

ROLE OF OXYGENATED FUEL TO REDUCE DIESEL EMISSIONS: A REVIEW

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ABSTRACT

Particulate matter (PM) and oxides of nitrogen (NO_x emissions) are the two important harmful emissions in diesel engine. Fuel companies and the researchers around the world are devoted to reduce such emissions with different ways. Fuel modification, modification of combustion chamber design and exhaust after treatment are the important means to alleviate such emissions. In this context, engine researchers are hunting suitable alternative fuels for diesel engine. Among different alternative fuels, oxygenated fuel is a kind of alternative fuel. Diethylene glycol dimethyl ether (DGM), dimethoxy methane (DMM), dimethyl ether (DME), diethyl ether (DEE), methyl tertiary butyl ether (MTBE), dibutyl ether (DBE), dimethyl carbonate (DMC), methanol and ethanol have played their role to reduce diesel emissions. These fuels can either be used as a blend with conventional diesel fuel or as a neat fuel. The presence of oxygen in the fuel molecular structure plays an important role to reduce PM and other harmful emissions from diesel engine. The present work reports on the effect of oxygenated fuel on diesel combustion and exhaust emissions. It has been found that the exhaust emissions including PM, total unburnt hydrocarbon (THC), carbon monoxide (CO), smoke and engine noise were reduced with oxygenated fuels. NO_x emissions were reduced in some cases were increased depending on the engine operating conditions. The reductions of the emissions were entirely depended on the oxygen content of the fuel. It has been reported that the combustion with oxygenated fuels were much faster than that of conventional diesel fuel. This was mainly due to the oxygen content in the fuel molecular structure and the low volatility of the oxygenated fuels. The lower volatile oxygenated fuel evaporated earlier and very good air-fuel mixing was achieved during combustion eventually resulted in lower exhaust emissions.

Key words: Diesel Engine, Alternative Fuel, Oxygenated Fuel, Diesel Combustion And Exhaust Emissions.

1. INTRODUCTION

Due to price hike in 80's and the rapid depletion of fossil fuels researchers concentrate their research on alternative fuel. Methanol and ethanol were proved to be effective alternative fuels long ago for internal combustion (IC) engines. The oxygen in the methanol and ethanol molecule helps to make complete combustion when combusted with atmospheric oxygen. Most recently DME, oxygen content of 34.7% has been noticed as one of the promising alternative fuels for IC engine. DME can be derived from natural gas, coal or even from biomass sources. Zhang et al. (1) reported lower diesel emissions including smoke, THC, carbon dioxide (CO₂), NO_x, while slight increase in CO was noticed with DME compared to those of conventional diesel fuel. Authors reported the reason of reducing exhaust emissions were the presence of oxygen in the DME, absence of C-C bond, shorter ignition delay and

the instantaneous vaporization of DME. Like DME, DEE is another oxygenated fuel that has a very high cetane number. Masoud et al. (2) reported lower smoke and THC emissions due to higher cetane number and oxygen content of DEE. Authors also found lower CO emissions at high load condition, but higher at low load condition Also lower NO_x emissions were realized with DEE-diesel blends. Kapilan et al. (3) conducted experiments with 5 % DEE and found lower CO, THC and smoke emissions while a slight improvement in thermal efficiency was observed. Yeh et al. (4) investigated the effect of fourteen different oxygenated fuels on diesel emissions, specially PM and NO_x emissions. Authors found that for PM reduction, the most effective oxygenates on equal oxygen content basis were the C₉ – C₁₂ alcohols in both the engine and vehicle testing. No significant NO_x emissions was increased with the oxygenates.

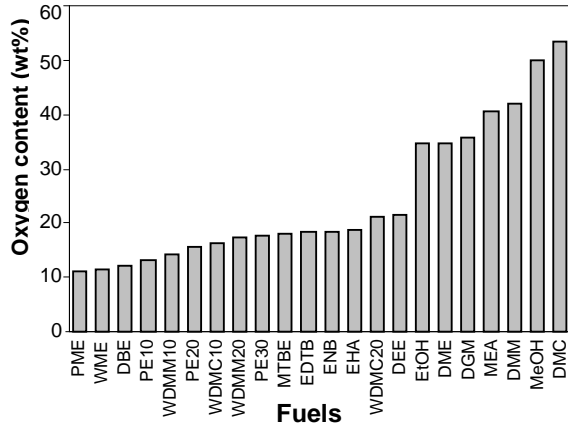


Fig 1 Oxygen content in different fuels

The current work focuses on diesel emissions, special emphasis on PM and NOx emissions with oxygenated fuels. The effects of liquid oxygenated fuels on diesel combustions are discussed in this work as many researchers worked on liquid oxygenated fuels. The advantages of using liquid fuel are: easy transportation, easy injection to the combustion chamber and require less space to store. The role of fuel oxygen on PM and NOx emissions is investigated with the previous research works. The target of the work is to make a correlation between fuel oxygen and the exhaust emissions.

