ALCOHOLS/ETHERS AS OXYGENATES IN DIESEL FUEL: PROPERTIES OF BLENDED FUELS AND EVALUATION OF PRACTICAL EXPERIENCES

IEA ADVANCED MOTOR FUELS

ANNEX XXVI FINAL REPORT

TEC TransEnergy Consulting Ltd
Befri Consult

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ABSTRACT

Oxygenates blended into diesel fuel can serve at least two purposes. Components based on renewable feedstocks make it possible to introduce a renewable component into diesel fuel. Secondly, oxygenates blended into diesel fuel might help to reduce emissions.

A number of different oxygenates have been considered as components for diesel fuel. These oxygenates include various alcohols, ethers, esters and carbonates. Of the oxygenates, ethanol is the most common and almost all practical experiences have been generated from the use of diesel/ethanol blends (E-diesel). Biodiesel was not included in this study. Adding ethanol to diesel will reduce cetane, and therefore, both cetane improver and lubricity additives might be needed. Diesel/ethanol emulsions obtained with emulsifiers or without additives are “milky” mixtures. Micro-emulsions of ethanol and diesel can be obtained using additives containing surfactants or co-solvents. The microemulsions are chemically and thermodynamically stable, they are clear and bright blends, unlike the emulsions.

Storage and handling regulations for fuels are based on the flash point. The problem with, e.g., ethanol into diesel is that ethanol lowers the flash point of the blend significantly even at low concentrations. Regarding safety, diesel-ethanol blends fall into the same category as gasoline. Higher alcohols are more suitable for diesel blending than ethanol.

Currently, various standards and specifications set rather tight limits for diesel fuel composition and properties. It should be noted that, e.g., E-diesel does not fulfil any current diesel specification and it cannot, thus, be sold as general diesel fuel. Some blends have already received approvals for special applications.

The critical factors of the potential commercial use of these blends include blend properties such as stability, viscosity and lubricity, safety and materials compatibility. The effect of the fuel on engine performance, durability and emissions is also of importance. So far, no engine manufacturers have indicated they will extend warranty coverage to their equipment when operating with E-diesel. They believe there are simply too many unanswered questions as well as the potential for liability exposure due to the increased flammability range of E-diesel.

The reports on field tests with oxygenated diesel fuels are rather scarce, especially reports on recent tests. There are, however, some reports available on engine tests and tests with trucks, buses and even off-road equipment. Most of the available test results identified fuel economy and cost as the only appreciable differences between E-diesel and conventional diesel fuel. Most emissions tests with heavy-duty engines confirm the effect of a substantial reduction in PM when running with E-diesel. The typical range for PM reduction is 20 – 40 %. Most studies also report reduced NO_x emissions.

Earlier, there were a lot of activities with E-diesel in Sweden. For the time being, California and Brazil are leading the development of E-diesel.

PREFACE

There is an ever growing interest in biofuels for transport. Ethanol is an attractive alternative fuel because it is a bio-based resource and it is oxygenated, thereby providing potential to reduce particulate emissions in compression-ignition engines. It is accepted that the addition of ethanol to diesel fuel will have a beneficial effect in reducing the PM emissions at least.

In Milan in April 2002, at its 27th meeting, the Executive Committee of the IEA Implementing Agreement of Advanced Motor Fuels (AMF) decided to start a new Annex on alcohols and ethers as oxygenates in diesel fuel (Annex XXVI). The report at hand is the final report of this Annex. Originally the Annex was designed to focus on practical experiences of using alcohols/ethers as oxygenates in diesel fuel. Compared with the original project plan, a more detailed chapter about fuel properties was added to the final report, also dealing with limitations of blending low-boiling components into diesel fuel.

The following countries took a decision to participate in Annex XXVI:

- Canada (Natural Resources Canada)
- Italy (Euron)
- Japan (Organization for the Promotion of Low Emission Vehicles LEVO and New Energy and Industrial Technology Development Organization NEDO)
- UK (Department for Transport)

The initial part of the work was carried out by Befri Konsult of Sweden. The report was finalised by TEC TransEnergy Consulting Ltd (Finland) in cooperation with Turku Polytechnic (Finland).

