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SOME CONSIDERATIONS ON THE OXYGENATED FUELS FOR DIESEL ENGINES

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Summary. The paper describes some properties of synthetic oxygenates and their influence on exhaust emissions from diesel engines. According to the results of examinations, oxygenates are an effective method for obtaining the reduction in the PM, CO and HC emissions without a significant increase in the NO_x emission. The high price and poor availability of oxygenates pose however a certain barrier for their common application.

Key words: diesel engine, exhaust emissions, diesel fuel, fuel additives, synthetic oxygenates

INTRODUCTION

Internal combustion engines, operating primarily on petroleum-based fuels, dominate land transportation propulsion. They also play a major role in marine and light aircraft propulsion. The diesel engines are the most efficient of all internal combustion engines. Along with great durability and reliability, these are some of the well-established reasons why so many consumers choose diesel engines over gasoline ones. In addition, recent development in diesel technology (Fig. 1) have significantly reduced the noise and improved the driveability and performance of modern diesel vehicles making them even more attractive to drivers. The use of diesel engines is growing. In the heavy-duty road transport sector a diesel engine is the engine of choice throughout the world due to its great torque and efficiency. The popularity of diesel passenger cars varies form region to region around the world. The highest demand for diesels is in Europe, where it accounts for over 50% of the passenger vehicle market [Hallgren and Heywood 2001]. The market for diesels is smaller in Japan because of stricter emission requirements and shorter distances travelled. As both diesel engine and fuel technologies improve, the market is likely to grow in Japan in coming years. In the United States of America diesel passenger car market is extremely limited because of the relatively low cost of gasoline. Nevertheless, there is growing awareness of the advantages of diesel, particularly the fact that diesel can help reduce CO_2 emissions and fossil fuel consumption rates [Why … 2004].

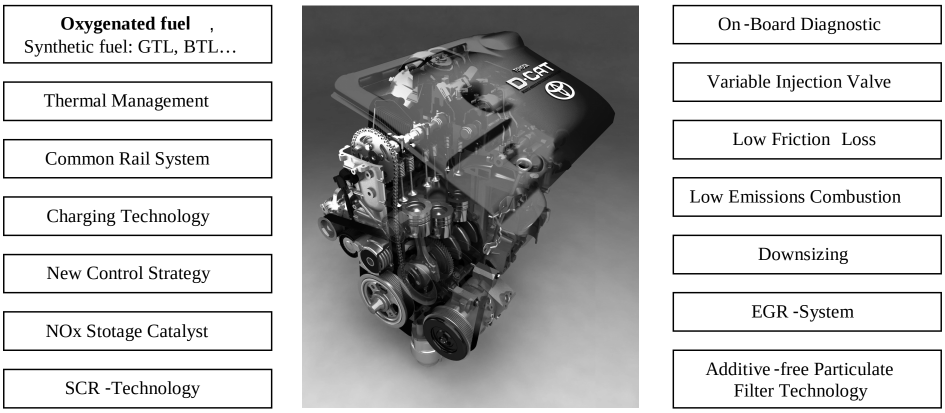

Fig. 1. Modern Diesel Engine Technology [Herrmann 2007]

One of the most important research topics on diesel engines is the reduction of emissions, but the suppression of in-cylinder emissions formation is normally hindered by the seemingly inherent trade-off between nitrogen oxides (NO_x) and particulate matter (PM). Without fundamental changes in combustion systems, one method alone has difficulty to significantly reduce NO_x and PM. Many of the methods for the reduction of diesel exhaust emissions have included modern diesel engine management/control technologies (see Fig. 1). The most effective methods are such as: exhaust gas recirculation (EGR), sophisticated fuel injection systems (e.g. Common Rail Systems), electronic controls and fuel properties modification. EGR has been applied to light-duty diesel engines and has mostly been effective in reducing tail-pipe NO_x emissions. However, the reduction in NO_x is at the expense of an increase in other emissions from the engine, increased engine wear and an increase in fuel consumption. Newly developed Common Rail injection systems allow for high injection pressures and pilot injections, which help to reduce the exhaust emissions and engine noise. Modern electronic controls have been used to optimise engine performance and to lower all the exhaust emissions evenly [Porai *et al*. 2004].

