



THE EFFECT OF TWO OXYGENATES ON DIESEL ENGINE EMISSIONS

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ABSTRACT

Improvement of fuel properties is essential for the suppression of diesel pollutant emissions along with the optimization of combustion-related design factors and exhaust after-treatment equipment. Studies conducted in the past have shown that a significant reduction of pollutants using oxygenates as alcohols, ethers, glycol ethers, methylals and carbonates. The present paper experimentally investigates the influence of oxygenated diesel fuels on the emissions with the use of two different synthetic oxygenated compounds namely Diphenyl ether (DPE) and Diethelene glycol dimethyl ether (DIGLYME). Several diesel fuel blends, which contain 10% and 15% by volume of DPE and DIGLYME, were prepared and the effect of these blends on emission characteristics were studied on a twin cylinder direct injection diesel engine. The blends were tested under the different load conditions and the results shows, there is significant reduction of engine emissions of hydrocarbon and carbon mono oxide emissions while the coefficient of light absorption of smoke opacimeter decreases by about 50% for DPE10, DIGLYME10 blend and it was reduced by about 60% for DPE15 and DIGLYME15 blend.

Keywords: oxygenated fuel, diesel engine, ether compounds, emissions.

INTRODUCTION

Reduction of exhaust emissions is extremely important for diesel engine development in view of increasing concern regarding environmental protection and stringent exhaust gas regulations. Diesel engines are the major contributors of various types of air polluting exhaust gases such as particulate matter, carbon monoxide, oxides of nitrogen and other harmful compounds. Increasingly stringent regulations governing particulate emissions, nitric oxides from diesel engines have prompted research directed toward methods for reducing the in-cylinder formation of pollutants by modifying fuels or controlling particles by after treatment technologies.

Despite the new promising diesel after treatment developments, the task to comply with ever more stringent regulations seems to be great. In the year 2005, the EURO IV fuel specification came into effect and the requirements of diesel fuel properties have become even more stringent.

Controlling diesel exhaust emissions through fuel modification seems to be promising because it would affect both the new and old engines. Modification of diesel fuel to reduce exhaust emission can be performed by increasing the cetane number, reducing fuel sulphur, reducing aromatic content, increasing fuel volatility and decreasing the fuel density. However, the potential of conventional diesel fuel for emissions reduction has already been to a large extent exploited and the most important fuel parameters mentioned above, can nowadays be changed in a narrow range only. Moreover, the shortfall in NO_x and PM emissions control in diesel engines is so great that much more drastic fuel changes will be needed (Stoner *et al.*, 1999).

To have the compromise between engine performance and engine out emissions, one such change has been the possibility of using diesel fuels with oxygenates. These blends usually enhance the combustion

efficiency, burn rates, power output, and the ability to burn more fuel, but first of all, these blends offer the reduction of exhaust emissions.

Many studies have shown that the addition of oxygen to a base diesel fuel will result in a reduction of particulate emissions (MišosŠaw Kozak *et al.*, 2008 and 2009). The primary parameter influencing the formation of particles appears to be the amount of oxygen in the fuel, and secondarily, the chemical structure of oxygenate providing the oxygen. The work of Miyamoto *et al.*, (1998) demonstrated that it was the oxygen content of the fuel additive that had the primary influence on soot reduction- not its chemical form. Curren *et al.*, (2001) done chemical kinetic modeling of selected oxygenates in N- heptane as a base diesel fuel and demonstrated that the generation of soot precursors decreased with the increasing oxygen content of the fuel mixture.

Andrea bertola *et al.*, (2000) has considered twenty seven oxygenated hydrocarbons as diesel fuel additives and concluded that the butylal offers significant advantages over most other oxygenates in that its physical properties are very close to that of common diesel fuel. Generally most of the oxygenated compounds when blended with diesel fuel decrease the pollution, but some of them only improve the performance (Brian *et al.*, 2001).