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1 PROJECT DESCRIPTION

In Milan in April 2002, at the 27th meeting of the Executive Committee of the IEA Implementing Agreement of Advanced Motor Fuels (AMF), Mr. Rolf Berg of Befri Konsult, Sweden, presented a proposal to start a new Annex on alcohols and ethers as oxygenates in diesel fuel.

The subject of oxygenates for diesel fuels had already been dealt within Annex XVIII, "Future Greener Diesel Fuels" by Battelle Memorial Institute. At the same meeting in Milan, the Executive Committee decided to close Annex XVII, after having approved the final report. Mr. Berg proposed a continuation to the work of Battelle, a new Annex with a practical approach, focusing on field tests around the world.

Mr. Berg's proposal was approved, and the new Annex, "Evaluation of practical experiences of ongoing projects around the world using alcohols/ethers as oxygenates in diesel fuel" was approved and designated number XXVI. In his project description, Mr. Berg listed the following objectives and tasks:

- The main objective is to get a truthful picture of the performance of such diesel blends containing alcohols or ethers that have reached pilot or commercial status.
- Identification of various types of diesel/oxygenate blends
- Evaluation of fuel properties such as combustion properties, lubricity, effect on vapour pressure and miscibility
- Evaluation of results from field tests, including issues such as emissions, fuel consumption, driveability and running costs

The original budget of the Annex was set at 40,000 USD. The following countries took a decision to participate in Annex XXVI:

- Canada (Natural Resources Canada)
- Italy (Euron)
- Japan (Organization for the Promotion of Low Emission Vehicles LEVO and New Energy and Industrial Technology Development Organization NEDO
- UK (Department for Transport)

At the 30th meeting of the AMF Executive Committee in Sao Paulo in October 2004, the participants of the Annex asked TEC TransEnergy Consulting Ltd of Finland to assist Befri Konsult in preparing the final report of Annex XXVI.

As the development of transportation fuels has been rapid, especially regarding the introduction of biocomponents, the review on field experience with oxygenated diesel fuels has been updated. Compared with the original project plan, a more detailed chapter on fuel properties, including limitations of blending low-boiling components into diesel fuel, has been added to the final report. Consequently the title of the final report has been modified slightly: “Alcohols/ethers as oxygenates in diesel fuel. Properties of blended fuels and evaluation of practical experiences”. Running costs are touched upon only very briefly. In the case of costs of diesel/ethanol blends, the main variable is the cost of ethanol and ethanol percentage. The price of ethanol can vary by a factor of three, depending on local conditions and processing technology. The cost for the additives needed is anyway smaller than the cost of the ethanol itself.

Biodiesel, i.e., esters of vegetable oils also contain oxygen. However, the study at hand focuses on alcohols and ethers as blending components for diesel. Special attention is given to diesel-ethanol blends. In this text “E-diesel” is used as a general denotation for diesel/ethanol emulsions, although “E-diesel” is also used as a trade mark.

2 RATIONALE FOR USING OXYGENATED FUEL COMPONENTS IN DIESEL

2.1 GENERAL ON ALTERNATIVE FUELS

Road transport typically accounts for some 20 to 30 % of the total energy usage, depending on the country. Moreover, the transportation fuel market (including international marine bunkers) represents about 53 % of the world refinery product demand (Gielen 2005).

As a consequence of cyclic combustion and highly variable load, the relative contribution of transport to certain emission components is even higher than the share of energy use. Thus the transportation sector is a major consumer of energy and additionally a major polluter, and is therefore facing many challenges. The number of vehicles around the world is increasing rapidly, and so are the environmental effects and the use of energy in transport. Whereas many other sectors of society have been able to stabilise or cut CO_2 emissions, transport related CO_2 emissions tend to be increasing both in relative and absolute terms (Figure 1).