Fujia et al. (5) investigated the effect of fuel oxygen on total PM and other exhaust emissions. Authors used CME, SME, RME, PME, WME and oxygenated fuels like ethanol, DMC and DMM. They reported that the total PM emissions were reduced with all biodiesels compared to that of diesel fuel (D160). THC emissions with all biodiesel reduced from 45-67%. Like THC, CO

emissions were reduced by 4-16% with the biodiesels. On the other hand, NOx emissions were increased with the addition of fuel oxygen content. Authors extended their research with three oxygenated fuels like ethanol, DMC and DMM. 10-30% ethanol was blended with PME, 10-20% DMC was added to WME and 10-20% DMM was added to DMM. The reductions in PM, THC and CO emissions and the increase in NOx emissions were due to the oxygen content in the fuel.

Zannis et al. (6) conducted engine experiments with oxygenated fuels. They used two oxygenated fuels, such as Diethylene Glycol Dimethyl Ether (Diglime – C₆H₁₄O₃) and Diethylene Glycol Dibutyl Ether (Butyl-Diglime – C₁₂H₂₆O₃), and one biodiesel (RME). These two oxygenated fuels and RME were blended with conventional diesel fuel (D1) maintaining oxygen content of 3 to 9%. The blended fuels were termed as DOX1, DOX2 and DOX3. The effect of fuel oxygen content on exhaust emissions at various engine loads was investigated. Authors reported relative changes of emissions between base fuel (diesel fuel) and oxygenated fuels DOX1 and DOX3. Soot, CO and THC emissions were reduced with increasing oxygen content for all loads. The reductions were higher for higher percentage of oxygen (9%) in the fuel blends and at high load condition. Authors reported that the reduction of soot, THC and CO emissions with increased fuel oxygen, which prevent to form soot emissions as less available carbon in fuel molecule. Authors also reported that the increase of local oxygen concentration enhances soot oxidation. On the other hand, NOx emissions were increased for higher oxygen content in the fuel. The additional oxygen in fuel rich region in conjunction with the increase in gas temperature due to the increase of cylinder pressure during combustion phase favors the formation of thermally generated NOx emissions.

Table 1 Oxygen content and molecular formula of different oxygenated fuels

Oxygenates	Oxygen (wt %)	Molecular formula
Dimethyl carbonate (DMC) (7)	53.30	C ₃ H ₆ O ₃
Diethyl ether (DEE) (8)	21.00	C ₄ H ₁₀ O
Diethylene glycol dimethyl ether (DGM) (7)	35.82	C ₆ H ₁₄ O ₃
Di-n-butyl ether (DBE) (7)	12.30	C ₈ H ₁₈ O
Dimethoxy methane (DMM) (7)	42.10	C ₃ H ₈ O ₂
Ethyl hexyl acetate (EHA) (7)	18.60	C ₁₀ H ₂₀ O ₂
Methyl tert-butyl ether (MTBE) (7)	18.18	C ₅ H ₁₂ O
Ethylene glycol di-t-butyl ether (EDTB) (7)	18.40	C ₆ H ₁₄ O ₂
Ethylene glycol mono-n-butyl ether (ENB) (7)	18.40	C ₆ H ₁₄ O ₂
Dimethoxy propane (DMP) (10)	-	(CH ₃) ₂ C(OCH ₃) ₂
2-methoxyethyl acetate (MEA) (13)	40.70	CH ₃ COOCH ₂ CH ₂ OCH ₃
Methanol (MeOH) (7)	50.00	CH ₄ O
Ethanol (EtOH) (7)	34.78	C ₂ H ₆ O
Palm oil methyl ester (PME) (5)	11.20	-
Waste cooking oil methyl ester (WME) (5)	11.30	-
Cottonseed oil methyl ester (CME) (5)	10.60	-
Rapeseed oil methyl ester (RME) (5)	10.50	-
PME 90% +EtOH (10%) (PE10) (5)	13.30	-
PME 80%+EtOH (20%) (PE20) (5)	15.50	-
PME 70%+EtOH (30%) (PE30) (5)	17.70	-
WME 90%+DMC10% (WDMC10) (5)	16.20	-
WME 80%+DMC20% (WDMC20) (5)	21.10	-
WME 90%+DMM10% (WDM10) (5)	14.20	-
WME 80%+DMM20% (WDM20) (5)	17.30	-

