, solid
🔴 – two phases, both clear
🔺 – two phases, one or both hazy
🟥 – two phases, solid

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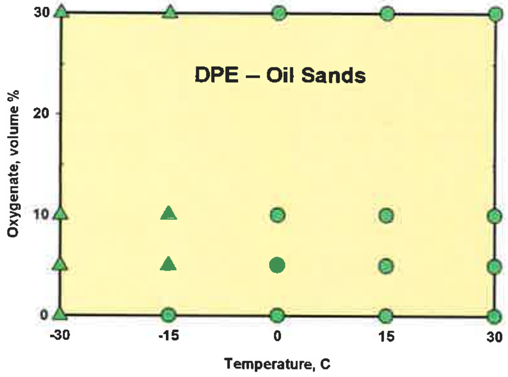
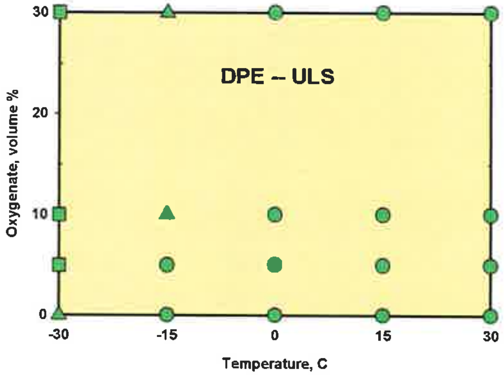
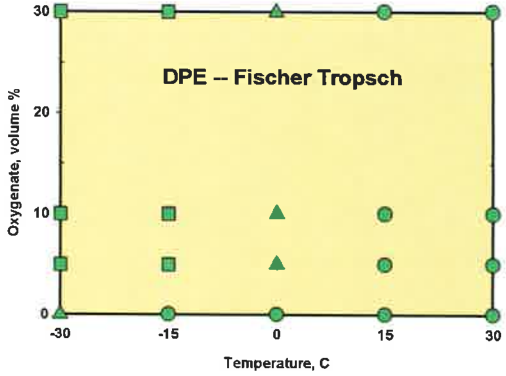
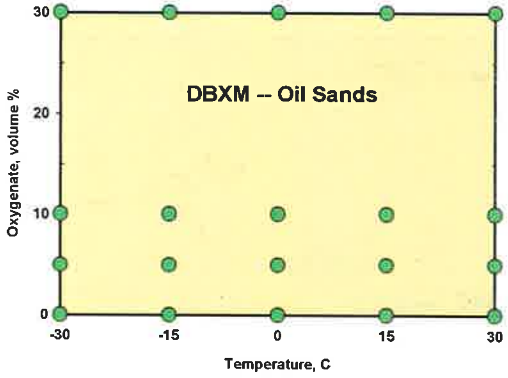
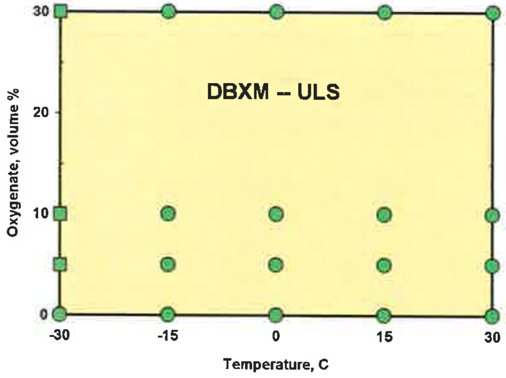
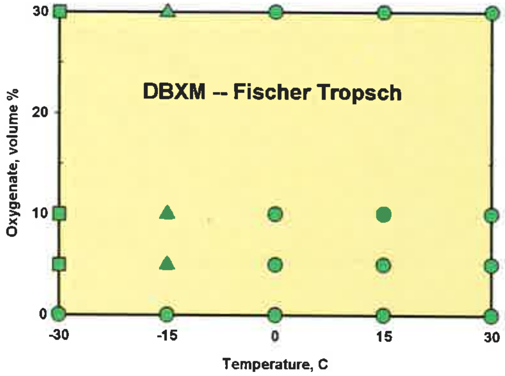