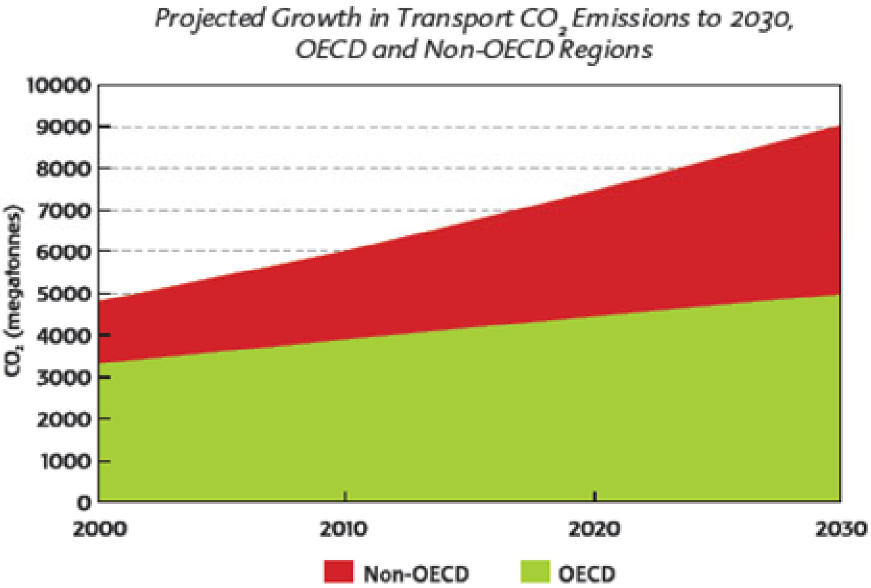


Figure 1. Projected transport CO_2 emissions. (IEA 2004)

At the same time new possibilities are opening up. The array of options is widening, not closing in. This is true for both fuel and vehicle technology options. We are closer than ever to a wide-scale use of alternative fuels. Today we have biofuels and natural gas on the agenda, for tomorrow there might be synthetic fuels and even hydrogen. (AMF 2004)

In general, there are several reasons to promote alternative fuels or alternative fuel components in transportation. The reasons can be as follows:

- reduction of oil dependency
- reduction of greenhouse gas emissions
- reduction of toxic exhaust emissions
- enhancement of overall energy efficiency
- reduction of fuel costs
- societal reasons (e.g., employment in the agricultural sector)
- any combination of the reasons mentioned above

In Europe, there is a Directive (2003/30/EC) in place calling for a 2 % fuel replacement by biofuels (energy base) in 2005 and a 5.75 % replacement in 2010. So far the target values are indicative, not mandatory. However, the Directive states that the Commission will monitor the development in biofuels, and if the development is not satisfactory, mandatory values might be introduced. The first review of the progress will be completed by the end of 2006.

Ethanol is an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression–ignition engines. It is accepted that the addition of ethanol to diesel fuel will have a beneficial effect in reducing the PM emissions at least. While there is considerable value in being able to use the fuel directly in an unmodified engine, small adjustments to fuel injection characteristics may result in further gains in reducing emissions. (Hansen et al 2005)

2.2 POSITION OF DIESEL

The diesel engine has taken its position as the leading prime mover for heavy-duty vehicles mainly on the grounds of high fuel efficiency and reliability. In most countries, diesel is in practise the sole fuel for heavy-duty vehicles, buses and trucks. The main drawbacks of the diesel engine are high particle emissions and high emissions of nitrogen oxides.

In Europe, diesel also has a very strong position in passenger cars. In 2004, the diesel share of newly registered passenger cars in Western Europe reached all-time high as 51.9 percent of newly registered passenger cars were diesel powered. (Bosch 2004). Stringent emission standards for passenger cars in the USA and Japan have hindered the penetration of diesel passenger cars to these markets. The overall share of light- and medium-duty diesels in the US was 3.37 % in 2004. (Green Car Congress 2005)

In Finland, the diesel share of new passenger cars was only some 15 % in 2004. Despite this fact, the share of diesel fuel sales of the total amount of transportation fuels was some 51 % (by weight) due to the diesel fuel use of the heavy-duty vehicle fleet. (Finnish Oil and Gas Federation 2005)

Overall, the relative share of diesel of the total fuel consumption by all highway vehicles has been steadily increasing. (Figure 2, DieselNet).