Nabi (7) also performed engine experiments with different oxygenated fuels. He investigated the effects of fuel oxygen on diesel emissions and combustion. In Figure 2, PM emissions were shown with soluble organic fraction (SOF) and insoluble fraction (ISF), which is actually termed as dry soot. The results in Figure 2 show the PM with neat diesel fuel, DGM100 and ENB100. Remarkable reduction in PM (Figure 2) and other emissions (not shown) were reported by the author. NOx emissions were also reduced with the oxygenated fuels (Figure 3). In Figure 2, only DGM was added to the conventional diesel fuel at volumetric percentages of 0, 25, 50, 75 and 100. Author concluded that it was oxygen, not the kinds or the chemical structures of the oxygenated fuels, was responsible for lower exhaust emissions. He also found the lower adiabatic flame temperature which caused the lower NOx emissions with oxygenated fuels. Author extended their research applying EGR in the exhaust system. Using EGR and an oxygenated fuel DGM, remarkable reductions in both smoke and NOx emissions were realized compared to those of diesel fuel.

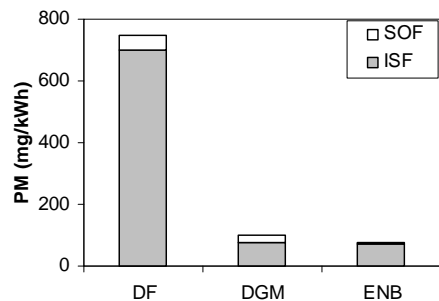


Fig 2. Improvement in PM with oxygenates (BMEP=0.75 MPa) (7)

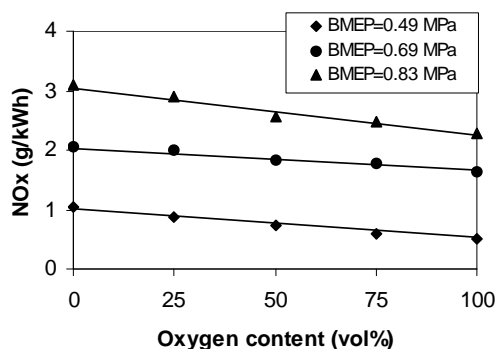


Fig 3. Improvement in NOx emissions with DGM at three BMEP conditions (7)

Nabi (7) attempted smokeless stoichiometric diesel combustion with a combination of high EGR, highly oxygenated fuels and a three way catalyst. Figure 4 shows the smoke emissions with DMM100 and different kinds of highly oxygenated liquid fuels at stoichiometric and high (30 vol%) EGR conditions. The smoke emissions formed easily at these conditions. 100 %DGM

and DGM based fuels blended with ordinary diesel fuel or different kinds of oxygenated fuels shown in Table 1. From Figure 4 it is observed that smoke emissions decreased sharply and linearly and became zero at an oxygen content of 38%. The smoke free diesel combustion was also confirmed with two other oxygenated fuels of oxygen content of 40 and 42%. From this study it was suggested that DGM80+MeOH20 (oxygen content of 38%), DGM80+DMC20 (oxygen content of 40%) and DMM100 (oxygen content of 42%) were suitable for partial load high EGR and high load stoichiometric diesel combustion.

Figure 5 (7) shows the influence of EGR on NOx emissions using DMM100. DMM100 realizes smokefree diesel operation at any engine conditions as discussed in Figure 4. The extreme right end points of Figure 5 represent to the stoichiometric condition where a three-way catalyst is believed to be effectively reduce NOx emissions. Significantly low NOx emissions were achieved by applying high EGR (30%) at different excess air conditions where high NOx emissions reductions with a three-way catalyst are difficult. It can be seen from the Figure that 30 % EGR produces NOx emissions below 100 ppm at any excess air condition. With oxygenated fuel and stoichiometric diesel operation significantly increase the maximum BMEP, which was found to be as high as 0.9 MPa without applying EGR. To achieve ultra low diesel emissions, author incorporated a three way catalyst in a diesel exhaust system. Figure 6 (7) shows the influence of a three way catalyst on three diesel emissions in partial load high EGR and high load stoichiometric diesel operation using DMM100. It can be seen from the Figure that the NOx emissions were reduced to as low as 100 ppm, while the THC and CO emissions were found to be about 200 ppm even at stoichiometric condition and without applying EGR. Thus it can be concluded that extremely low NOx and smokefree diesel operation was realized with the combination of a three way catalyst, high EGR and DMM100.

