# LOW EMISSION OXYGENATED DIESEL FUEL

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## ABSTRACT

New diesel engines and fuels are required to meet stricter world-wide emission standards. Challenges include both lower particulate and $NO_X$ emissions. MTBE, ETBE, and TAME utilization in gasoline results in emissions reductions. Similarly, oxygen containing additive use in diesel fuel applications gives substantial particulate emission reduction. In combination with diesel ignition improvement additives, a typical "on-road" 30% aromatic content oxygenated diesel fuel can give an emission profile similar to a 10% aromatic California reference diesel fuel. Oxygenate selection criterion and emission reductions in heavy duty engines are detailed for several commercial P-series glycol ethers and for a new ether oxygenate, di-t-butyl glycerol. A di-t-butyl glycerol product mixture is prepared by etherification of glycerol available as a by-product from commercial biodiesel manufacture. Various strategies for oxygenate use to enhance diesel fuel performance are discussed.

## INTRODUCTION

The trend toward low emission diesel fuels is growing worldwide. In the United States, **Clean Air Act** legislation will mandate reduced particulates in 1994 and lower $NO_X$ emissions in 1998. Emission reductions beyond these targets will require a combination of new engine technology, additives, and reformulated diesel fuels (1). The production of economically viable low emission diesel fuels will remain a substantial challenge into the years to come. Oxygenated diesel fuel may offer one possible solution.

Oxygenate utilization to produce "cleaner burning" diesel fuels has been known for over fifty years. Oxygenates are well known to reduce particulate emissions. Low molecular weight alcohols, such as methanol, ethanol, and t-butyl alcohol, have been reported to reduce emissions (2). Higher alcohols (3), carbonates (4), diethers (5), such as diglyme, and various glycol ethers (6) have also been reported. Particularly attractive are P-series glycol ethers which contain both an ether and a propylene glycol end-group.

This paper deals with oxygenate selection criterion and emission reductions in modern diesel engines. Various application strategies to reduce emissions and enhance diesel fuel performance are discussed.

## OXYGENATE SELECTION

Key oxygen selection criterion include: cost, toxicity, environmental impact, fuel blending properties, and engine performance. Critical fuel blending properties, which were used to screen and identify viable oxygenate candidates, included: high oxygen content, diesel fuel solubility, flashpoint, viscosity, water solubility in the resultant fuel blend, oxygenate extractability from the fuel, and minimal impact on the natural diesel fuel cetane number.

The oxygenate should be soluble in diesel fuel from 1.0 to 5.0% to achieve maximum emissions reduction and improved engine performance. Above 5.0%, oxygenate cost per gallon of fuel treated is prohibitive. A number of high oxygen containing materials, such as ethylene and propylene carbonate, and most E - series glycol ethers, which

are based on ethylene glycol, were eliminated from consideration due to poor diesel fuel solubility. As aromatic content in future reformulated diesel fuels is reduced from 35% to 10 - 20%, oxygenate solubility in the less polar hydrocarbon fuels will become acute.

The oxygenated diesel fuel flashpoint needs to be over 52°C, as specified by ASTM D975, to reduce the transportation flammability risk. Many inexpensive ethers with high oxygen content, including MTBE, ETBE, TAME, and DIPE, were eliminated from consideration due to the low flashpoints of the resulting 1.0% oxygenated fuel blends. Fuel blends containing 1.0% or more of inexpensive dimethyl carbonate and diethyl carbonate, were also eliminated because the resulting blends had flashpoints lower than the target.

A key issue is how the additive behaves if the oxygenated blend becomes exposed to water. Both high degree of water solubility in the fuel blend and high degree of water extractability of the oxygenated additive from the fuel are unacceptable. Dimethyl and diethyl carbonate both have high water extractability from the fuel. Similarly, most fuel soluble E - series glycol ethers are easily extracted and are thus eliminated from consideration. P - series glycol ethers, generally, have acceptable partitioning characteristics.