DPE – Oil Sands
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

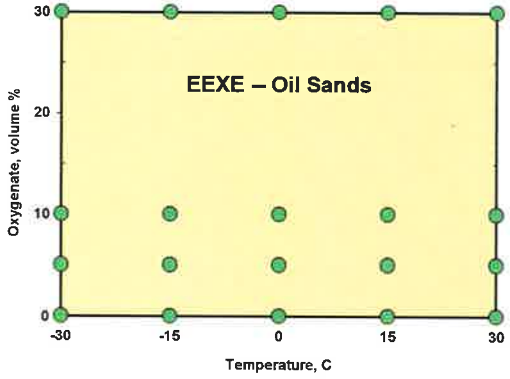

DPE -- ULS
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

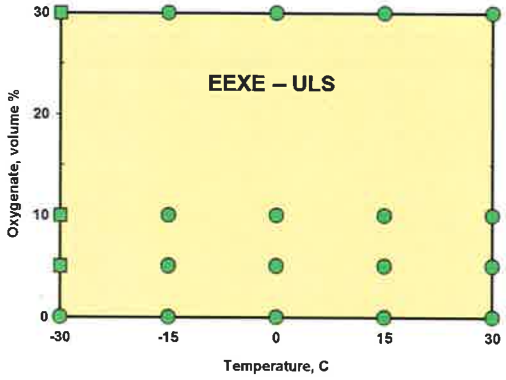

DPE -- Fischer Tropsch
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

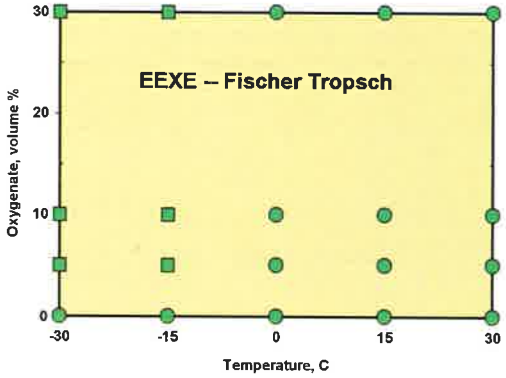

DBXM -- Oil Sands
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

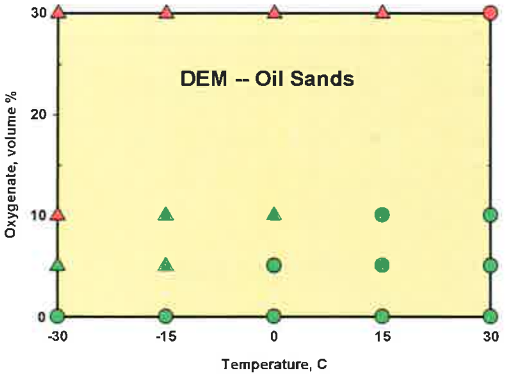

DBXM -- ULS
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

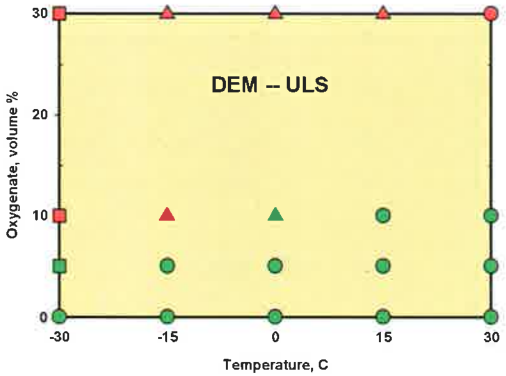

DBXM -- Fischer Tropsch
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

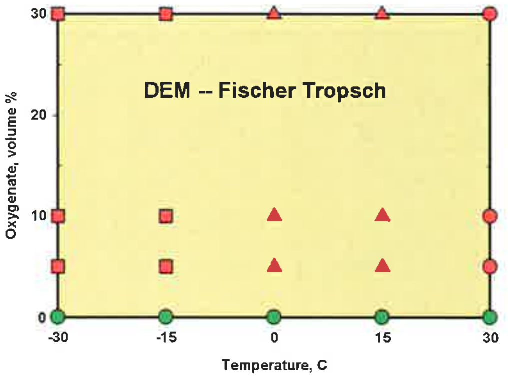

EEXE – Oil Sands
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

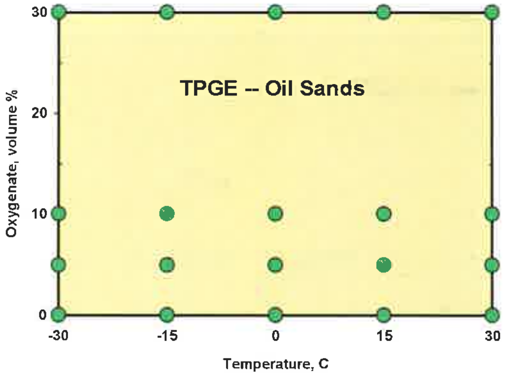

EEXE – ULS
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

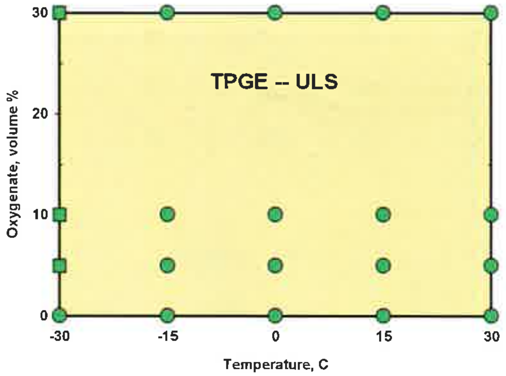

EEXE -- Fischer Tropsch
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

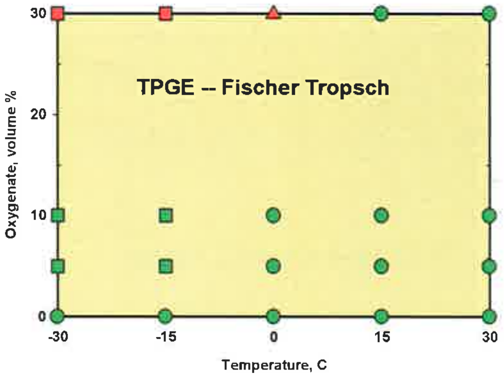

DEM -- Oil Sands
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

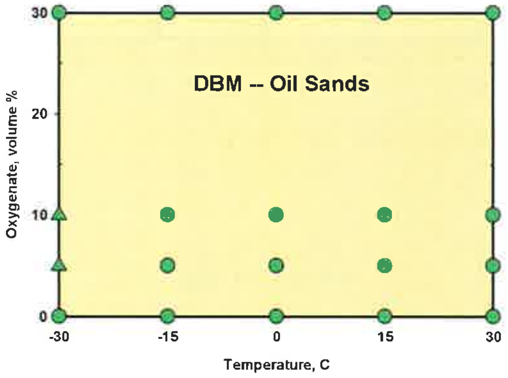

DEM -- ULS
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

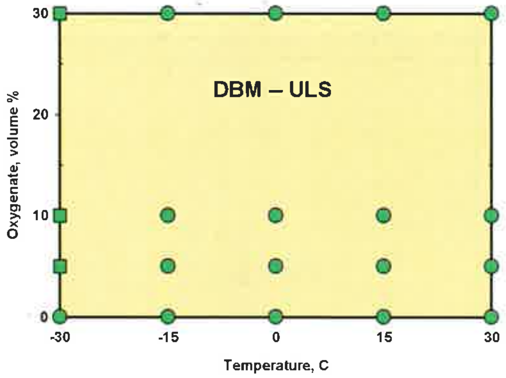

DEM -- Fischer Tropsch
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

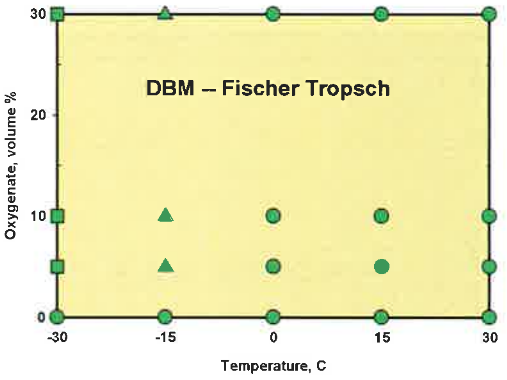

TPGE -- Oil Sands
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

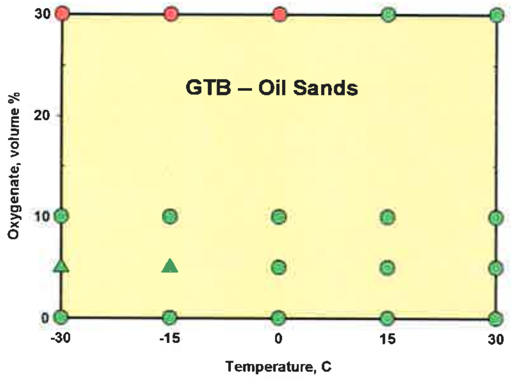

TPGE -- ULS
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

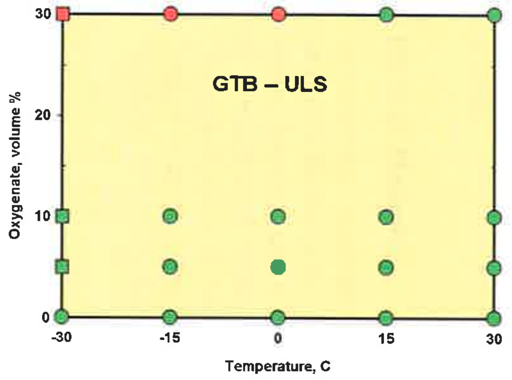

TPGE -- Fischer Tropsch
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C

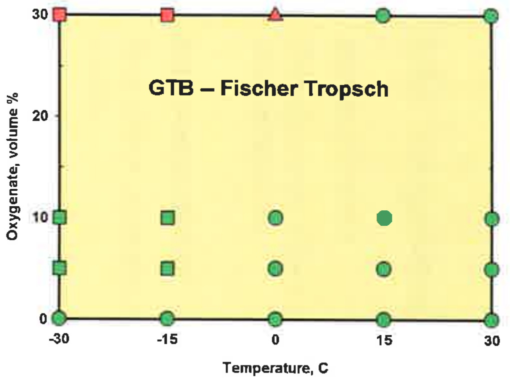

DBM -- Oil Sands
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C


DBM -- ULS
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C


DBM -- Fischer Tropsch
Oxygenate, volume %
30
20
10
0
-30
-15
0
15
30
Temperature, C







Legend for Miscibility Graphs

Number and Appearance of Phases

🟢 – one phase, clear
▲ – one phase, hazy
🟩 – one phase, solid
🔴 – two phases, both clear
🔺 – two phases, one or both hazy
🟥 – two phases, solid

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3.5 Discussion of Miscibility Results

3.5.1 Oxygenates

Dipentyl Ether

The dipentyl ether (DPE) showed good miscibility with all three diesel fuels at all temperatures.

Dibutoxymethane

The dibutoxymethane (DBXM) was miscible with all the diesel fuels at all blend levels.

2-Ethoxyethyl Ether

The 2-ethoxyethyl ether (EEXE) was miscible with all the diesel fuels at all blend levels.

Diethyl Maleate

The diethyl maleate (DEM) formed two layers with the oil sands diesel at the 30 percent blend level, with the ultra-low sulfur diesel at the 10 and 30 percent blend levels, and with the Fischer-Tropsch diesel at all blend levels. In the case of the diethyl maleate, the relatively short ethyl group apparently did not provide enough hydrocarbon properties to allow solubility in diesel fuel hydrocarbons. Figure 7 shows the appearance of a sample of 30 percent DEM in Oil Sands and Fischer-Tropsch diesel fuels.

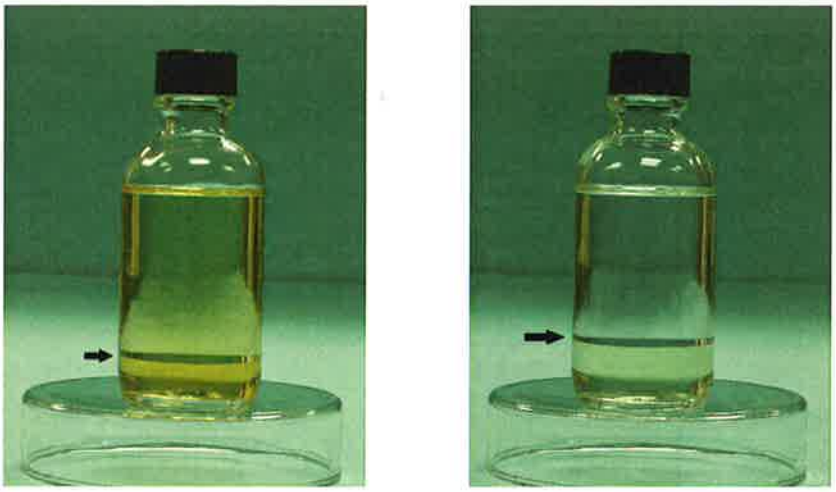

Figure 7. Appearance of Samples of 30 Volume Percent DEM Blended with Oil Sands and Fischer-Tropsch Diesels

Arrow indicates phase boundary.