Anand et al. (8) investigated the influence of EGR and oxygenated fuel on diesel combustion and exhaust emissions. Authors used DEE as oxygenated fuel and blended with diesel fuel up to 30 vol%. Authors incorporated 5% EGR using 20 vol% DEE to diesel fuel. Without applying EGR, lower NOx emissions were resulted from DEE blended fuels compared to diesel fuel, while higher smoke emissions were realized with the same blends. Authors also reported simultaneous NOx and smoke emissions with DEE20 when applied EGR. 80% NOx emissions were reduced with 15% EGR using 20 vol% DEE to diesel fuel. At full load under 15 vol% EGR conditions with 20 vol% DEE, the smoke emissions were reduced to 2.1 Bosch smoke units (BSU) from the baseline smoke level of 4.2 BSU. The reductions were due to the oxygen availability in DEE, which supplies oxygen during combustion.

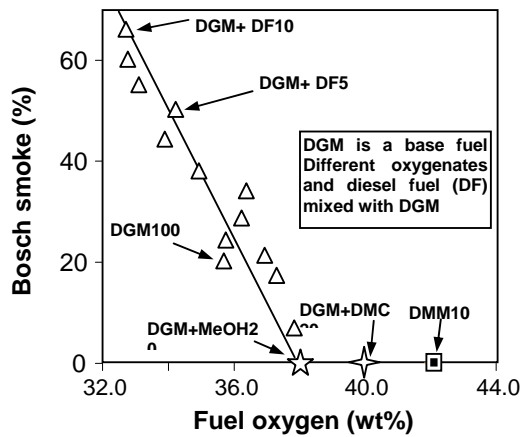


Fig 4. Smoke emissions with highly oxygenated fuels ($\phi = 1.0$, EGR = 30%) (7)

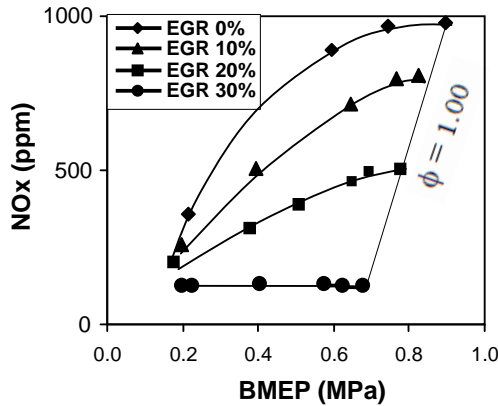


Fig 5. Influence of EGR on NOx emissions with DMM100 (7)

Miyamoto et al. (9) conducted experiments with eight kinds of oxygenated fuels to investigate the effect of low content oxygenate additive (maximum 10 vol%) on diesel emissions. The oxygen contents of the neat oxygenated fuels were ranging from 12.3 to 53.3 wt%. When blended these oxygenates with conventional diesel fuel, particulate and smoke emissions were suppressed significantly without increasing NOx. THC and CO emissions were also decreased slightly. Oxygen content in the blended fuels and the low volatility of the fuel were the reasons for decreasing the emissions.

Sathiyagnanam et al. (10) conducted diesel engine experiments with DMM and dimethoxy propane (DMP). Authors blended DMM and DMP as additives (1 ml to 3 ml) to diesel fuel. They conducted the experiments by introducing a diesel particulate filter (DPF). The experimental results were compared with and without DPF using the two oxygenated additives (DMM and DMP) and diesel as a base fuel. It was found that smoke and PM emissions were reduced with the addition of

DMM and DMP to diesel fuel. Smoke and PM emissions reduction was higher with DPF. NOx emissions, on the other hand were higher with DMM and DMP blended fuels. It was reported that NOx emissions were higher by 13 g/kWh with DMM and 16 g/kWh by DMP.