Despite the new promising diesel aftertreatment developments, the task to maintain stringent regulations appears to be great. This fact has encouraged automotive researchers to look for other options to help control diesel emissions. One such option is to control diesel exhaust emissions through fuel modification because it would affect both new and old engines. Modification of diesel fuel in order to reduce exhaust emissions can be performed by [Bielaczyc *et al*. 2003] increasing cetane number, reducing fuel sulphur, reducing aromatic content, increasing fuel volatility and decreasing the fuel density. While such changes can clearly provide some emissions benefits, the shortfall in NO_x and PM emissions control in diesel engines is so great that much more drastic fuel changes will be needed for a compromise. 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, even during cold-start and warm-up of the engine.

DIESEL OXYGENATES: SYNTHETIC OR BIO-COMPONENTS?

The fuel oxygenates, in case of gasoline, has been used for years. Ethanol is used most often, higher alcohols and ethers alternatively. The oxygen content in amount of up to 2,7% m/m is accepted by the European Standard EN 228:2004, European Directive 2003/17/EC and the Worldwide Fuel Charter. The advantageous effects of oxygenates on the gasoline engine exhaust emissions has thoroughly been examined and their use has commonly been established.

Table 1. Properties of some diesel oxygenates [Nabi *et al.* 2000, Hallgren and Heywood 2001, Miyamoto *et al*., Kozak *et al*. 2007]

Oxygenate	Molecular formula	Oxygen content % m/m	Density @20°C kg/m^3	Boiling point °C	Cetane number	Calorific value MJ/kg
Ethylene glycol dimethyl ether (monoglyme)	CH_3-O-$(CH_2)_2$-O-CH_3	36.6	867	85	86	23.6
Diethylene glycol dimethyl ether (diglyme)	CH_3-O-$(CH_2)_2$-O-$(CH_2)_2$-O-CH_3	35.8	943	162	126	24.5
Di n-butyl ether	CH_3-$(CH_2)_3$-O-$(CH_2)_3$-CH_3	12.3	771	142	ca. 140	38.7
Dimethyl carbonate	$CH_3O(CO)OCH_3$	53.3	1079	91	11	13.5
2-ethylhexyl acetate	$CH_3(CH_2)_7O(CO)CH_3$	18.6	878	199	–	35.2

The question of oxygenates for diesel fuels is different, as in this case their use is not regulated by any rules (except vegetable diesel esters). So far intensive examinations have been performed with use of the bio-oxygen-agents i.e. ethanol, which is not very useful as diesel fuel because of its high octane number and low boiling point, as well as with fatty acid methyl esters (FAME). The addition of FAME to diesel fuel generally ensures the reduction in the emission of the incomplete combustion products (CO, HC and PM). However, there is only about 10% m/m of oxygen in FAME, i.e. significantly less than in the synthetic oxygenates, where the oxygen content can be higher than 50%, and therefore FAME must be added in significantly larger amounts. Moreover, FAME is a mixture of many compounds and it is difficult to maintain its stable composition and parameters during a longer storage. The synthetic diesel oxygenates (Tab. 1) are free of such disadvantages and with regard to diesel fuels they have usually other advantages, as very high cetane number, for instance.

THE INFLUENCE OF SYNTHETIC DIESEL OXYGENATES ON EXHAUST EMISSIONS

There are not many papers available in which the examinations performed while using the synthetic diesel oxygenates have been presented. The reports concerning such examinations come mostly from the USA [Cheng and Dibble 2001, Hallgren and Heywood 2001, Cheng *et al*. 2002, Layton and Marchetti 2002, Upatnieks and Mueller 2004 and Japan [Asakara and Sakurai 1994, Murayama T. *et al*. 1995, Miyamoto *et al*. 1998, Nabi *et al*. 2000, Takei *et al*.] however, some European papers can also be found [Beatrice *et al*. 1999, Delfort *et al*. 2002, Bielaczyc *et al*. 2006, Kozak *et al*. 2007]. Most of the examinations deal with the PM emissions, as the CO and HC emissions can be easily reduced with the use of the oxidation catalyst and the NO_x emissions cannot be radically reduced by the modification of fuel.