Tripropylene Glycol Methyl Ether

The tripropylene glycol methyl ester (TPGE) was not fully miscible with the Fischer-Tropsch diesel fuel at the 30 percent concentration. At a temperature of 0 C the 30 percent blend formed two layers, the bottom layer was yellow and cloudy (this oxygenate had a yellowish cast), and the top layer was white and cloudy.

Portions of the TPGE molecule that are very electronegative[*] undoubtedly results in a difficulty in mixing with non-polar hydrocarbons.

Dibutyl Maleate

The dibutyl maleate (DBM) was miscible with all the diesel fuels at all blend levels.

Glycerol Tributrate

The glycerol tributrate was not miscible with any of the diesel fuels at the 30 percent blend level. Like TPGE, glycerol tributrate has portions of the molecule that are very electronegative.

3.5.2 Fuels

Of the three fuels, the Fischer Tropsch diesel showed the greatest tendency towards miscibility problems. This fuel is composed mainly of paraffins, which have low electronegativity. Fuels with more aromatic constituents had fewer miscibility problems; only the diethyl maleate formed two layers

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[*] Which also results in an unusually high de-shielding on an NMR spectrum.

4 Water Tolerance

4.1 Background

In handling fuels commercially, it is not possible to keep the fuel tanks entirely dry. Tanks of petroleum fuels, including diesel fuel frequently have "water bottoms," layers of water that lie at the bottom of a fuel storage tank, of varying extent. The water arises from condensation of humid air, influx of rain, or various other sources; it is found at the bottom because the water is more dense than the fuel. Because the water exists in a separate phase, the amount of such water can be controlled through housekeeping practices, such as selective removal of tank bottoms.

However, in the case of an oxygenate-diesel fuel blend, a situation may arise where exposure to water causes the formation of to form a second fuel phase. Typically this happen when an oxygenate-fuel blend absorbs enough water that a separate phase forms consisting of the oxygenate and water. The generally accepted explanation for this behavior is that water molecules are polar and can interact with the polar portion of the oxygenate to form a solution whose overall polarity has increased to the point that it is no longer miscible with the hydrocarbons in diesel fuel.

4.2 Need for Water Tolerance Data

Some water tolerance data are available as part of the "ad hoc" oxygenate study.[13] Data from this study indicated that tripropylene glycol monomethyl ether (TPGE) exhibited unacceptable water tolerance behavior.

4.3 Water Tolerance Test Procedures

The water tolerance test procedure consisted of additions of 0.2 and 1.0 percent by volume water to the various oxygenate-diesel fuel blends. The water tolerance test was performed at two temperatures: –30 C and 15 C.

After the addition of the measured volume of water, each sample was shaken, allowed to settle, and observed under a strong light.

4.4 Results of Water Tolerance Tests

The results of most of the water tolerance tests were unremarkable. In general, the added water simply remained as droplets of liquid water. However, in the case of the TPGE, the addition of a small amount of water caused a previously miscible oxygenate to form a separate phase. This occurred with all three diesel fuels. The results of these tests are shown graphically in Figure 8.

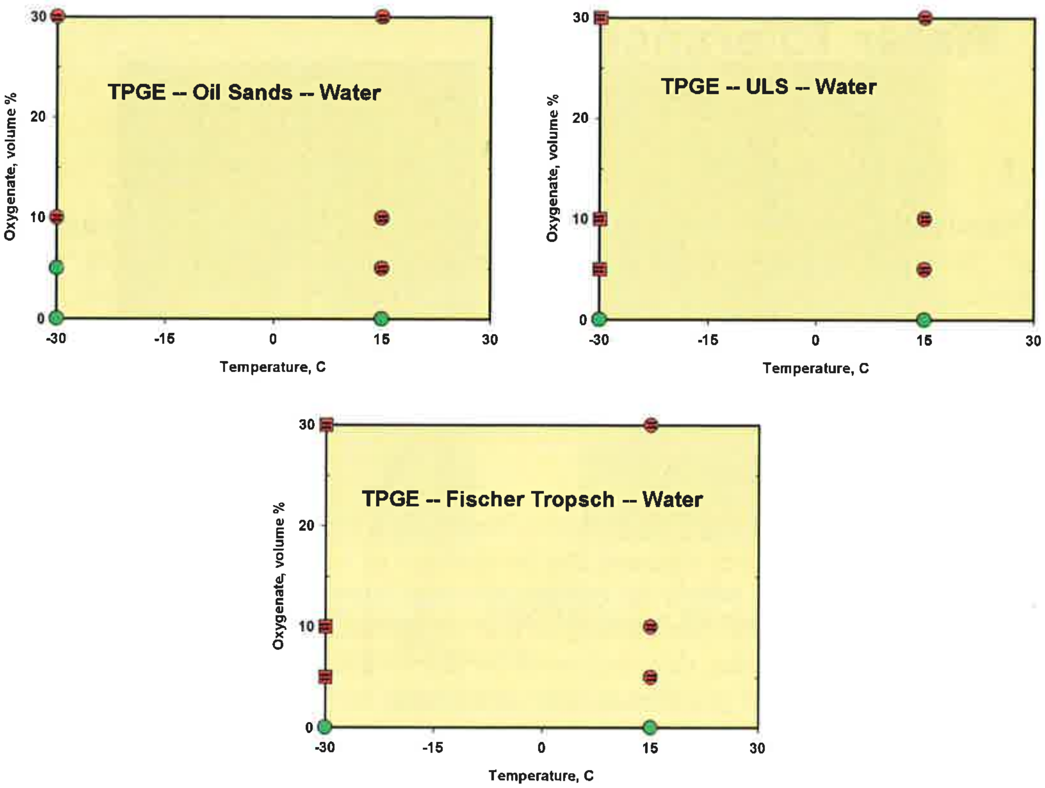
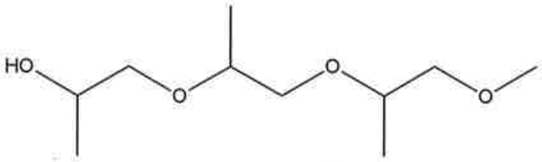


Figure 8. Water Tolerance Test Results for TPGE

4.5 Discussion of Water Tolerance Results

In order for water tolerance problems to occur, the oxygenate must dissolve enough water to make a mixture that is too polar to remain miscible with hydrocarbons. The TPGE structure,



has an – OH group that facilitates this water solubility.

5 Cloud Point

5.1 Background

The cloud point of a fuel is that temperature at which a fuel shows a cloud or haze when cooled. The cloud or haze is often stated to be composed wax crystals on the assumption that paraffinic components of the fuel will be the first to form solid crystals upon cooling. The cloud point is generally measured according to ASTM D 2500.

The cloud point is an important indicator of the ability of a diesel fuel to exhibit good cold weather operation without causing filter plugging or other operational problems.

5.2 Need for Cloud Point Data

Cloud point data are generally not available for the oxygenate-diesel fuel blends under study in this program.

5.3 Cloud Point Test Procedures

The cloud point test procedures were similar to those described in ASTM D 2500. The principal differences were the omission of the jacket and the use of a glass vessel of somewhat different dimensions.

5.4 Results of Cloud Point Tests

Cloud point results for the neat oxygenates are shown in Table 5. The cloud points of the diesel fuels are shown in Table 6. Results for the oxygenate-diesel fuel blends are shown in Table 7.

Table 5. Cloud Point Results for Neat Oxygenates

Oxygenate	Cloud Point, C
DPE	<-30
DBXM	<-30
EXEE	<-30
DEM	<-30
TPGE	<-30
DBM	<-30
GTB	<-30

Table 6. Cloud Point Results for Diesel Fuels

Diesel Fuel	Cloud Point, C
Oil sands diesel	<-30
Ultra-low sulfur	-18
Fischer-Tropsch	-2

Table 7. Cloud Point Results for Oxygenate-Diesel Fuel Blends

Oxygenate or Blend	Cloud Point, C						
	DPE	DBXM	EXEE	DEM	TPGE	DBM	GTB
Melting point [a]	-69	-58	-45	-9	-78	-69	-75
Neat oxygenate	<-30	<-30	<-30	<-30	<-30	<-30	<-30
5% in OS diesel	-10	<-30	<-30	-12	<-30	-25	-24
10% in OS diesel	-12	-30	<-30	7	<-30	-27	<-30
30% in OS diesel	-5	<-30	<-30	22	<-30	<-30	<-30
5% in ULS diesel	-18	-18	-18	-17	-16	-19	-16
10% in ULS diesel	-18	-20	-18	6	-16	-18	-16
30% in ULS diesel	-28	-27	-20	19	-16	-17	-16
5% in F-T diesel	-5	-3	-1	22	-2	-1	-1
10% in F-T diesel	-10	-3	-1	19	-1	0	-1
30% in F-T diesel	-30	-4	3	19	5	-1	2

[a] Melting points are literature values included for reference.