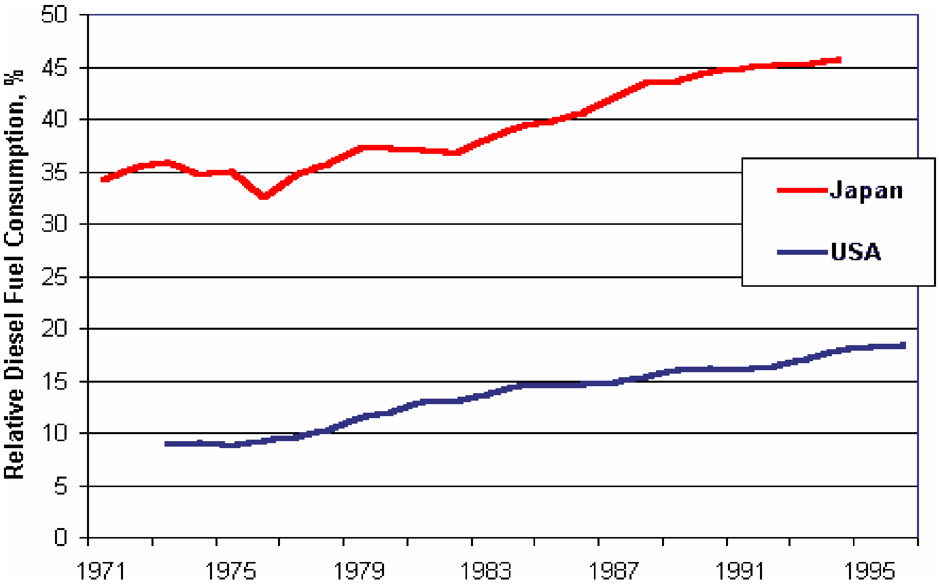


Figure 2. Overall share of diesel fuel in Japan and USA. (DieselNet)

For evident reasons, when planning the implementation of alternative fuels or, e.g., biocomponents, diesel vehicles and diesel fuel cannot be overlooked, as diesel by volume in most cases is very close to gasoline. In addition, the greater part of the commercial vehicle operations rely on diesel vehicles.

Fuel modifications provide an interesting option to emission reductions for the existing vehicle fleets. Sulphur-free low aromatic, low density fuel like the Swedish Environmental Class 1 diesel fuel can reduce NO_x emissions by some 10 % and particle emissions by some 25 % relative to ordinary diesel fuel. (Nylund 2005)

The main advantages of fuel modifications are that the lead time for implementation is relatively short, and that in the best cases no modifications are needed to the fuel distribution system or the vehicles.

2.3 OXYGENATES FOR DIESEL FUELS

Oxygenates blended into diesel fuel can serve at least two purposes. Components based on renewable feedstocks make it possible to introduce a renewable component into diesel fuel. Such components could be bio-ethanol, biodiesel or synthetic components made from biomass via gasification and synthesis gas.

Depending on the fuel component and the overall fuel chain, the biofuel options can be anything from comparable to significantly better compared with diesel fuel regarding greenhouse gas or carbon dioxide emissions. Regardless of the effects on CO_2 emissions, every biocomponent will contribute to fuel diversification.

Secondly, oxygenates blended into diesel fuel might help to reduce emissions. Especially for heavy-duty vehicles, the most critical emission components are particles and oxides of nitrogen. Several studies have shown that oxygenated fuel components help to bring down particle emissions.

In the case of oxides of nitrogen, oxygenates can work in two directions. Conventional biodiesel tends to increase NO_x emissions, alcohol based fuels and emulsions (diesel + alcohol, diesel + water) tend to lower NO_x emissions.

In Chapter 4, the effects of oxygenates on emissions and the mechanisms behind the changes will be discussed in detail.