Generally, the oxygenated diesel blends show a great reduction in the PM emissions, to an extent far greater than their amount of addition. Interesting research concerning an effect of the oxygenated compounds on the PM emissions has been presented by B. Delfort and co-workers [Delfort *et al*. 2002]. Oxygenates were selected among dialkyl ethers, dialkyl acetals, polyacetals and dialkyl carbonates. They have been blended in base diesel fuel (Euro III) in a concentration of 5% v/v. The PM emissions of these blends have been compared to the base fuel emissions. The PM reduction was determined using the same vehicle on chassis dynamometer, during NEDC test.

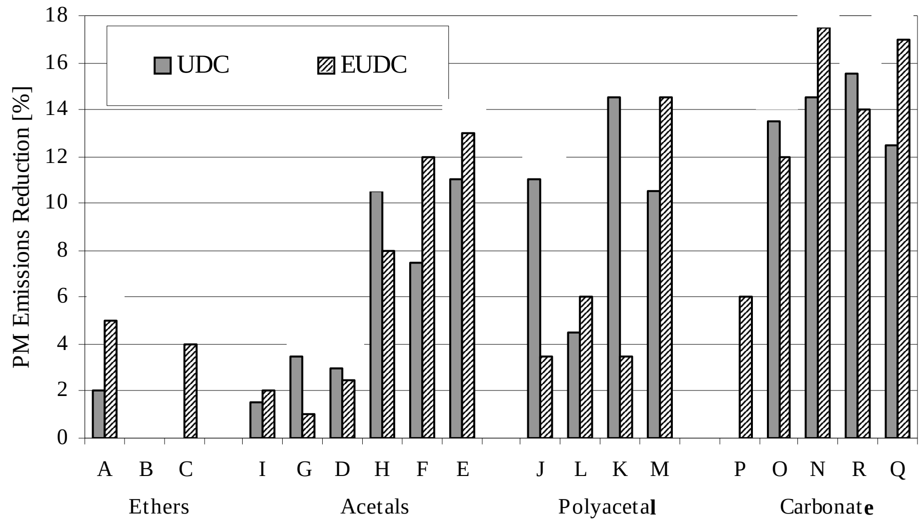

Fig. 2. Influence of chemical structure of various oxygenates on PM emissions reduction during NEDC test (UDC+EUDC); the numbers over chart's columns shows the oxygen content in an oxygenated fuel [Delfort *et al*. 2002]

The research has shown that PM emissions reduction is generally dependent on oxygen content in fuel, however, there is no absolute relationship between PM reduction and global fuel oxygen content. Fuel oxygen content is the most important parameter only within the same chemical family (Fig. 2). It seems that at constant volume of oxygenate, carbonate compounds have the best results in terms of the PM reduction.

It is of great importance that the reduction in the PM emission caused by oxygenates is not accompanied by a significant increase in the NO_x emission, which in some cases can even be reduced (Fig. 3 and Tab. 2) resulting in a favorable shift in the PM/NO_x trade-off. With a fuel-inducted reduction in PM, engine adjustment (e.g. high

EGR rate) and modification can be subsequently employed to reduce NO_x, with overall effect being a simultaneous reduction in both pollutants.