Many intermediate molecular weight aliphatic, cycloaliphatic, and aryl alkyl alcohols meet the fuel blending selection criteria. Poly(ether) polyols based on propylene oxide or butylene oxide are viable oxygenate candidates. Methyl soyate, which is a form of biodiesel, meets selection criterion and was evaluated. Several commercial P - series glycol ethers and a new glycol ether oxygenate, di-t-butyl glycerol, are potentially inexpensive, and meet all the other selection criterion. Diglyme, which is associated with health risks, and too expensive to be economically viable, was also included in the test program so that benchmark comparisons can be made with previous studies. Various emission reduction strategies which utilize oxygenated diesel fuel are outlined in this paper.

## OXYGENATED DIESEL APPLICATIONS

There are many opportunities to use an oxygenated diesel fuel for emission reduction. A standard 1993 E.P.A. certification D2 diesel fuel reformulated with oxygenate has the potential to reduce emissions from both pre-1991 engines, which are required to meet a 0.60 gram / brake horsepower - hour particulate target, and post-1991 heavy-duty diesel engines which must meet a 0.25 gram / brake horsepower - hour Clean Air Act particulate emissions target. In addition, oxygenated diesel fuel could has the potential to benefit 1994 and 1998 heavy-duty diesel engine emission performance.

To demonstrate operability in older engines, an E.P.A 13-mode emission test was conducted in a 1990 Cummins L-10 heavy-duty diesel engine. Results show a 39 cetane number diesel fuel containing 43% aromatics and 0.25% sulfur, when blended with 5.0% GE-C (commercial P - series glycol ether), have the potential to reduce particulates emission with little impact on $NO_x$. Similar results are expected in other older engines.

Most of the results reported in this paper focus on oxygenated diesel fuel performance in modern heavy-duty diesel engines. Emission testing was conducted in the prototype 1991 Detroit Diesel Series 60 CARB certification engine at Southwest Research Institute. Hot-start transient emissions, including hydrocarbons, carbon monoxide, $NO_x$, and particulate matter, were measured using the standard E.P.A. transient test cycle and are shown in Table 1. The reference fuel is a E.P.A. certification D2 diesel fuel with a 43 cetane number, 0.037 Wt.% sulfur, and a 31% aromatic content. Various oxygenates were blended into this reference fuel at concentrations from 1.0 to 5.0%. The cetane number of the oxygenated fuel blends were adjusted to 43 using ethyl hexyl nitrate.

Oxygenates significantly reduce hydrocarbon, carbon monoxide, and particulate

emissions, but give a sight increase in $NO_X$ emissions. There is little or no increase in fuel consumption when an oxygenated diesel fuel is utilized. Results clearly demonstrate that reduced particulate matter emissions is a key benefit achieved through oxygenated diesel fuel use. In addition, 5.0% GE-C reduces unregulated aldehyde and ketone emissions by around 25%.

Not all oxygen containing additives are effective in reducing particulate emissions. 1-Phenyl ethanol and 1-cyclohexyl ethanol, for example, do not significantly reduce particulate emissions and methyl soyate is only marginally effective. Diethers, such as diglyme, and P - series glycol ethers; however, are very effective in reducing particulates. Based on a large amount of data, most of which could not be presented in a short paper, it can be concluded that particulate reduction is directly proportional to the ether oxygen content of the blended fuel. Results show GE-C at 1.0 wt.% oxygen gives around a 15% particulate emission reduction.