3 GENERAL REQUIREMENTS FOR DIESEL FUELS

3.1 GENERAL

There are a number of fuel properties, both physical and chemical, which are crucial for the proper operation of a diesel engine. National and regional regulations and standards control diesel fuel quality. Fuel quality requirements are in place partly to secure the operability and integrity of vehicles and engines, partly to control exhaust emissions.

Included on the list of regulations and standards are, among others, the European Fuels Directives 98/70/EC and 2003/17/EC, the European diesel standard EN 590, US EPA's diesel fuel requirements, US ASTM diesel fuel standards, and Japanese JIS K 2204 fuel standards. In addition, the auto- and engine manufactures have compiled a common document on fuel quality requirements called the World Wide Fuel Charter (WWFC 2002).

In Europe, the fuel Directives set limit values only on cetane number, density, 95 % point of distillation, content of polycyclic aromatic hydrocarbons and sulphur content. Cetane, density and distillation are directly related to the general performance of the engine, the rest of the parameters mainly to exhaust emission control. The EN 590 standard, on the other hand, also covers fuel properties like flash point, water content, copper strip corrosion, oxidation stability, lubricity, viscosity, and cold properties. (DieselNet 2005)

In principle, the following discussion of diesel fuel properties follows the order in the EN 590 standard. Some comments on, e.g., ethanol as a fuel component are included already here, although a more detailed discussion about the characteristics of various oxygenates follows later in Chapter 5.

Appendix 1 presents the European Directive 2003/17/EC on fuel quality, the 1999 version of the EN 590 standard, and two different classes (Categories 3 & 4) for diesel fuel quality defined in the WWFC.

3.2 IGNITION QUALITY

The diesel process is based on auto-ignition of the fuel. The fuel is delivered by a high-pressure injection system directly into the combustion chamber. Two distinct phases of the combustion can be identified, premixed and diffusion type (mixing controlled) combustion.

Fuel injected during the ignition delay period (time from start of injection to start of combustion) is atomized, evaporated, mixed with air, ignited through auto-ignition and burned in premixed mode. Once combustion has started, the fuel discharging from the injector is evaporated and ignited almost immediately, burning in diffusion mode.

The compression ignition combustion process, including the formation of pollutants, is extremely complicated because the three-dimensional process is by nature unsteady and heterogeneous. (Heywood 1988)

The rate of heat release of the premixed combustion is higher compared with the diffusion type of combustion. Using fuels with low ignition quality increases the ignition delay, the amount of fuel injected during the ignition delay period and the share of premixed combustion. All this results in high pressure gradients, rough engine operation, high noise levels, and even in increased NO_x emissions. Good ignition properties are, thus, important.

For conventional hydrocarbon fuels, either cetane number determined by a special CFR test engine or a calculated cetane index is used to describe ignition quality. Straight-chain paraffinic compounds (normal alkanes) have the highest ignition quality, which improves as the chain length increases. Aromatic compounds have poor ignition quality, as do the alcohols. Figure 3 shows the effect of hydrocarbon structure on ignition delay.