Cheng A.S. Ed *et al.*, (2002) tested diglyme and other oxygenates to show that particulate matter reduction is controlled largely by the oxygen content of the blend fuel and the effect of chemical structure was observed to be small. But the results of Micheal D Boot *et al.*, (2007) confirms the importance of oxygen mass fraction of the fuel blend, but at the same time illustrates the effect of chemical structure.

The fuel oxygenates have been widely used for years for gasoline. However the gasoline oxygenates is not suitable, to be used in fuel for diesel engines due to their



very low cetane numbers, low values of boiling point, their poor viscosity.

The use of the synthetic additives is a more advantageous way of oxygenizing diesel fuels. Such groups of chemical compounds as ethers, acetals, carbonates, esters and higher alcohols, should be taken into consideration (Irshad Ahmed *et al.*, 2001). Some compounds of the mentioned groups have physical and chemical properties very similar to that of diesel fuel. Moreover, they are characterized with a very high cetane number (often above 100) and very high oxygen content (often above 50% m/m). All this shows that these compounds should be effective even if a small amount is added to the base fuel (K. B. Spreen *et al.*, 1995).

Mani Natarajan *et al.*, and Manuel A *et al.*, (2001) have suggested the screening and selection methodologies for oxygenates based on a set of physical and chemical properties, that will be eligible for diesel engine testing.

OXYGENATED DIESEL ADDITIVES

To acquire information on the performance of the compression ignition engines operated with oxygenated fuels, a detailed literature study was under taken. The majority of the technical documents report on alcohols, ethers (Yeh L.I *et al.*, 2001 and Delfort *et al.*, 2002). The properties being considered for use with diesel fuel as oxygenated additives include volatility, toxicity, solubility, odour, seal compatibility, ignition quality, cost, low temperature pumpability, and stability of the fuel/additive mixture (Tsurutani K., *et al.*, 1995). From the literature study various oxygen containing hydro carbons were considered and then evaluated in relation to engine application in compression ignition engines.

Requirements of good oxygenate properties

Oxygenates that are to be blended with diesel fuel must have fuel properties appropriate for motor fuel. In particular

- The blend must exhibit an adequate water tolerance.
- The oxygenate must be miscible with various diesel fuels over the range of environmental temperature seen in vehicle operation.
- The blend must have an adequate cetane number and preferably allow the blend to show an increased cetane number.
- The oxygenate blend must not exhibit excessive volatility when mixed with various diesel fuel base.

Selection of oxygenates

The selection of oxygenates was guided by several considerations

- Boiling point and flash point in diesel fuel range: Since this study was based on a 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 to meet commonly adopted diesel fuel fire safety requirements.

- Exiting reviews and experimental data: Some oxygenates have been the subject of previous investigations, including the generation of engine emission data. For example Andrea Bertola *et al.*, (2000) recently considered 27 oxygenates as diesel fuel additives.

- Necessary requirements, concerning fire safety and combustion properties of the pure substances defined the elimination criteria for the first selection.

Boiling point > 60 °C

Flash point > 55 °C

Self ignition temperature < 350 °C

Kinematic viscosity < 4 mm²/s

Eleven oxygenated compounds met the necessary requirements. In addition other criteria (e.g. oxygen content, density, lower heating value ...) were set to choose the more suitable oxygenated additives in reducing the exhaust opacity of automotive diesel engines. The best two oxygenated candidates as diesel fuel additives, in accordance with this part of technical evaluation, are:

- a) Diethylene glycol dimethyl ether (DIGLYME)
- b) Diphenyl ether (DPE)

The properties and chemical structure of the two oxygenates studied are given in Table-1.

Table-1. Oxygenates and properties.

Oxygenate	DPE - Diphenyl Ether CAS 101-84-8	DIGLYME - Diethylene glycol dimethyl ether CAS 111-96-6
Linear formula	C ₁₂ H ₁₀ O	C ₆ H ₁₄ O ₃
Boiling point, °C	258	162
Oxygen %	10.11	35.8
Density g/mL	1.073	0.937
Flash point, °C	115	67
Chemical structure		

The names, fire point, flash point and kinematic viscosity for the oxygenates blends studied are shown in Table-2. It also shows the oxygenate name abbreviations used elsewhere in this report.