Lu et al. (11) investigated the spray characteristics and diesel exhaust emissions with three oxygenated fuels, namely ethanol, DMC and DMM. Authors investigated the spray characteristics (Sauter mean diameter (SMD) and axial mean velocity distribution) with DMM-diesel hybrid fuels, while the engine

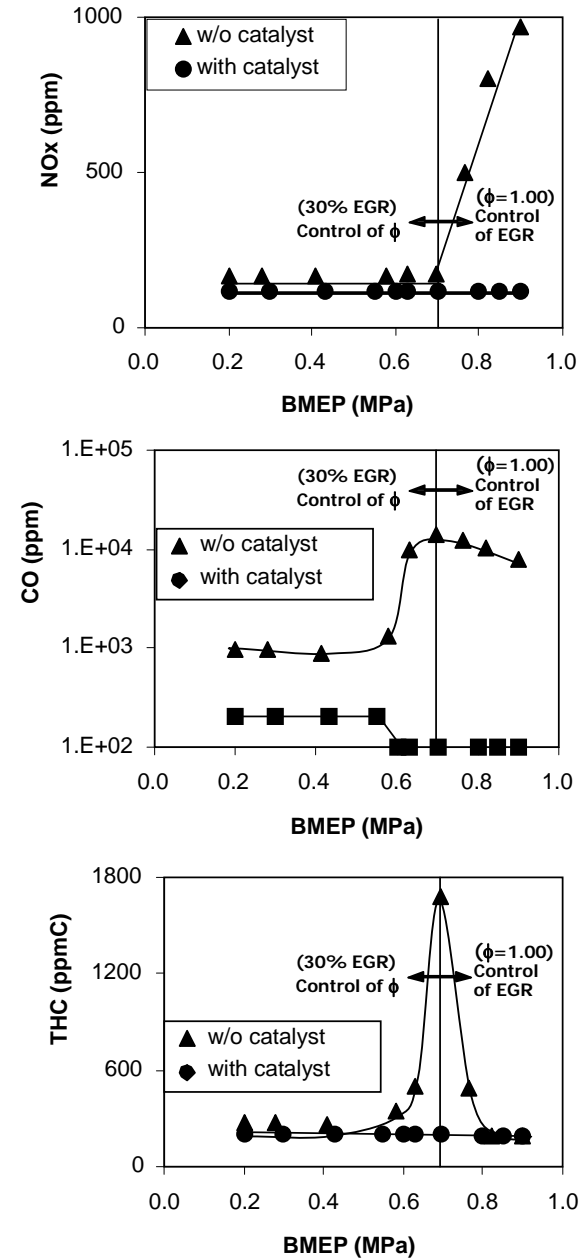


Fig 6. Influence of a three way catalyst on three diesel emissions (7)

experiments were performed with DMC-diesel hybrid fuels. For spray analysis DMM was blended to diesel fuel at blending ratios of 25 and 50 vol%, while for DMC the ratios were 10, 20 and 30 vol%. It was found that the droplet diameter of the DMM-diesel hybrid fuels decreased with increased axial distance from the injector tip. Compared to diesel fuel, the mean axial velocities of DMM-diesel hybrid fuels were higher. The lower SMD and higher axial mean velocity with DMM-diesel hybrid fuels were due to the inherent properties of lower kinematic viscosity and surface tension of neat DMM. Concerning exhaust emissions it was reported that the smoke and NOx emissions were reduced markedly with DMC-diesel hybrid fuels. The reductions were higher with the higher percentages of DMC to diesel fuel. The reduction of NOx emissions was due to the shorter combustion duration, while presence of oxygen in hybrid fuels was additional reason for reduction in smoke emissions.

Wang et al. (12) carried out engine experiments with several oxygenated fuels like biodiesel, ethanol, DMM and DMC. They made different oxygenated blends with diesel fuel. The biodiesels used in the experiments were derived from palm oil, waste cooking oil and acidified oil. It was found that the dry soot in PM emissions decreased significantly as the fuel oxygen content increased. SOF, which is a constituent of PM were found to be higher. Authors also investigated the effect of cetane number on SOF emissions. It was found that with the increase in fuel cetane number SOF emissions decrease. Authors found that an oxygenated fuel blend of 50% biodiesel, 15% DMC and 35% diesel fuel (oxygen content of the blend is 15.46%) met the Chinese 4th stage standard, which is equivalent to Euro IV for heavy duty engines without modifying or using any after treatment device.

Yanfeng et al. (13) did experiments with a new kind of oxygenated fuel, 2-methoxyethyl acetate (MEA) of oxygen content of 40.7 wt%. Authors reported significant reduction in smoke emissions with MEA blends. THC and CO emissions were also reduced with higher blending percentages of MEA to diesel fuel. However, the MEA blends had almost no effects on NOx emissions. Authors suggested that 15% MEA blend is suitable for diesel emissions, engine power and fuel economy.