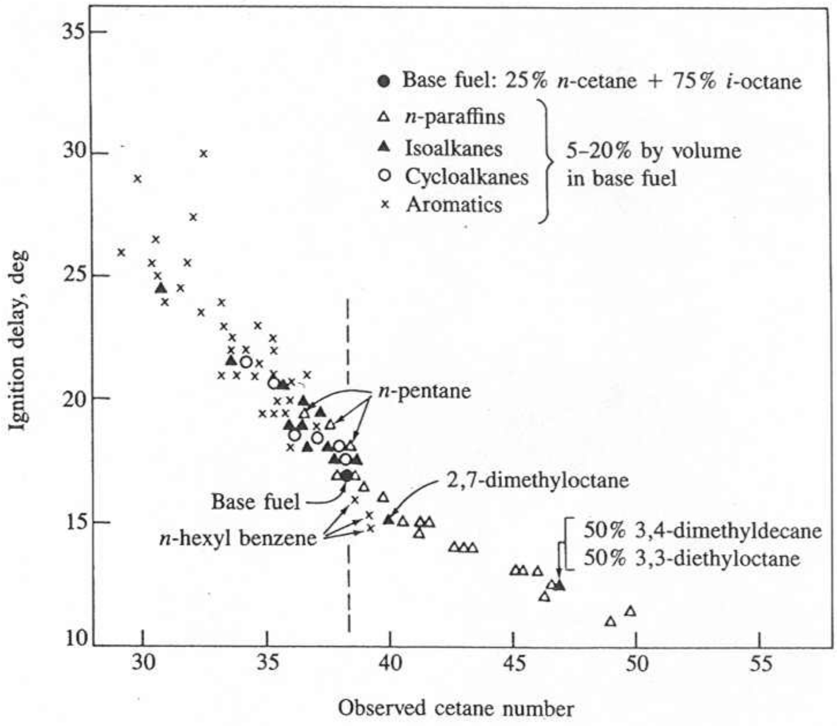


Figure 3. Effect of type of hydrocarbon structure on ignition delay. (Heywood 1988)

Today, the European fuels Directive requires a minimum cetane number of 51. If, e.g., ethanol is blended into diesel at major concentrations, the blend has, most probably, to be treated with an ignition improver additive. It is not possible to operate a conventional diesel engine with neat alcohol, as the fuel simply will not ignite. To run a diesel type engine on neat alcohol, either the fuel has to be treated with an ignition improver additive (organic peroxides, nitrates and nitrites, typically hexyl nitrates), or the engine has to be modified (ignition secured by pilot injection of diesel, or ignition by a sparkor glow-plug). Scania has employed fuel modifications for its heavy-duty ethanol engines, while Detroit Diesel opted for glow-plug assistance. (Aakko 2004)

3.3 DENSITY AND HEATING VALUE

All diesel fuel injection systems are based on volumetric metering. In order to control maximum engine output and emissions, EN 590 sets a relatively narrow band for density, 820 – 845 kg/m^3 at +15 ^{o}C. At a constant heating value, lower density means reduced maximum power output, higher density increased output and increased particle formation.

For conventional diesel fuel, heating value per volume is some 36 MJ/l. The corresponding value for ethanol is some 21 MJ/l (Bosch 2002). If ethanol were metered at the same rate as ordinary diesel fuel, the engine output with ethanol would be some 60 % relative to diesel. For a given power output, the volumetric fuel consumption with ethanol would be some 1.7 times higher compared with diesel. For engines running on neat alcohol, the fuelling rate has to be modified. Modifications may also be needed when running on blended fuels. Increased fuelling rates lengthen the injection period, and may thus affect engine and emission performance.

3.4 FLASH POINT

Flash point is the limit temperature for the formation of an ignitable air-fuel vapor mixture. Storage and handling regulations for fuels are based on the flash point. In Europe, diesel fuel has to have a flash point higher than 55 °C. In the US, the Class II liquid requirement for flash point is higher than 38°C. The problem with, e.g., ethanol blended into diesel is that ethanol lowers the flash point of the blend significantly even at low concentrations. Regarding safety, diesel-ethanol blends fall into the same category as gasoline. Similar procedures for safety, handling and storage are required for diesel-ethanol blends as for gasoline.

3.5 WATER CONTENT

The solubility of water into conventional diesel fuel is very limited. Any free water will cause problems, i.e., freezing at low temperatures and, even more serious, damages and corrosion in the high-pressure injection system. The solubility of ethanol into diesel is also limited. Ethanol has therefore to be emulsified with diesel. A high water content will increase the risk of phase separation and even the risk of biological instability. (Reynolds 2002)

3.6 CORROSION, LUBRICITY

The high-pressure injection system is prone to wear and corrosion. Most diesel fuels are treated with multi-functional additive packages to improve lubricity and suppress corrosion. Wear of injection systems was a big issue when low-sulphur or sulphur-free diesel fuels were introduced. The 1999 version of the EN 590 fuel specification (Euro 3) contains a requirement of a HFRR (High Frequency Reciprocating Rig) test for lubricity. Just like for water, the lubricity of ethanol is poor. When operating a diesel type engine with neat ethanol, the fuel has to be treated with both ignition improver and lubricity additives.