**Table 1 Oxygenate Additive Effect On Hot-Start Transient Emissions**
(Grams/Brake Horsepower - Hour)*

| Additive; Conc. (Vol.%) | Oxygen Content (wt.%) | HC Ref. Fuel Cand Fuel | CO Ref. / Cand. | $NO_X$ Ref. / Cand. | PM Ref. / Cand. |
|---|---|---|---|---|---|
| MBA; 5 | 0.78 | 0.425 (.029)<br>0.468 (.059) | 1.852 (.043)<br>1.867 (.045) | 4.155 (.032)<br>4.327 (.087) | 0.180 (.006)<br>0.174 (.002) |
| Cyclohexyl Ethanol; 5 | 0.68 | 0.388 (.029)<br>0.466 (.017) | 1.933 (.088)<br>1.994 (.015) | 4.091 (.027)<br>4.181 (.063) | 0.180 (.005)<br>0.177 (.008) |
| Methyl Soyate; 5 | 0.59 | 0.392 (.011)<br>0.319 (.066) | 2.004 (.029)<br>1.843 (.127) | 4.303 (.056)<br>4.331 (.097) | 0.182 (.007)<br>0.174 (.006) |
| Diglyme; 5 | 2.05 | 0.421 (.036)<br>0.307 (.021) | 1.939 (.082)<br>1.634 (.033) | 4.231 (.086)<br>4.340 (.065) | 0.174 (.007)<br>0.146 (.007) |
| Poly(ether) Polyol; 1 | 0.34 | 0.385 (.012)<br>0.305 (.037) | 1.919 (.030)<br>1.676 (.009) | 4.175 (.029)<br>4.213 (.065) | 0.176 (.005)<br>0.166 (.003) |
| GE-C, 1 | 0.37 | 0.424 (.037)<br>0.395 (.025) | 1.990 (.086)<br>1.920 (.116) | 4.242 (.102)<br>4.239 (.034) | 0.171 (.002)<br>0.163 (.008) |
| GE-C, 2 | 0.74 | 0.433 (.040)<br>0.407 (.035) | 1.946 (.081)<br>1.866 (.020) | 4.159 (.070)<br>4.166 (.103) | 0.183 (.003)<br>0.159 (.010) |
| GE-C, 5 | 1.82 | 0.384 (.019)<br>0.291 (.008) | 1.872 (.034)<br>1.568 (.021) | 4.159 (.045)<br>4.235 (.042) | 0.183 (.004)<br>0.154 (.003) |

*** Emission testing was conducted in the prototype 1991 Detroit Diesel Series 60 CARB Certification engine at Southwest Research Institute. Hot-start transient emissions (hydrocarbons, carbon monoxide, $NO_X$, and particulate matter) were measured using the standard EPA transient test cycle and sampling techniques were based on 1992 Federal Test Procedures (FTP). The reference fuel is a standard EPA certification D2 diesel fuel with a 43 cetane number, 0.037 Wt.% sulfur, and 31% aromatic content. Oxygenates were blended into this reference diesel at the volume % indicated. Emissions are reported in Grams / Brake Horsepower - Hour. ( ) is one standard deviation. MBA is 1-phenyl ethanol. GE-C is a typical commercial P - series (propylene glycol based) glycol ether.**

Emission regulations are directed at reducing both particulate matter and $NO_X$ emissions. Table 1 show ether oxygenates reduce particulates, but this particulate reduction is typically accompanied by a small increase in $NO_X$ emissions. Increasing the oxygenated diesel fuel cetane number using chemical cetane improvers, such as ethylhexyl nitrate or di-t-butyl peroxide, has been shown to reduce $NO_X$ emissions. Thus, the oxygenate / chemical cetane improver combination gives a diesel fuel with both lower particulate and $NO_X$ emissions. Results outlined in Table 2 suggest this combination strategy provides an opportunity to prepare an oxygenated diesel fuel which will meet current California emission standards.

**Table 2** **Oxygenated California Diesel Fuel***
(Grams / Brake Horsepower - Hour)

| Fuel Type | Cetane No / Arom.(%) | HC | CO | $NO_X$ | PM |
|---|---|---|---|---|---|
| EPA Base Ref. | 43<br>31 | 0.433 | 1.979 | 4.17 | 0.174 |
| Low Arom. Ref. | 51<br>15 | 0.143 | 1.303 | 3.99<br>(3.98) | 0.153<br>(0.159) |
| GE-C & Peroxide | 53<br>31 | 0.153 | 1.225 | 4.04 | 0.160 |

*** Transient protocol and data analysis are identical to those described in Table 1. The glycol ether, GE-C, blend concentration is 2.0% and enough di-t-butyl peroxide was used to increase the diesel fuel cetane number of the GE-C & paroxide experiment by 10.0 units. Since a 10% aromatic CARB reference fuel could not be purchased, a 15% containing aromatic fuel was used as the CARB low aromatic reference fuel. The Coordinating Research Council's (CRC) VE-1 Model (7) waa used to correct emissions from the 15% aromatic fuel to CARB certification fuel properties on cetane, aromatic content, and sulfur. The number in ( ) is the adjusted emissions value. Considerable CRC data suggests the VE-1 Model is valid for this type of adjustment.**