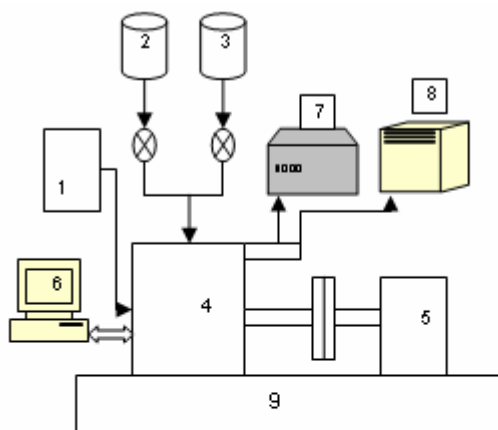
**Table-2.** Properties of fuel blends.

	Kinematic viscosity (mm ² /sec)	Flash point (°C)	Fire point (°C)
Base diesel	3.2	63	76
90 % Diesel + 10 % DPE (DPE10)	2.2	60	73
85 % Diesel + 15 % DPE (DPE15)	1.98	58	69
90 % Diesel + 10 % Diglyme (DIGLYME10)	2.7	61	74
85 % Diesel + 15 % Diglyme (DIGLYME15%)	2.01	60	71

The objective of the current paper is to present a summary of experimental results obtained for a two different oxygenated blends using a kirloskar twin cylinder direct injection diesel engine.

EXPERIMENTAL SETUP

The test engine is twin cylinder 4-stroke water cooled direct injection diesel engine. To give a brief comparison the engine parameters are not modified and the coolant temperature is kept at 80°C during the experiments.



1. Air box
2. Diesel
3. Diesel & Oxygenate blend
4. Test engine
5. Eddy current dynamometer
6. Engine controller
7. Exhaust gas analyser
8. Smoke meter
9. Engine base

Figure-1. Schematic diagram of the experimental setup.

In order to investigate the effects of blends containing different proportions of DPE and DIGLYME on engine combustion and emission characteristics, pure diesel and blends of diesel with 10% DPE and 15% of

DPE and then 10% of DIGLYME and 15% of DIGLYME by volume were prepared and the experiments were conducted. NO_x, CO and HC were measured by exhaust gas analyzer and the smoke intensity was measured by smoke meter. The schematic of the experimental setup was shown in the Figure-1.

Engine specifications

Facilities to monitor and control engine variables were installed on a twin cylinder test bed kirloskar DM20 experimental engine. A complete description of the engine specifications is tabulated in Table-3.

Table-3. Specifications of the test engine.

Make	Kirloskar
Model	DM20
Type of engine	Four stroke, naturally aspirated, water cooled, direct injection
No. of cylinders	Two
Bore x stroke	102 x 116 mm
Displacement volume	1896 cc
Compression ratio	17.5 : 1
Rated output as per BS5514 / ISO 3046 / IS 10001	14.8 kW (20.0 bhp) @ 1500 rpm

Instrumentation details

The test engine is coupled to an eddy current dynamometer. The main measuring instruments were ; a viscous type laminar air flow meter, tanks and flow meter for fuels, temperature sensors for the exhaust gas, inlet air, cooling water, lubricating oil, a TDC marker (a magnetic pickup), a rpm indicator, and a kistler piezo electric transducer for the combustion chamber pressure, and a data acquisition system.

Exhaust gas analyzers were used to measure smoke, nitrogen oxides (NO_x), total unburned hydrocarbon (HC), and carbon monoxide (CO) at the exhaust pipe.