3.7 VISCOSITY

Viscosity and fuel density are two important parameters when designing fuel systems. As the fuel density, viscosity should also be kept in a rather narrow window. Low viscosity will increase leakage and delay start of injection in fully mechanical injection systems. High viscosity will impose additional loads on the injection system.

3.8 OTHER FUEL PARAMETERS

Some of the fuel properties and parameters listed in the standards are not restricting the use of, e.g., ethanol as a blending component in diesel fuel. Such properties include sulphur content, content of polycyclic aromatic hydrocarbons (PAH), carbon residue, and end of distillation. In the case of sulphur and PAHs, ethanol acts as a diluent.

Table 1 presents a qualitative summary of ethanol in comparison with conventional diesel fuel. The listing of fuel properties is based on EN 590.

Table 1. Ethanol in comparison with conventional diesel fuel.

Fuel property	**Ethanol in comparison with diesel fuel**
Ignition quality	much worse, need for additives (or engine modification)
Density	slightly lower, 40 % lower volumetric heating value
Sulphur	sulphur-free
PAH	zero aromatics
Flash point	low, creates security problems if blended into diesel
Carbon residue	low
Ash	low
Water content	ethanol is water soluble and hygroscopic, emulsions may suffer from stability problems
Total contamination	low
Copper strip corrosion	promotes corrosion
Oxidation stability	oxidation and biological stability depend on water content, little information available
Lubricity	low, need for additives
Viscosity	low
Distillation	fixed distillation point 78 ^{o}C

4 EFFECTS OF OXYGENATES ON EMISSIONS

4.1 GENERAL

From an air quality point of view, particles and nitrogen oxides are considered to be the most troublesome emission components in diesel exhaust.

Figure 4 shows a summary of pollutant formation mechanisms in a direct injection diesel engine. Figure 4 makes a distinction between the premixed and the mixing controlled combustion phase. In the premixed phase, nitrogen oxide formation and hydrocarbon emissions due to over-lean mixture dominate. In the mixing controlled phase, soot is formed in the rich zones of the fuel jets (Heywood 1988). There are different views on the contribution from premixed and mixing controlled combustion to the formation of nitrogen oxides. Stone (1999) emphasises the contribution from mixing controlled combustion to formation of nitrogen oxides.

Relations of all the variables affecting the combustion process are presented in a schematic diagram in Figure 5. Fuel quality is only one of many factors, although a very important one.