Effective October 1, 1993 all diesel fuel used in California must have an emission footprint which is equivalent to a low sulfur - 10% aromatic containing CARB reference fuel. Southwest Research Institute's prototype 1991 Detroit Diesel Series 60 engine, which is utilized for the oxygenate study, is the CARB certification engine. The emissions from an oxygenated diesel fuel, which contains 2.0% glycol ether (GE-C) and enough di-t-butyl peroxide ignition improver to increase the cetane number by 10.0 units, are nearly identical to the "pseudo-CARB" low aromatic reference diesel fuel used in this study. These results predicts that a combination of an oxygenated diesel fuel and chemical cetane improver provides an opportunity to produce a California "alternative" oxygenated diesel fuel with a 31% aromatic content Which has an emission performance equivalent to a low sulfur - 10% aromatic CARB reference fuel.

Cost is a significant issue in the preparation of a California diesel fuel. Clearly, a 30% aromatic containing oxygenated diesel fuel, which uses commercially available, P - series glycol ethers, is more cost effective than using a low sulfur - 10% aromatic fuel. Refinery hydrogenation to reduce diesel fuel aromatic content to 10% is an expensive option. The strategy used by most refiners is to reformulate with a 20% aromatic base fuel using high levels of chemical cetane improver. The California Air Resources Board (CARB) indicate costs for qualified fuels of this type will increase the diesel fuel costs by five to eight cents per fuel gallon. The oxygenated diesel fuel cost currently fits into the upper part of this cost range. Less expensive oxygenates are needed to make an oxygenated California diesel fuel a viable option.

One "non-commercial" oxygenate, which has the potential for reduced cost, is di-t-butyl glycerol. A di-t-butyl glycerol product mixture is prepared by etherification of glycerol which is available as a by-product from commercial biodiesel manufacture. The envisioned strategy is to blend 5% of an 80:20 methyl soyate / di-t-butyl glycerol oxygenate mixture with conventional low sulfur D2 diesel to create an inexpensive oxygenated diesel fuel. The cost and availability of by-product glycerol is leveraging. Biodiesel is a commercial reality in Europe and would provide the best opportunity for implementation.

Coupled with new heavy-duty diesel direct injection engine technology, reformulated oxygenated diesel fuels offers a potential option for achieving the 1998 **Clean Air Act** target which mandates a $NO_X$ reduction from 5.0 to 4.0 grams / brake horsepower - hour. The engine strategy for 1994 is to modify the engine design to give the 0.10 gram particulate target. Fortunately, $NO_X$, carbon monoxide, and hydrocarbon emissions are acceptable. In 1998 engines, an oxygenated diesel fuel, which reduced particulates by 15%, would allow the OEM's to tune less rigorously for particulates, thus providing more flexibility on the $NO_X$ tuning.

There are numerous other opportunities to use oxygenates in specialty fuel applications where reduced emissions are of interest. For example, transit authority buses will use high quality low sulfur D1 or kerosene, particulate traps, and post-combustion catalysts to achieve a 0.07 gram particulate target for 1994. The downside for these specialty fuels is less power and higher fuel consumption. An oxygenated D2 diesel fuel has the potential to provide the same low emissions without increased fuel consumption. Other specialty fuel opportunities for an oxygenated fuel include: stationary powerplants, underground mining, marine diesel, locomotive diesel, and fuels for many smaller volume "off-road" applications.

## CONCLUSIONS

Cleaner burning diesel fuels can be produced through the use of oxygenated additives. Carefully selected "commercially" available P -series glycol ethers, which have the desired characteristics, are effective in reducing hydrocarbon, carbon monoxide, and particulate matter emissions. The magnitude of the particulate emissions reduction is directly proportional to the "oxygen" content of the ether oxygenate containing fuel. A combination of a glycol ether oxygenate with a cetane improver results in further emission reductions, especially $NO_X$. One application strategy for the combination oxygenate / ignition improver diesel fuel formulation is a 30% aromatic containing oxygenated fuel which has the same emissions performance profile as the mandated low sulfur - 10% aromatic California diesel fuels.

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