Experimental procedure

The engine tests were conducted at a constant engine speed of 2000 rpm. After stable operating conditions were experimentally achieved, the engines were subjected to similar loading conditions. Starting from no load the observations were recorded at 20%, 40%, 60% and 80%, all as percentages of the rated load. The engine was stabilized before taking all measurements. All measurements were taken at constant static injection timing. An attempt was made to conduct all experiments without significant fluctuations in inlet air temperature and lubricating oil temperature as a method to prevent possible discrepancies in engine operation during the tests and mainly, to avoid variations in engine loading.



The experimental procedure consisted of the following three steps;

- Initially, engine tests using the base reference diesel fuel were conducted covering all engine loads examined to determine the engine operating characteristics and pollutant emissions constituting the engine base line operations.
- The previous procedure was repeated at the same operating conditions with the engine fueled consecutively with fuels of additive DPE10, Diglyme10 and DPE15, DIGLYME15.
- Emphasis was made to confine and if possible to diminish the scattering of the measurements for pollutant emissions around the mean value by repeating the measurements at each operating conditions.

During the engine tests the following parameters were recorded at each operating conditions considered.

- In cylinder pressure
- Exhaust gas temperature
- Fuel consumptions.
- Exhaust smokiness
- Exhaust gas emissions.

RESULTS AND DISCUSSIONS

The key findings from the experimental engine testing are summarized below

The presence of additional oxygen in the blends always increases the possibility of burning of carbon particle in the exhaust gases which resulted in high exhaust gas temperature and it also increases with the increase in percentage of blends in the base fuel as it can be seen from Figure-2.

As it can be seen from Figure-3 and Figure-4, Oxygenated fuel additives such as glycol ethers and phenyl ethers considered in this work have a significant impact on CO and HC emissions from diesel engines. The effectiveness of the oxygenated additives in the reduction of the CO and HC emissions was not directly dependent on the oxygen content. This was proven by the fact that the highest reduction was obtained for the additive with the lowest oxygen content, in this case diphenyl ether (Table-1). In this situation it can be concluded that the physical/chemical properties of the additives, e.g. boiling point, play an important role. It is also known that PM emissions reduction is generally dependent on the oxygen content in fuel, whereas CO and HC emissions reduction depends also on the molecular structure of the oxygenate

Because of the availability of additional oxygen there is better combustion and so the CO₂ levels are greater than the base fuel.

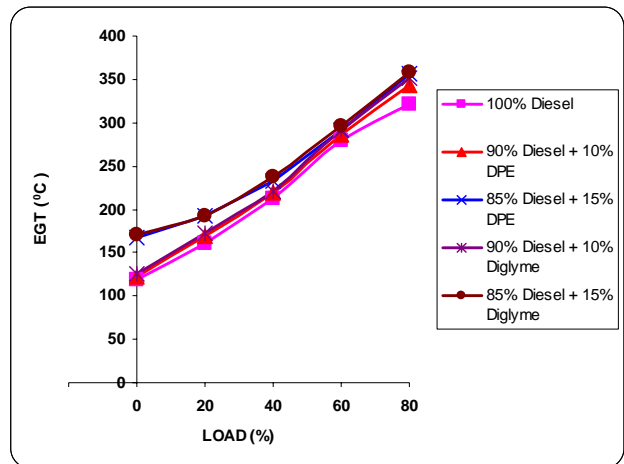


Figure-2. Comparison of EGT for base diesel and diesel + blends of DPE and Diglyme.

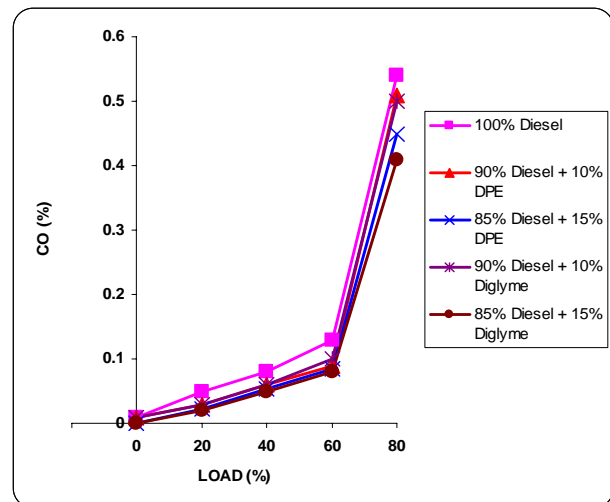


Figure-3. Comparison of CO for base diesel and diesel + blends of DPE and Diglyme.