5.5 Discussion of Cloud Point Results

Accuracy Note

According to the ASTM D 2500 method upon which the cloud point determination was modeled, the repeatability of the method is ± 2 C, and the reproducibility of the method is ± 4 C. Thus, the caution should be exercised in the interpretation of differences in cloud point temperature.

Dipentyl Ether

The presence of the dipentyl ether helped lower the could point of the Fischer-Tropsch diesel, but raised the cloud point of oil sands diesel. It left the ULS diesel cloud point largely unchanged at the 5 and 10 percent blend levels, but reduced the cloud point by 10 C at the 30 percent blend level.

Dibutoxymethane

The dibutoxymethane appeared to lower the cloud point of the ULS diesel and perhaps lowered the cloud point of the Fischer Tropsch diesel slightly. DBXM raised the cloud point of the oil sands diesel.

2-Ethoxyethyl Ether

The 2-ethoxyethyl ether did not make a significant change in the cloud point of any of the diesel fuels.

Diethyl Maleate

Although the literature value of the melting point of diethyl maleate is listed at –8 to –10 C, no cloud was observed to –30 C in these tests. The diethyl maleate used in these tests was a commercial grade of 97 percent purity. Apparently the listed melting point can only be obtained with a higher purity level. Inasmuch as any commercial use in fuels would be with a commercial grade, this melting point discrepancy was not deemed to be serious.

The presence of the diethyl maleate raised the cloud points of the all three diesel fuels substantially, with the exception of the 5 percent blend with the ULS diesel.

Tripropylene Glycol Methyl Ether

The addition of the tripropylene glycol methyl ether left the cloud points of the diesel fuels basically unchanged, although the 7 C rise in cloud point for the 30 percent blend with Fischer Tropsch diesel is probably significant.

Dibutyl Maleate

The dibutyl maleate had little effect on the cloud points of any of the diesel fuels.

Glycerol Tributrate

The presence of the glycerol tributrate did not make a significant change in the cloud point of any of the diesel fuels.

6 Flash Point

6.1 Background

The flash point of a fuel is the temperature at which sufficient quantity of vapor is present over the surface of the liquid to allow the propagation of a flame. The flash point is mainly a measure of the volatility of the fuel, particularly of the more volatile components.

6.2 Need for Flash Point Data

Fire safety authorities in many jurisdictions regulate fuels and other potentially flammable substances according to their flash points. The ASTM D 975 Standard Specification for Diesel Fuel Oils requires that No. 2 diesel fuel have a minimum flash point of 52 C and that No. 1 diesel fuel have a minimum flash point of 38 C. In the U.S. the National Fire Protection Association (NFPA) classifies diesel fuel as a combustible, rather than a flammable, liquid because its flash point is greater than 38 C. Lower flash points would require more stringent (and more expensive) fire protection measures, such as explosion-proof electrical wiring.

6.3 Flash Point Test Procedures

Flash point determinations were made by a commercial testing laboratory using the ASTM D 93 procedure. Flash point determinations were made on the each of the seven oxygenates and three diesel fuels, and on 58 of the 63 oxygenate-diesel fuel blends. Five blends consisted of two phases at room temperature and these samples were eliminated from the flash point tests. The reproducibility of the ASTM D 93 test is from 3 to 8 C over the range of flash points covered in this study. Thus, smaller differences in flash point values may not be significant.

6.4 Results of Flash Point Tests

Results of the flash point tests are shown in Table 8 and Table 9.

Table 8. Results of Flash Point Tests for Base Fuels

Diesel Fuel	Flash Point, C
Oil sands	48
Ultra-low sulfur	68
Fischer Tropsch	93

Table 9. Results of Flash Point Tests on Oxygenates and Blends

Oxygenate or Blend	Flash Point, C						
	DPE	DBXM	EXEE	DEM	TPGE	DBM	GTB
Neat oxygenate	58	62	58	98	110	110	95
5% in OS diesel	48	49	47	49	51	49	44
10% in OS diesel	47	49	48	49	49	48	46
30% in OS diesel	51	48	47	*	52	51	51
5% in ULS diesel	67	66	66	69	69	69	68
10% in ULS diesel	67	65	64	71	71	67	67
30% in ULS diesel	63	64	61	*	75	71	67
5% in F-T diesel	78	85	84	*	94	94	86
10% in F-T diesel	82	81	78	*	89	91	91
30% in F-T diesel	76	71	65	*	95	90	87

* Indicates that no flash point data were taken because two phases were present

6.5 Discussion of Flash Point Results

Notes on Diesel Fuels

The oil sands diesel had a flash point of 48 C. Although this is slightly less than the 52 C minimum in the ASTM D 975 Standard Specification for Diesel Fuel Oils, according to the same specification, a flash point as low as 38 C would be acceptable for a winter grade fuel.

The ultra-low sulfur diesel had a flash point that was within the range commonly seen for diesel fuels.

The Fischer-Tropsch diesel had an unusually high flash point for a diesel fuel.

Dipentyl Ether

For the oil sands diesel the lower flash point of the fuel dominated. For the ultra-low sulfur diesel the flash point is noticeably lowered only by 30 percent oxygenate. For the Fischer-Tropsch diesel, which has a flash point 35 C higher than the oxygenate, there is significant lowering of the fuel flash point.

Dibutoxymethane

For the oil sands diesel and the ultra-low sulfur diesel the lower flash point of the fuel dominated. For the Fischer-Tropsch diesel, the flash point of the oxygenate was 31 C lower than the flash point of the fuel and the flash point of the blend decreased significantly as the proportion of oxygenate increased.

2-Ethoxyethyl Ether

For the oil sands diesel the lower flash point of the fuel dominated. For the ultra-low sulfur diesel, there was a slight lowering of the flash point, and for the

Fischer-Tropsch diesel, where the oxygenate flash point was 35 C lower than the flash point, the flash point of the blend decreased significantly as the proportion of oxygenate increased.

Diethyl Maleate

Diethyl maleate was not miscible with diesel fuel over the full range of blends studies. For the lower percentage blends where miscibility was not an issue, the flash point of the fuel was not significantly changed by the presence of the oxygenate.

Tripropylene Glycol Methyl Ether

For the oil sands diesel, the lower flash point of the fuel dominated. This was also true for the ultra-low sulfur diesel. For the Fischer-Tropsch diesel, the fuel flash point was not significantly changed by the presence of the oxygenate.

Dibutyl Maleate

For blends with dibutyl maleate, the flash points of all three fuels were not significantly changed by the presence of the oxygenate.

Glycerol Tributrate

In the case of the glycerol tributrate, the flash point of all three fuels was essentially unchanged by the oxygenate.

7 Vapor Pressure

7.1 Background

The vapor pressure is the pressure exerted by the vapors of a volatile substance. Vapor pressure data on oxygenate-diesel fuel blends are key to several issues:

- Assessing the flammability of vapor spaces in tanks with oxygenate-fuel blends in a more basic way than is possible from flash point tests.
- Assessing the extent and composition of evaporative emissions from oxygenate-fuel blends.
- Obtaining insight into the strength of fuel odors.
- Understanding the chemical behavior of oxygenate-diesel fuel blends and the extent to which the various oxygenates mix in an ideal or non-ideal manner with diesel fuel hydrocarbons.

Vapor pressure data for the range of temperatures to motor vehicles may be exposed are of interest. And, of course, similar vapor pressure data on the neat oxygenates and fuels are necessary for comparison.

7.2 Need for Vapor Pressure Data

Volatility, as measured by vapor pressure data, is a fundamental property of organic liquids. Volatility is important for droplet vaporization and fire hazard prediction. Vapor pressure data are also important for the estimation of evaporative and refueling emissions.

Literature vapor pressure data were found for some of the oxygenates under study in this Annex. In some cases these data were presented in the form of Antoine Equation parameters; in other cases the data were in the form of temperatures at which benchmark vapor pressures, such as 10 or 100 Pa were achieved. For three of the oxygenates, no vapor pressure data were located, but data on the heat of vaporization were available. These data could be used in conjunction with the normal boiling point and the Clausius-Clapeyron equation to estimate vapor pressures. All these data are summarized in Table 10.

No literature data were found for the vapor pressures of any of the oxygenate-diesel fuel blends.