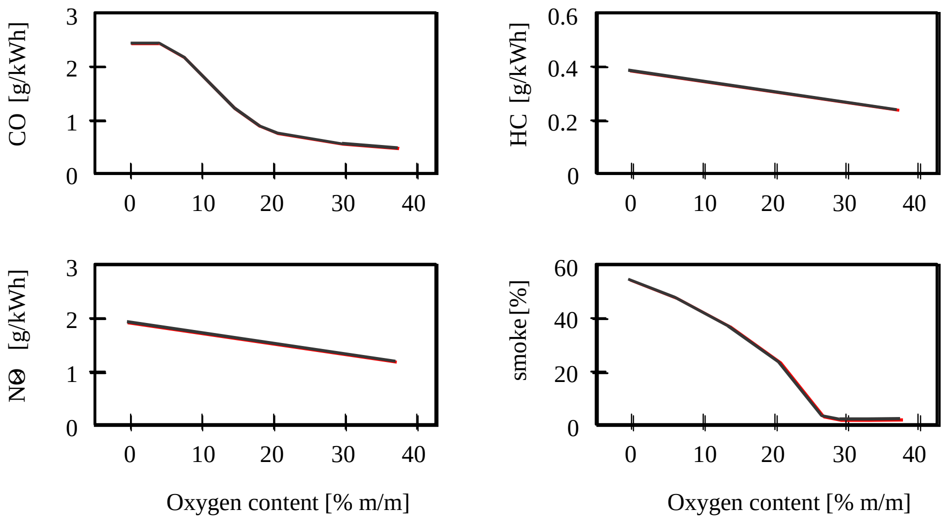

Fig. 3. Exhaust emissions as a function of diesel fuel oxygen content;
Light-duty DI diesel engine at 1320 rpm and bmep = 0.75 MPa [Miyamoto *et al*. 1998]

Table 2. Percentage reduction of exhaust emissions of the diglyme blends
with respectto the neat diesel fuel (Euro IV);
FIAT M724 1.9 JTD engine at 2000 rpm and bmep = 0.2 MPa [Beatrice *et al*. 1999]

Fuel	HC	CO	NO_x	PM
Diesel fuel + 10% Diglyme	29%	26%	5%	11%
Diesel fuel + 20% Diglyme	24%	36%	8%	48%
Diesel fuel + 30% Diglyme	33%	29%	8%	57%

The authors of this paper are fairly experienced in research on diesel oxygenates and their influence on exhaust emissions. Our experiments were mainly performed at a chassis dynamometer over the New European Driving Cycle (NEDC). So far, we have tested about 12 different diesel oxygenated additives at low concentrations (≤10%). The oxygenated additives proved their effectiveness in reducing exhaust emissions. As far as the effectiveness of oxygen is concerned – 1% of oxygen in fuel was reduced (depending on oxygenate): CO and HC emissions by up to 30% and PM emissions by up to 10% during the NEDC. In general, application of oxygenated additives slightly increased NO_x emissions – up to 5% during the NEDC. The results of our experiments were presented at the FISITAWorld Automotive Congress [Bielaczyc *et al*. 2006] and SAE Fuels&Emissions Conference [Kozak *et al*. 2007] and more detailed results of our research can be found in the appropriate conference proceedings. Our more discerning research on diesel oxygenates influence on combustion process and exhaust emissions is still in progress. Oxygenated fuels are evaluated at a in-cylinder combustion pressure characteristics, heat release and combustion phasing. In-cylinder optical measurements of flame lift-off length and natural luminosity are obtained simultaneously with engine-out emissions measurements. Some recent results are presented in Figures 4 and 5.