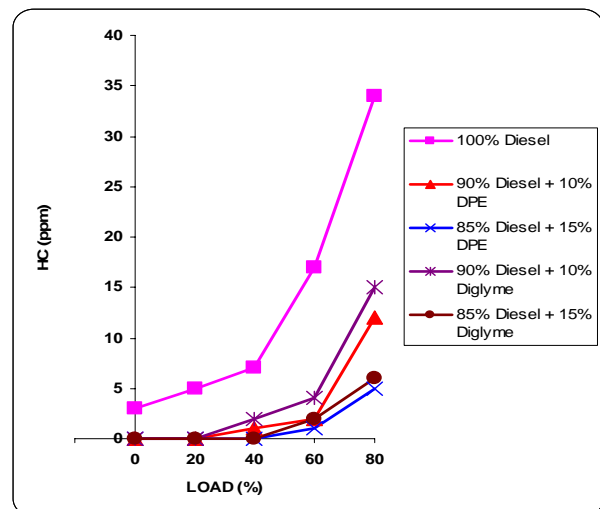


Figure-4. Comparison of HC for base diesel and diesel + blends of DPE and Diglyme.



One of the objectives of this work was to ascertain whether or not some oxygenates were more effective than others in the decrease in the formation of HC, CO and NOx. The obtained results show that the fuel which effectively reduces the CO and HC emissions is less effective in reducing the NOx emissions, as it can be seen from Figure-6.

It is also seen that the oxygen enrichment of the conventional fuel is not accompanied by a sharp increase of the in-cylinder NO concentration as expected due to decrease of the local temperature as a result of the lower fuel heating value.

The influence of DPE and DIGLYME on the exhaust opacity is shown in Figure-7. There were very large differences between the coefficients of light absorption of smoke opacimeter. There was about 50% reduction of opacity when blends DPE10 and DIGLYME10 are used and also 60% reduction when the blends DPE15 and DIGLYME15 were used. Both DPE and DIGLYME show almost the same effect as far as opacity is concerned. They consistently gave us the lowest opacity under both high and low load engine testing as well as for the different blend proportions.

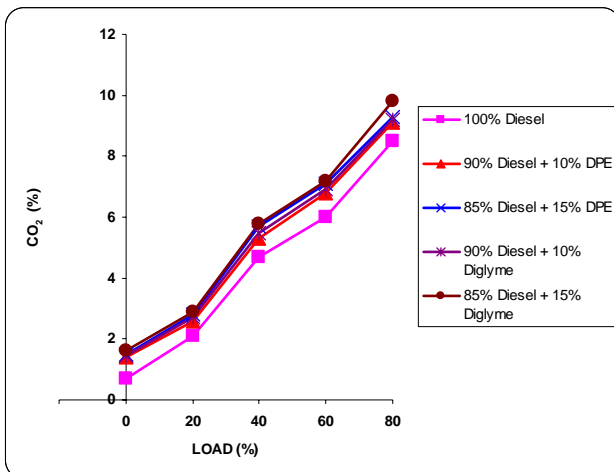


Figure-5. Comparison of CO₂ for base diesel and diesel + blends of DPE and Diglyme.