Table 10. Available Literature Data on Neat Oxygenates

No.	Oxygenate	Antoine Equation Parameters	T, C for vp = 10, 100 Pa	vp at 15 C, Pa
DPE	Dipentyl ether	A = 3.87244 B = 1396.465 C = -98.829 (14)	-8, 22 (15)	
DBXM	dibutoxymethane (butylal)	ΔHvap = 57.3 kJ/mol (16)		
EXEE	2-Ethoxyethyl ether (diethylene glycol diethyl ether)	ΔHvap = 58.40 kJ/mol (17)	-7, 25 (18)	
DEM	diethyl maleate	A = 5.04064 B = 2324.474 C = -36.819 (19)	20, 52.2 (20)	
TPGE	Triproplylene glycol methyl ether			
DBM	Dibutyl maleate		50.4, 94.0 (21)	
GTB	Glycerol tributrate (tributyrin)	ΔHvap = 107.1 kJ/mol (22)|		

References in parentheses. Blank cell indicates that no literature data were found.

7.3 Vapor Pressure Test Procedures

A gas chromatographic technique was used to determine the vapor pressures. This technique not only allowed the accurate determination of the vapor pressures of diesel fuels, oxygenates and blends, but also provided insights into the relative contributions of the fuel hydrocarbons and the oxygenate to the total vapor pressure. The gas chromatographic method also identified any effects from impurities in the commercial-grade oxygenates used. The overall procedure was modeled somewhat after the procedure used by Mackle, et al.[23] to determine relative vapor pressures and heats of vaporization.

7.3.1 Sample Preparation Procedure

The sample preparation procedure was as follows.

A sample of the oxygenate, diesel fuel, or blend was placed in a 50-mL capacity glass vessel that could be connected through a valve to a vacuum line and had a septum for withdrawing a sample from the vapor space with a syringe. This vessel is shown in Figure 9. The sample was frozen in liquid nitrogen, as shown in Figure 10 and the vessel evacuated through the vacuum line. The vacuum line was closed and the sample was warmed. The sample was then frozen and evacuated again. The two successive evacuations were intended to remove air and/or volatile impurities from the liquid and from the space above the liquid.

02-008

Figure 9. Glass Vessel for Vapor Pressure Determinations

02-016

Figure 10. Cooling and Evacuation Procedure

After these evacuations, the sample was allowed to warm and equilibrate at –30, -15, 0, 15, or 30 C. A gas-phase sample was then withdrawn with a gas-tight syringe. This sample was then analyzed using gas chromatography.

7.3.2 Gas Chromatographic Analysis Procedure

A Varian 3400 gas chromatograph was used for all analyses. The GC system incorporated a liquid injection port with septum and a splitter. The splitter was active, set constant at all times. A J&W Scientific capillary column was used. The column was 60 meters long and had an inside diameter of 0.32 mm; the stationary phase was a 0.1 μm film of dimethylpolysiloxane.

Hydrocarbon Calibration

Three standard blends were used to correlate peak area with the concentration of hydrocarbons in ppm carbon. One blend was a 24-component gas-phase standard that contained normal alkanes, iso-alkanes, alkenes, and aromatics ranging in molecular mass from methane to n-dodecane. This standard was certified and was directly traceable to a standard reference material.* The analytical uncertainty in the concentration of each component at the 95 percent confidence level for this standard was stated by the manufacturer† to be less than 5 percent. Considerable experience has shown this standard to be consistent and reliable.

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* Standard reference material SRM 1665b with 2.97 ppm of propane in air.

† Scott Specialty Gases

The second standard blend was similar, but contained only methane, ethane, propane, butane, pentane, and hexane.

The third standard blend was a liquid standard[*] that contained the following diesel-range hydrocarbons: decane, dodecane, tetradecane, hexadecane, octadecane, eicosane, docosane, tetracosane, hexacosane, and octacosane.

Peak area data from all these standards were combined to obtain calibration coefficients for number of peak area units per ppm of carbon for an injection of 10 µL of gas-phase sample. The calibration was found to be consistent for all three standards.

Oxygenate Calibration

First, an oxygenate standard solution in hexane was prepared for each oxygenate. The initial dilution contained 100 µL of oxygenate in 50 mL of hexane. Successive dilutions of 10:1 and 5:1 were used to reduce the oxygenate concentration further for the oxygenate standard solution. The density of each component was used to calculate the mass of each component in the diluted solutions and then to calculate the mass of oxygenate in a 10 µL sample of oxygenate standard solution injected into the GC.

Analysis of Vapor Samples

A 10 µL gas-tight syringe was used to take a sample of vapor from the glass vessel containing the oxygenate-diesel fuel blend (or neat oxygenate or neat diesel fuel). This sample was then injected in to the GC. All the peaks[†] on the resulting chromatogram were assigned as being either oxygenate or hydrocarbon. The previously determined calibrations were used to calculate the ppm carbon in the sample from both oxygenate and hydrocarbon vapor. The gas chromatograms showed that most of the samples had small amounts of dissolved C1 through C4 hydrocarbons. However, these small amounts had no significant effect on the aggregate hydrocarbon partial pressure. Figure 11 shows an example of a gas chromatogram for one of the oxygenate-diesel fuel blends.

From the molecular weight of the oxygenate and the average molecular weight of the hydrocarbon vapor, the ideal gas law could be used to calculate partial pressures of each. (The average molecular weight of the hydrocarbon vapor was determined from a weighted average of the hydrocarbon peaks on the chromatogram and their respective carbon numbers as estimated from their retention times.)

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[*] Manufactured by Cerilliant.

[†] Most chromatographs also had a peak from remnants of methylene chloride solvent used to clean the glass vessel and the syringe. This peak was ignored.

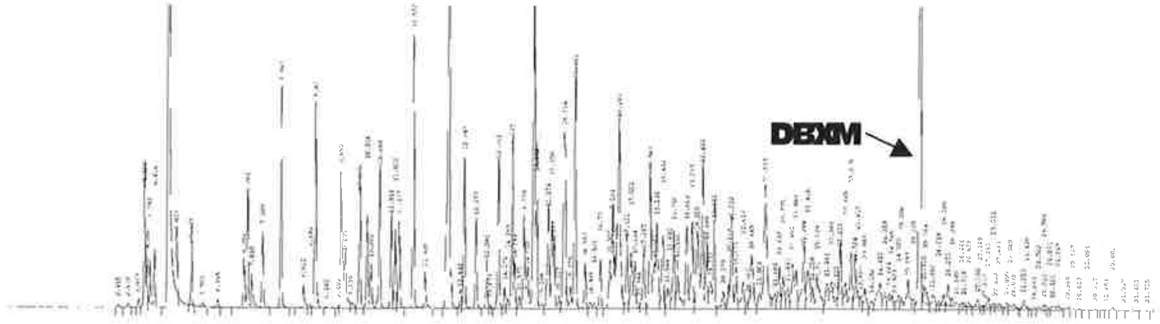


Figure 11. Gas Chromatogram for 30 Volume Percent Dibutoxymethane (DBXM) in Oil Sands Diesel at 15 C

Data Reduction

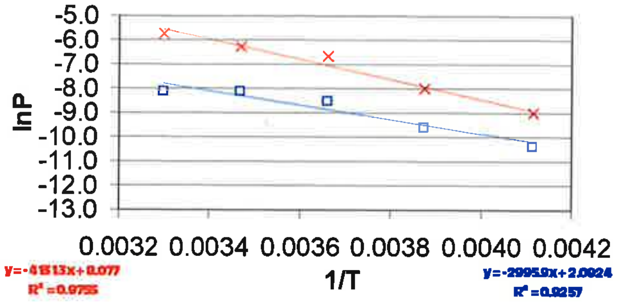
For each oxygenate, oxygenate blend, and diesel fuel, the results of the vapor pressure tests at –30, -15, 0, 15, and 30 C were plotted as ln P versus 1/T, as suggested by the Clausius-Clapeyron equation, which is in integrated form

$$\ln(P) := \frac{\Delta H_{vap}}{R \cdot T} + C$$

where
P = vapor pressure
ΔHvap = heat of vaporizatior
R = ideal gas constant
T = temperature
C = constant

For each sample, separate fitted plots were obtained for the oxygenate vapor pressure and for the fuel hydrocarbon vapor pressure. Figure 12 shows an example of these plots.

Heats of vaporization were obtained from the slope of these plots, and this heat of vaporization was used in conjunction with the Clausius-Clapeyron equation to provide best estimates vapor pressures at a given temperature. (A temperature of 20 C was chosen for data presentation.) The total vapor pressure was the sum of the partial pressures of hydrocarbon and oxygenate.