Guo et al. (14) attempted engine experiments with a new oxygenated fuel, methyl 2-ethoxyethyl carbonate (MEEC) by introducing an ether group to DMC molecule. MEEC was blended with diesel fuel from 15 to 25 vol%. For a 25% MEEC blend with full load condition, CO was lessened by 29.2 to 40.5%, smoke by 0.3 to 0.5 BSU. NOx emissions were also lessened by 15.9% when the 15% MEEC was blended with diesel fuel. Output power of the engine was not noticeably changed with MEEC blends; however 2.5 to 5.5% fuel consumption was increased with 20% MECC. BSEC was improved by 10% when the engine was fuelled with 20%MECC.

Cheng et al. (15) carried out experiments with two oxygenates, DMM and DEE blended with conventional diesel fuel and a Fischer-Tropsch (F-T) diesel fuel to investigate their exhaust emissions reduction potential. Both DMM and DEE reduced PM emissions. Like PM, NOx emissions were also reduced with these blends. 35% less PM was observed with DMM30, while 30% less PM emissions were resulted in with DEE30. Compared to diesel fuel. F-T fuel also reduced PM emissions by 29%. NOx emissions, on the other hand were reduced by 1-10% with F-T, DMM and DEE blends. Fuel conversion efficiency (thermal efficiency) was reduced with the tested fuels compared to diesel fuel.

Chen et al. (16) investigated the effect of fuel oxygen on diesel emissions and performance. Authors blended ethanol and biodiesel to diesel fuel. The blending percentages of ethanol to diesel fuel were 10, 20 and 30%, while the biodiesel percentages were 5 and 10%. Engine torque was reduced and BSFC was increased with blended fuels. Using the diesel ethanol and biodiesel blends the PM was reduced significantly and the reduction was found to be significant at higher percentages of oxygen in the fuels. NOx emissions were slightly increased or the same as baseline diesel fuel. THC emissions with oxygenated blends were reduced under most operating conditions. CO emissions were increased at low to medium load conditions, but reduced at high load condition.

Tat et al (17) investigated diesel exhasut emissions with biodiesel. Authors used soy methyl ester (soy biodiesel) and high oleic methyl ester to investigate the brake specific NOx, THC, CO and smoke emissions. Both biodiesels are some sort of oxygenated fuels as approximately 11 wt% oxygen contain in their molecular structures. The brake specific THC and the smoke emissions were lower with the two biodiesels compared to diesel fuel. The brake specific NOx emissions with two biodiesels were higher than those of diesel fuel. The reasons of higher NOx emissions with biodiesels are as follows: the higher proportion of unsaturated fatty acid compositions in the biodiesels, advance injection timing leads to earlier ignition, which leads to higher peak cylinder temperatures. Biodiesels produce less soot than diesel fuel, which may increase NOx emissions.

2. CONCLUSIONS

This paper reports on the role of oxygenated fuels on diesel emissions. The results of the different research papers were analyzed and can be summarized as follows:

1. NOx, smoke and PM emissions with oxygenated fuels were reduced in most cases. However, the increase in NOx emissions were also reported with oxygenated fuels. The reductions in emissions were mainly dependent on fuel oxygen. The reductions were found maximum at the maximum percentage of fuel oxygen.
2. The increase in NOx emissions with biodiesel which is also an oxygenated fuel were the higher percentage of

unsaturated fatty acid compositions, lower soot emissions with biodiesels. Advance injection timing with biodiesels lead to earlier ignition. Earlier combustion with biodiesels resulted in higher peak cylinder temperatures. Higher cylinder temperatures with biodiesels eventually lead to higher NO_x emissions.

3. CO emissions were reduced with all oxygenated fuels at wide operating load ranges. The reductions were significant at higher load range. The fuel oxygen, which was responsible for reducing CO emissions made complete combustion in the fuel rich region.

4. Like CO emissions, THC emissions were also reduced with oxygenated fuels for all loading conditions, but a few reports showed higher THC emissions at lower load condition.

5. It is established that the reductions in smoke, PM, CO and THC emissions were dependent on fuel oxygen content. Lower boiling points and lower volatility of oxygenated fuels were the additional factors for the reduction in these emissions.

6. The engine thermal efficiency was reduced and in some cases increased with oxygenated fuels.

3. ACKNOWLEDGEMENTS

The opinions, findings and conclusions discussed in this paper are those of the authors mentioned in the list of reference and do not reflect opinions or views of the authors of this paper.

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