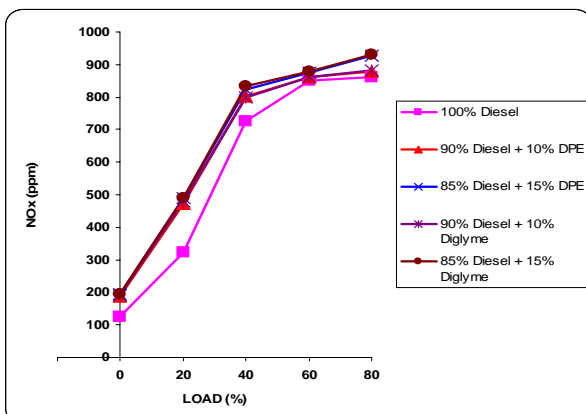


Figure-6. Comparison of NO_x for base diesel and diesel + blends of DPE and Diglyme.

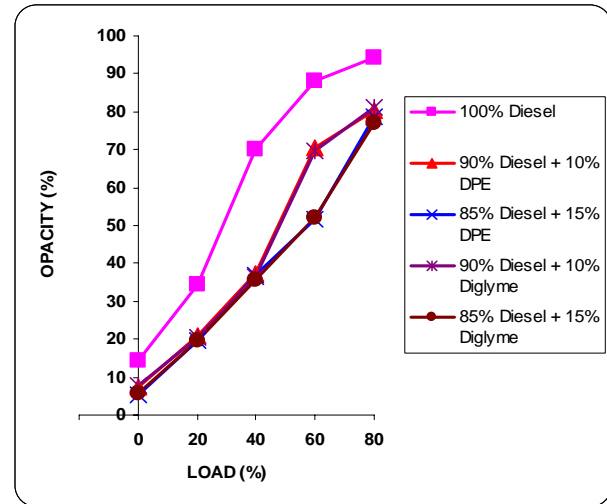


Figure-7. Comparison of Opacity for base diesel and diesel + blends of DPE and Diglyme.

CONCLUSIONS

In this research a preliminary investigation was carried out to study the effects of on exhaust emissions by DPE and DIGLYME blends in a twin cylinder direct injection diesel engine. The results obtained for constant engine speed with various engine loads can be summarized as follows:

- Both DPE and DIGLYME blends substantially lowers the exhaust gas opacity. The maximum reduction 60% was observed by DPE15 and DIGLYME15 blends as compared to base reference diesel fuel.
- The oxygenated diesel fuel blends has shown significant reduction in CO and HC emissions with only a slight penalty in NO_x emissions.
- Oxygen enrichment of the conventional fuel is not accompanied by a sharp increase of the in-cylinder NO concentration due to decrease of the local temperature as a result of the lower fuel heating value.
- Oxygenated diesel fuels produce a favorable shift in PM/NO_x trade-off.

In the near future, we will consider the application of both oxygenated fuel additive mixture and exhaust gas recirculation for a further improvement in the engine exhaust emissions trade off.