Legend: red = hydrocarbon, blue = oxygenate

Figure 12. Example of Use of the Clausius-Clapeyron Equation for Fitting Vapor Pressure Data for 30 percent Dibutoxymethane in Oil Sands Diesel Fuel

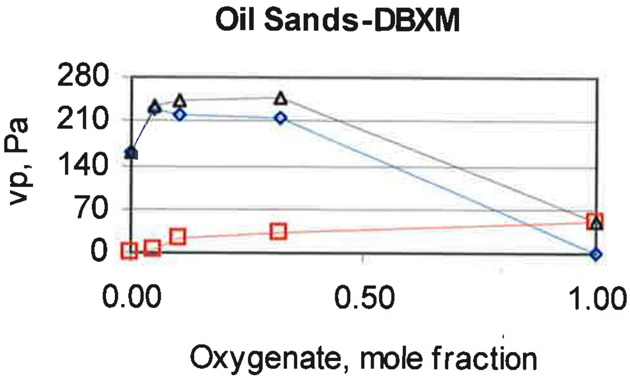


Figure 13. Vapor Pressure Diagram for 30 Volume Percent Dibutoxymethane in Oil Sands Diesel at 20 C

Legend: red – oxygenate, blue – hydrocarbon, black – total

7.4 Results of Vapor Pressure Tests

The results of the vapor pressure tests are summarized in tabular form in Table 11. All data are for 20 C.

Table 11. Vapor Pressure Results

Fuel-Oxygenate Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Oil Sands	0	0.00	0	161	161
	5	0.05	12	269	282
	10	0.10	11	213	224
	30	0.30	17	143	159
DPE	100	1.00	68	0	68

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
ULS	0	0.00	0	96	96
	5	0.06	7	70	77
	10	0.12	7	60	68
	30	0.34	24	61	86
DPE	100	1.00	68	0	68

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Fischer-Tropsch	0	0.00	0	11	11
	5	0.07	6	49	55
	10	0.13	12	19	31
	30	0.38	25	29	53
DPE	100	1.00	68	0	68

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Oil Sands	0	0.00	0	161	161
	5	0.05	7	229	236
	10	0.11	24	220	244
	30	0.32	30	217	247
DBXM	100	1.00	49	0	49

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
ULS	0	0.00	0	96	96
|	5	0.06	7	55	62
|	10	0.13	9	49	58
|	30	0.36	7	47	54
DBXM	100	1.00	49	0	49

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Fischer-Tropsch	0	0.00	0	11	11
|	5	0.07	10	19	28
|	10	0.14	19	13	32
|	30	0.39	33	20	53
DBXM	100	1.00	49	0	49

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Oil Sands	0	0.00	0	161	161
|	5	0.06	7	191	198
|	10	0.11	7	207	214
|	30	0.33	12	191	203
EXEE	100	1.00	22	0	22

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
ULS	0	0.00	0	96	96
|	5	0.07	10	120	130
|	10	0.14	8	95	104
|	30	0.37	19	127	146
EXEE	100	1.00	22	0	22

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Fischer-Tropsch	0	0.00	0	11	11
|	5	0.08	7	23	29
|	10	0.15	9	35	44
|	30	0.41	22	80	102
EXEE	100	1.00	22	0	22

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Oil Sands	0	0.00	0	161	161
|	5	0.05	0	188	188
|	10	0.10	1	194	195
|	30	0.29	0	168	168
TPGE	100	1.00	1	0	1

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
ULS	0	0.00	0	96	96
|	5	0.06	1	76	77
|	10	0.11	0	62	62
|	30	0.33	0	40	40
TPGE	100	1.00	1	0	1

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Fischer-Tropsch	0	0.00	0	11	11
|	5	0.08	0	16	16
|	10	0.13	0	25	26
|	30	0.36	1	13	14
TPGE	100	1.00	1	0	1

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Oil Sands	0	0.00	0	161	161
|	5	0.05	0	131	132
|	10	0.09	1	223	224
|	30	0.28	0	143	143
DBM	100	1.00	1	0	1

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
ULS	0	0.00	0	96	96
|	5	0.05	1	83	83
|	10	0.11	1	92	93
|	30	0.31	0	40	41
DBM	100	1.00	1	0	1

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Fischer-Tropsch	0	0.00	0	11	11
|	5	0.06	0	14	14
|	10	0.12	0	22	22
|	30	0.35	1	29	30
DBM	100	1.00	1	0	1

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Oil Sands	0	0.00	0	161	161
|	5	0.04	1	249	249
|	10	0.07	0	174	175
|	30	0.23	0	164	165
GTB	100	1.00	0	0	0

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
ULS	0	0.00	0	96	96
|	5	0.04	0	74	75
|	10	0.09	0	63	63
|	30	0.26	0	106	107
GTB	100	1.00	0	0	0

Blend	Oxygenate, vol. %	Oxygenate, mole fraction	Oxygenate vp, Pa	Diesel vp, Pa	Total vp, Pa
Fischer-Tropsch	0	0.00	0	11	11
|	5	0.05	0	45	45
|	10	0.10	1	29	30
|	30	0.29	2	85	88
GTB	100	1.00	0	0	0

7.4.1 Comparison with Raoult's Law

According to Raoult's Law, the vapor pressure of each component of an ideal solution is equal to the mole fraction of that component in the liquid solution. In order to compare the results of the vapor pressure measurements to those predicted by Raoult's Law, the blend concentrations were converted from volume percent to mole fraction.

For this conversion, it was necessary to know the molecular weights of the oxygenates and the diesel fuels. The molecular weights of the oxygenates could be computed simply from the chemical formulae. The average molecular weight of each of the three diesel fuels was determined using the method of Riazzi as described in reference [24]. This method consists of the following correlation, which is reported to be accurate to within 5 percent:

$$MW := 42.695\left(\exp\left(2.097\cdot 10^{-4}\cdot T_{50} - 7.78712\,SG + 2.08476\cdot 10^{-3}\cdot T_{50}\cdot SG\right)\right)\cdot\left(T_{50}^{\,1.26007}\cdot SG^{4.98308}\right)$$

where MW = average molecular weight
T50 = mid-boiling temperature, K
SG = specific gravity

Classic vapor pressure versus composition plots for the oxygenate–diesel fuel blends are shown in Figure 14. All data are for 20 C.

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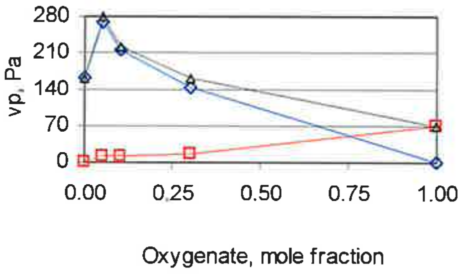
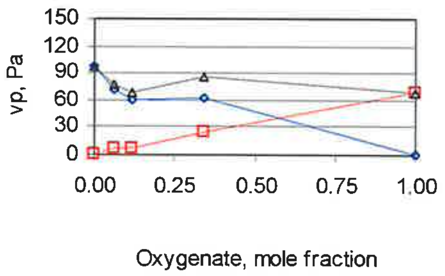
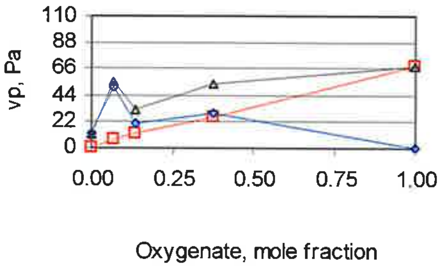