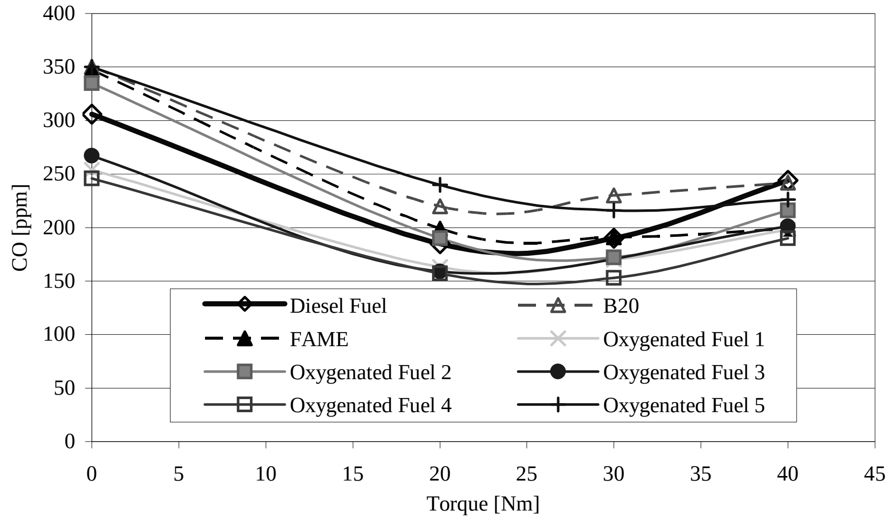

Fig. 4. CO concentration in exhaust gas as a function of load torque; SB 3.1 engine at 1600 rpm, prototype CR injection system, injection pressure 80 MPa; oxygenated fuels contained various synthetic oxygenates at 10% concentration

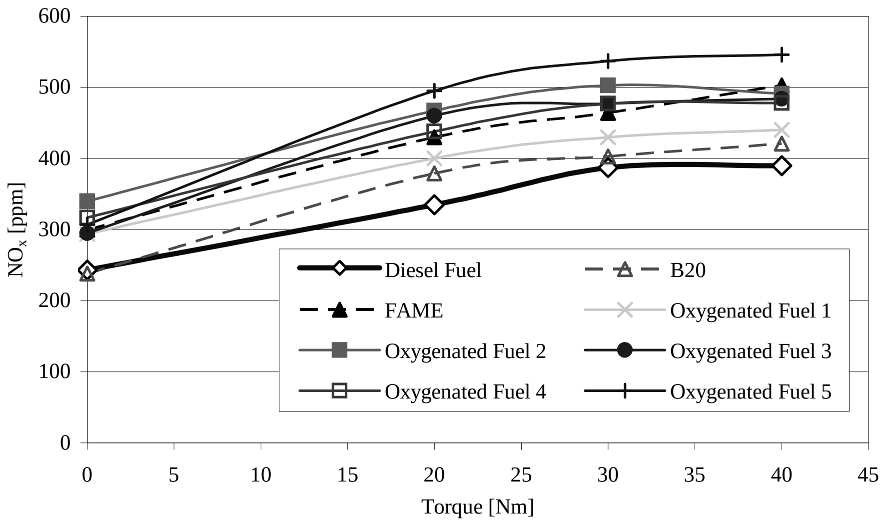

Fig. 5. NO_x concentration in exhaust gas as a function of load torque; SB 3.1 engine at 1600 rpm, prototype CR injection system, injection pressure 80 MPa; oxygenated fuels contained various synthetic oxygenates at 10% concentration

CONCLUSION

Oxygenates, in addition to their numerous advantages, have also some disadvantages, such as high price and a poor availability. The oxygenates for diesel fuels certainly do not present any panacea for the exhaust emissions. The time for any single actions aiming at the radical reduction in the emissions is over. The oxygenates can, and in the authors' opinion they should, be one of the elements of the complex action limiting the emissions from the diesel engines. On one hand lack of „the connected vessels system" existing in case of the oxygenates is very valuable. On the other hand the results of their long-lasting influence on the engine and exhaust gas treatment system are still not known. Well to wheel CO_2 balance needs also to be checked. Theoretically, the ease with which the oxygenates can be used and a wide range of possible effects support the idea of their application in all vehicles. Practically, the modification of fuel, including the use of the oxygenates, is only a rational way for reducing the emissions from old vehicles which are the most troublesome for the environment.

According to the authors' opinion the oxygenated diesel blends will be initially used in the areas exposed to the highest ecologic risk, e.g. the large urban agglomeration. So the situation will develop in a similar way as in the case of reformulated gasoline. Increase in the production of oxygenates will result in their low price and more and more common use.

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