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REFERENCES

- Andrea Bertola and Konstantinos Boulouchos. 2000. Oxygenated Fuels for Particulate Emissions Reduction in Heavy-Duty DI-Diesel Engines with Common-Rail Fuel Injection. SAE Paper No. 2000-01-2885.
- Brian E. Hallgren and John B. Heywood. 2001. Effects of Oxygenated Fuels on DI Diesel Combustion and Emissions. SAE Paper No. 2001-01-0648.
- Curran H. J., Fisher E. M., Glaude P.-A., Marinov N. M., Pitz W. J., Westbrook C. K., Layton D. W., Flynn P. F., Durrett R. P., zur Loye A. O., Akinyemi O. C. and Dryer F. L. 2001. Detailed Chemical Kinetic Modeling of Diesel Combustion with Oxygenated Fuels. SAE paper No. 2001-01-0653.
- Cheng A. S. (Ed) and Robert W. 2002. Dibble, Bruce A. Buchholz, The Effect of Oxygenates on Diesel Engine Particulate Matter. SAE Paper No. 2002-01-1705.
- David W. Layton and Alfredo A. Marchetti. 2002. Comparative Environmental Performance of Two Diesel-Fuels Oxygenates: Dibutyl Maleate (DBM) and Tripropylene Glycol Monomethyl Ether (TGME). SAE Paper No. 2002-01-1943.
- Delfort B. Oxygenated Compounds and Diesel Engine Pollutant Emissions Performances of New Generation of Products. SAE Paper 2002-01-2852.
- Gong Yanfeng, Liu Shenghua, Guo Hejun, Hu Tiegang, Zhou Longbao *et al.*, 2007. A new diesel oxygenate additive and its effects on engine combustion and emissions. Applied Thermal Engineering. 27: 202-207.
- Hejun Guo, Xianxiang Huang, Jian Zhang, Hongyun Zhang and Limei Li Xi'an. 2005. Study on Methyl 2-Ethoxyethyl Carbonate Used as an Oxygenated Diesel Fuel. SAE Paper No. 2005-01-3142.
- Irshad Ahmed. 2001. Pure Energy Corp. Oxygenated Diesel: Emissions and Performance Characteristics of Ethanol-Diesel blends in CI engines. SAE Paper No. 2001-01-2475.
- Mani Natarajan, Manuel A. González D *et al.*, 2001. Oxygenates for Advanced Petroleum-Based Diesel Fuels: Part 1. Screening and Selection Methodology for the Oxygenates. SAE Paper No. 2001-01-3631.
- Manuel A. González D, Eleanor Liney. 2001. Oxygenates Screening for Advanced Petroleum- Based Diesel Fuels: Part 2. The Effect of Oxygenate Blending Compounds on Exhaust Emissions. SAE Paper No. 2001-01-3632.
- Miyamoto N., Ogawa H., Nurun N. M., Obata K. and Arima T. 1998. Smokeless, Low NO_x, High Thermal Efficiency, and Low Noise Diesel Combustion with Oxygenated Agents as Main Fuel. SAE paper No. 980605.
- Michael D. Boot, Peter J.M. Frijters. 2007. Oxygenated Fuel Composition Impact on Heavy-Duty Diesel Engine Emissions. SAE Paper No. 2007-01-2018.
- MišosŠaw Kozak and Jerzy Merkisz. 2008. The Influence of Synthetic Oxygenates on Euro IVDiesel Passenger Car Exhaust Emissions - Part 3. SAE Paper No. 2008-01-2387.
- Miłosław Kozak and Jerzy Merkisz. 2009. The Influence of Oxygenated Diesel Fuels on a Diesel Vehicle PM/NO_x Emission Trade-Off. SAE Paper No. 2009-01-2696.
- Stoner M. and Litzinger T. 1999. Effects of Structure and Boiling Point of Oxygenated Blending Compounds in Reducing Diesel Emissions. SAE paper No. 1999-01-1475.
- Spreen K. B, T. L. Ullman, *et al.*, Effects of cetane number, aromatics, and oxygenates on emissions from a 1994 heavy-duty diesel engine with exhaust catalyst. SAE Paper No. 950250.
- Tsurutani K., *et al.*, the Effects of Fuel Properties and Oxygenates on Diesel Exhaust Emissions. SAE Paper No. 952349.
- Yeh L. I., D. J. Rickeard J. L. C. Duff and J. R. Bateman *et al.* 2001. Oxygenates: An Evaluation of their Effects on Diesel Emissions. SAE Paper No. 2001-01-2019.

Abbreviations

- CO - Carbon Mono oxide
 CO₂ - Carbon Di oxide
 NO_x - Nitrogen Oxides
 HC - Hydro Carbon
 EGT - Exhaust Gas Temperature
 DPE - Di phenyl Ether
 DPE10 - 90 % Diesel + 10 % DPE blend
 DPE15 - 85 % Diesel + 15 % DPE blend
 DIGLYME - Di ethelene Glycol Di methyl Ether
 DIGLYME10 - 90 % Diesel + 10 % DIGLYME blend
 DIGLYME15 - 85 % Diesel + 10 % DIGLYME blend.