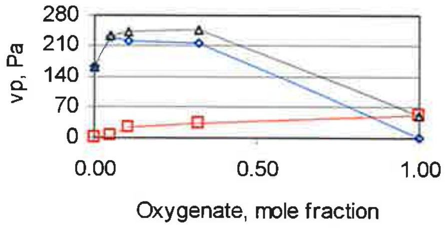
Oil Sands-DPE



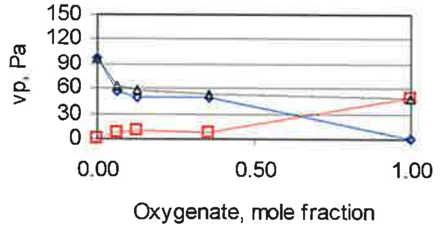
ULS-DPE



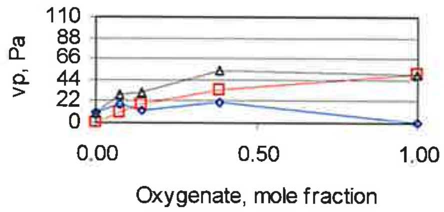
FT-DPE



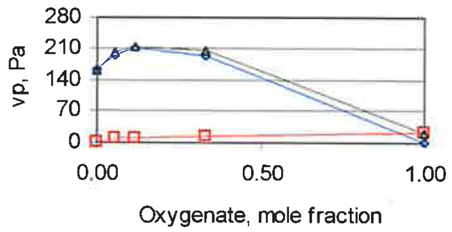
Oil Sands-DBXM



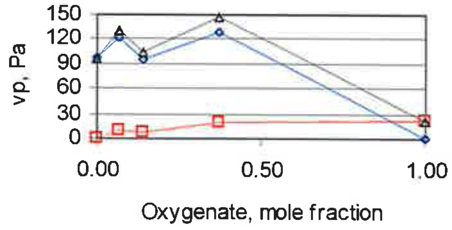
ULS-DBXM



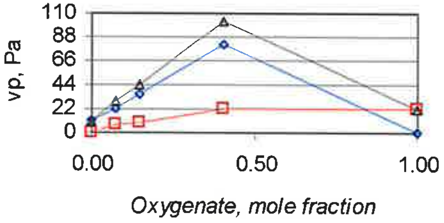
FT-DBXM



Oil Sands-EXEE



ULS-EXEE



FT-EXEE

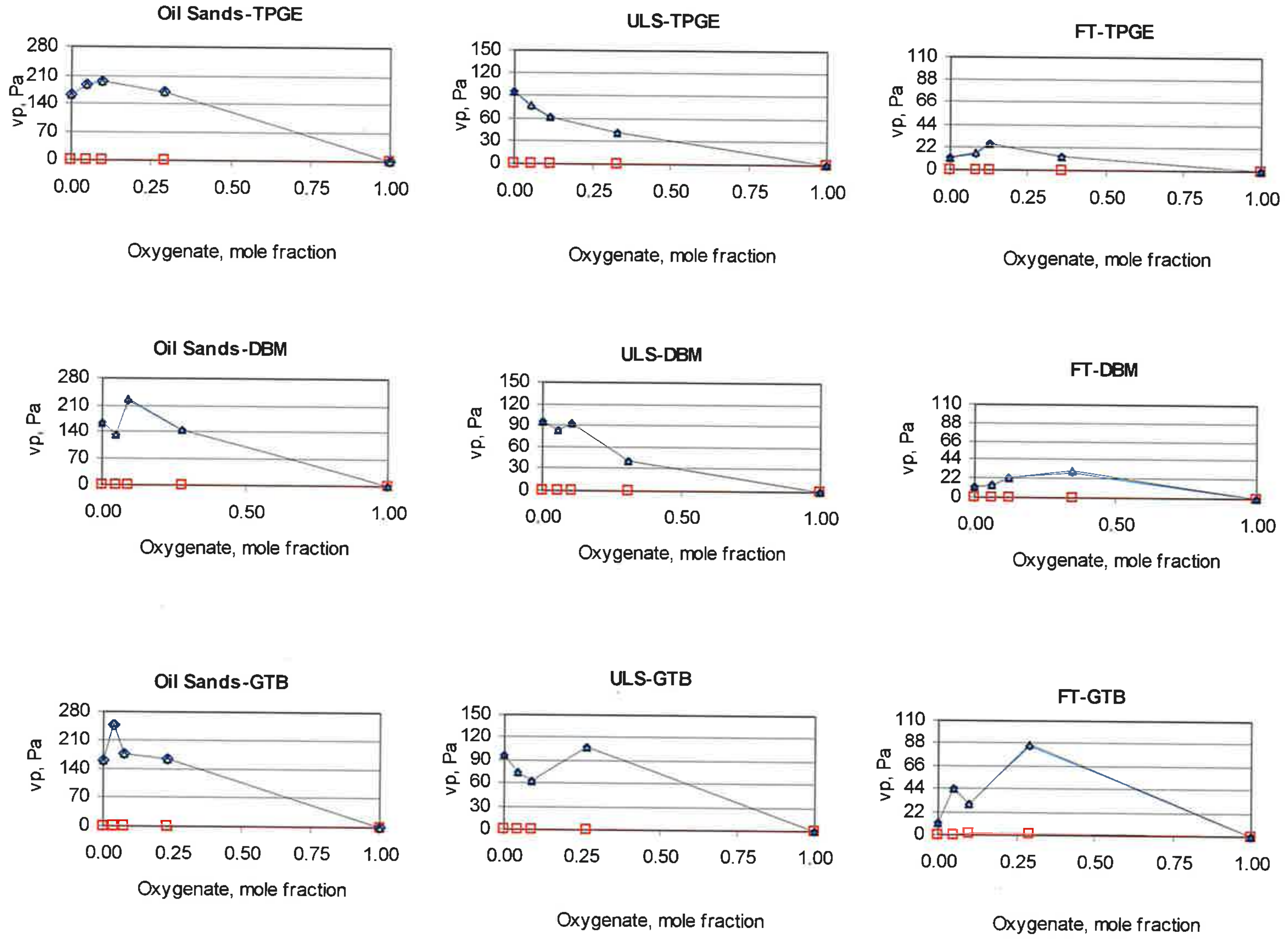


Figure 14. Vapor Pressure versus Composition Plots for Oxygenate - Diesel Fuel Blends

Legend: red = vp of oxygenate component, blue = vp of hydrocarbon component, black = total vapor pressure

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7.5 Discussion of Vapor Pressure Results

7.5.1 General Discussion

The oxygenate-diesel fuel system is a complex one, unlike the simple two- or three component systems generally discussed in physical chemistry texts. There are hundreds of diesel fuel components that vary in chemical structure and differ widely in volatility. The oxygenates included in this study were specifically chosen to represent a variety of chemical structures. Thus, it is not surprising that the vapor pressure results exhibit a variety of behaviors.

In many cases the highest vapor pressure was observed with the 5 volume percent blend. A literature example of similar, though less pronounced, behavior may be seen in Figure 15, where the highest total vapor pressure, indicated by a colored symbol, is observed at blend level of about 5 percent.

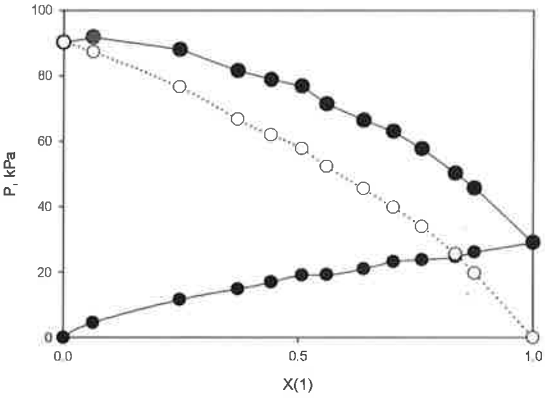

Figure 15. Vapor Pressure of Diethyl ketone – n-Hexane System[25]

7.5.2 Discussion of Individual Oxygenates

Dipentyl Ether

Blends of this oxygenate with the oil sands diesel had the highest vapor pressure of all the blends studied – a peak of 280 Pa at 20 C. For comparison, the vapor pressure of nonane at 20 C is 340 Pa and that of decane is 94 C. The oil sands diesel and the Fischer-Tropsch diesels tended to produce a non-ideal response. The oxygenate was a significant contributor to the total vapor pressure.

Dibutoxymethane

Particularly for the Fischer-Tropsch diesel, the oxygenate was a significant contributor to the total vapor pressure.

2-Ethoxyethyl Ether

With all three fuels, the 30 percent solution produced a maximum in total vapor pressure.

Tripropylene Glycol Methyl Ether

With this oxygenate, the vapor pressure contribution of the oxygenate is negligible. However the presence of the oxygenate influences the vapor pressure of hydrocarbons, as shown by the dependence of the vapor pressure on the amount of oxygenate.

Dibutyl Maleate

Likewise for the dibutyl maleate, the vapor pressure contribution of the oxygenate is negligible. However the presence of the oxygenate influences the vapor pressure of hydrocarbons, as shown by the dependence of the vapor pressure on the amount of oxygenate. The 10 percent blend produces the maximum total pressure with the oil sands and the ULS fuels.

Glycerol Tributrate

Similar comments hold for the glycerol tributrate, which is the least volatile of the oxygenates tested: the vapor pressure contribution of the oxygenate is negligible, but the presence of the oxygenate influences the vapor pressure of hydrocarbons.

8 Ignition Quality

8.1 Background

One of the most basic qualities of a fuel for compression ignition engines is that it must ignite through compression. Generally, the cetane number is taken as a measure of the ignition quality of fuels for compression ignition engines.

8.2 Need for Ignition Quality Data

Ignition quality data for these diesel fuel oxygenates are sparse. Available data are summarized in Table 12.

Although some oxygenates have been reported to have high cetane numbers, the data are not consistent. Moreover cetane numbers of blend components often combine in non-linear fashion. Thus, actual data are needed to assess the ignition quality of various oxygenates and blends.

Table 12. Literature Data for Ignition Quality of Diesel Fuel Oxygenates

Oxygenate	Cetane Number and Ref.
DPE	111-130[26]
DBXM	>74[27]
EXEE	113-136[28]
DEM	
TPGE	
DBM	
GTB	

Blank indicates that no literature data were found on ignition quality of this oxygenate

8.3 Ignition Quality Test Procedures

This screening study made use of the ignition quality test (IQT). This test is based on a heated, constant volume combustion chamber into which a single injection of the fuel sample is made. The time delay between the beginning of the injector needle lift and the combustion pressure recovery point* is taken as a measure of ignition delay for that fuel.

Early development of the technique occurred at Southwest Research Institute.[29,30,31] The method was been further developed by Advanced Engine

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* Initially the pressure decreases due to cooling from the evaporation of the fuel. As combustion begins, the pressure rises; the time at which the pressure has risen to equal the initial pressure is termed the combustion pressure recovery point.

Technology, Ltd. [32,33] Recently, work at Advanced Engine Technology Ltd. has proceeded on refining, validating, and commercializing this technique, [34] and on gaining approval as an ASTM standard method.[35]

8.4 Ignition Quality Test Results

The results of the ignition quality tests are summarized in Table 13 and Table 14.

Table 13. Ignition Quality Test Results for Diesel Fuels

Diesel Fuel	IQT Cetane Number
Oil sands diesel	41.4
Ultra-low sulfur diesel	44.5
Fischer-Tropsch diesel	79.5

Table 14. Ignition Quality Test Results for Oxygenates and Oxygenate-Diesel Fuel Blends

Oxygenate or Oxygenate-Diesel Fuel Blend	IQT Cetane Number					
	DPE	DBXM	EXEE	TPGE	DBM	GTB
Neat oxygenate	344	86.6	>1000	74.5	26.5	6.7
5% in oil sands diesel	43.6	42.5	44.7	42.1	41.8	40.1
10% in oil sands diesel	45.9	44.3	49.1	42.7	40.8	38.6
30% in oil sands diesel	59.3	48.7	73.4	46.6	38.0	32.8
5% in ULS diesel	48.1	45.5	47.8	45.1	44.4	42.8
10% in ULS diesel	51.2	46.7	53.3	45.7	43.3	40.7
30% in ULS diesel	66.4	52.2	77.0	50.4	39.8	33.5
5% in F-T diesel	90.3	81.7	91.1	80.2	78.1	75.9
10% in F-T diesel	98.3	85.0	96.7	79.4	74.0	71.3
30% in F-T diesel	114.1	86.5	161.6	77.8	62.7	53.0

8.5 Discussion of Ignition Quality Results

8.5.1 Neat Oxygenates

The observed cetane numbers of the neat oxygenates in the study, as determined by the IQT apparatus, varied widely, from 6.7 for GTB and 26.5 for DBM to 344 for DPE and over 1000 for EXEE.

In every case the cetane numbers of the blend increased smoothly from 0 to 100 percent oxygenate.

Although cetane numbers have been in use for a long time, the understanding of the relationship between fuel composition and cetane number is imperfect. For hydrocarbons,* the cetane number tends to rise with carbon number, and a number of general relationships between cetane number hydrocarbon type have been observed, such as those shown in Figure 16.[36]

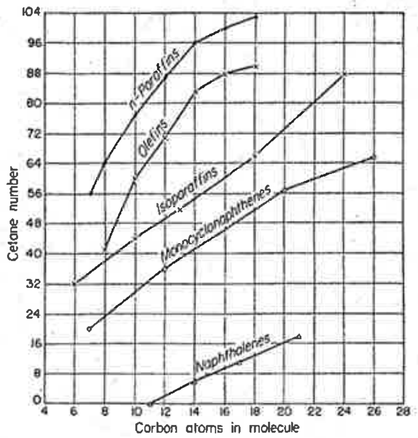

Figure 16. Relationship of Hydrocarbon Type and Size on Cetane Number

However, for oxygenates the relationship between molecular structure and cetane number is not as well-known† and undoubtedly much more data are required before generalizations can be made with confidence. Looking at the limited data from this study, it is noted that:

- The two esters had low cetane numbers.
- The cetane number of the DBXM was much lower than that of EXEE, even though the structures and carbon numbers were somewhat similar. However, the DBXM still had a cetane number that is high for diesel fuel.

8.5.2 Diesel Fuels

As Table 15 shows, the agreement between the cetane numbers of the diesel fuels, as determined by the IQT in this study, with cetane numbers determined by the D 613 test was excellent.

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[*] In the strict sense of compounds of hydrogen and carbon only.

[†] A study by the U.S. National Renewable Energy Laboratory (NREL) reexamining the relationship between fuel molecular structure and cetane number is currently under way. Oxygenates will be a particular focus of this study.

Table 15. Comparison of Diesel Fuel Cetane Numbers from D 613 and IQT Tests

Diesel Fuel	Cetane Number, D 613	Cetane Number, IQT
Oil sands diesel	40.2	41.4
Ultra-low sulfur	44.8	44.5
Fischer-Tropsch	81	79.5

8.5.3 Blending Cetane Numbers

Table 16 shows blending cetane numbers for the 10 volume percent oxygenate-diesel fuel blends.

Table 16. Blending Cetane Numbers for 10 Volume Percent Oxygenate-Diesel Fuel Blends

Oxygenate or Blend	Blending Cetane Number					
	DPE	DBXM	EXEE	TPGE	DBM	GTB
Neat oxygenate	344	86.6	>1000	74.5	26.5	6.7
10% in OS diesel	86	70	118	54	35	13
10% in ULS diesel	112	67	133	57	32	6
10% in F-T diesel	268	135	252	76	25	-3

Note that:

- The blending cetane number for an oxygenate varies significantly with the diesel fuel.
- The blending cetane numbers of the DPE, EXEE and TPGE are significantly lower than for the neat oxygenate. However, the neat DPE and EXEE have such high neat cetane numbers that the lower blending cetane numbers are still very high.
- Blending cetane numbers tend to be accentuated with the Fischer-Tropsch diesel fuel: oxygenates with high cetane numbers have higher blending cetane numbers when blended with this diesel fuel as compared to the other two diesel fuels, and oxygenates with low cetane numbers have lower blending cetane numbers when blended with this diesel fuel.

9 Health and Toxicity Information

While this study was not primarily directed towards an investigation of potential health effects of diesel fuel oxygenates, health and toxicity information identified during the course of this investigation was to be reported. Two recent reviews of diesel fuel oxygenates were identified that discuss health effects. Both reviews emphasize the preliminary and incomplete nature of the available health and toxicity information. Table 17 shows the coverage of these reviews of the oxygenates included in the present effort.

Table 17. Coverage of Oxygenates in Reviews

	Oxygenate	Murphy[37]	Natarajan, et al.[38]
DPE	Dipentyl ether	✓	
DBXM	dibutoxymethane	✓	
EXEE	2-Ethoxyethyl ether	✓	✓
DEM	diethyl maleate		✓
TPGE	Triproplylene glycol monomethyl ether		✓
DBM	Dibutyl maleate		✓
GTB	Glycerol tributrate		✓

10 Future Work

In the initial planning workshop in Toronto for this Annex, preliminary discussions were held concerning further activities that might form the basis for a Phase II and/or Phase III activities.

10.1 Future Phase II Activities

At that time there was some consensus that Phase II activities should focus on combustion properties, such as:

- Spray parameters
- Soot formation tendency
- Calculated adiabatic flame temperature
- Chemical kinetics of NO_x formation

as well as on fuel properties related to engine operation, such as:

- Material compatibility, with both metals and polymers
- Viscosity
- Lubricity
- Thermal stability
- Cold flow.

Also, Phase II could include studies of the miscibility, vapor pressure, and ignition quality of oxygenates not included in Phase I.

10.2 Future Phase III Activities

Phase III of the Future Greener Diesel Fuels Annex was expected to focus on investigating the following aspects of those fuels and blends identified in Phases I and II activities as most promising:

- Engine tests
- Development of fuel specifications
- Life cycle analyses of fuel emissions.

Both the proposed Phase II activities and the proposed Phase III activities were tentative and no commitment was made to fund or perform these activities, but there was consensus that they should be discussed at the conclusion of Phase I.

Acknowledgements

Funding for a Workshop in Toronto in June 1998 to plan the work was provided by the IEA-AMF common fund. Many helpful comments were received at that workshop.

Dr. Lisa Lanning of Automotive Testing Laboratories prepared the oxygenate-diesel fuel blend samples and performed the miscibility, water tolerance, cloud point, and gas chromatographic vapor pressure analyses. Flash point testing was performed by Paragon Laboratories.

Ralph McGill of ORNL provided guidance and graciously presented two interim reports.

We wish to thank Lambiotte & Cie S.A. for providing the dibutoxymethane (butylal), Shell Canada for supplying the oil sands diesel, and Equilon for providing the Fischer-Tropsch diesel fuel.

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