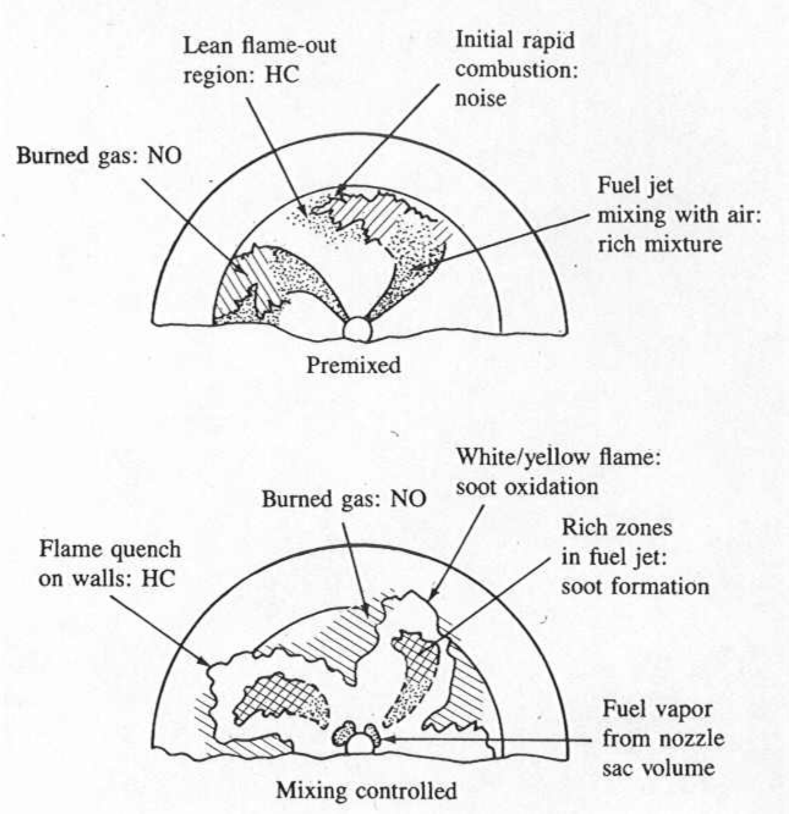


Figure 4. Summary of pollutant formation in a direct-injection diesel engine. (Heywood 1988)

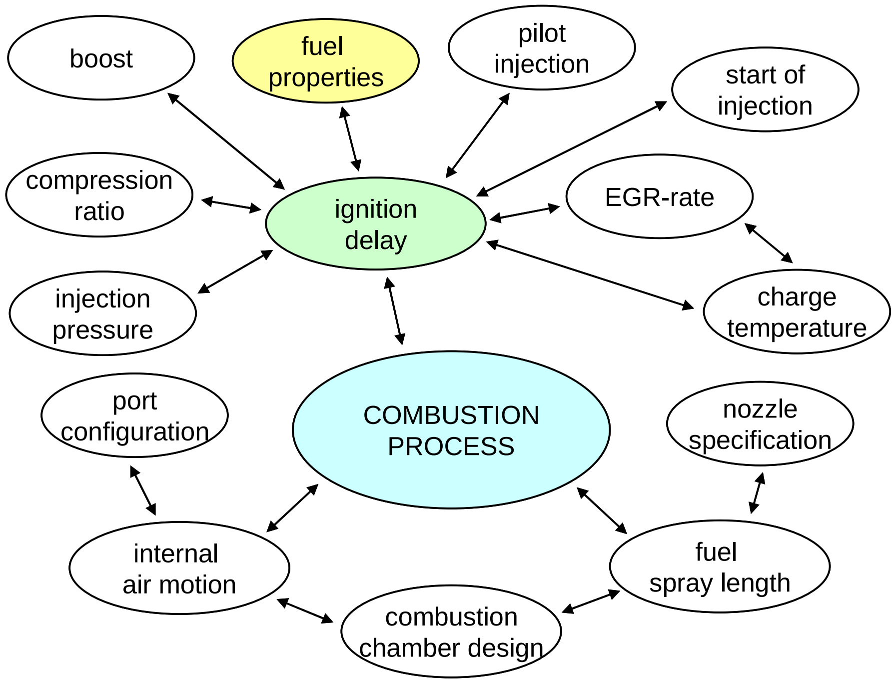


Figure 5. Parameters affecting the combustion process. (Karila et al 2004)

Fuel effects on regulated emissions can be divided into two main categories, physical effects and chemical effects. For combustion and emission formation, Heywood (1988) deems the chemical properties of the fuel much more important (hydrocarbon structure, aromatic vs. paraffinic etc.).

Of the physical characteristics, fuel properties like viscosity and density may affect injection timing, fuel atomization and evaporation and, thus, exhaust emissions. Much depends on the engine itself. Increases in fuel viscosity advance actual injection timing in older engines with fully mechanical injection systems, thus increasing NO_x emissions and reducing PM emissions. This is what happens when biodiesel is used in older engines. Figure 6 shows the conventional interrelationship between injection timing, NO_x, particle emissions and fuel consumption.

For many new generation engines, start of injection is not affected by fuel properties anymore, as start of injection in, e.g., Common-Rail type injection systems is fully electronically controlled. In most cases, the fuel effects are a combination of both physical and chemical properties.

When evaluating greenhouse gas or carbon dioxide emissions, both fuel production and end-use have to be taken into consideration. Significant amounts of fossil energy (e.g., fertilizers, transport, processing, etc.) is needed for some biofuel options, resulting in a total CO_2 balance which is not very favourable.

As in Chapter 3, the following discussion contains some brief general remarks on ethanol.

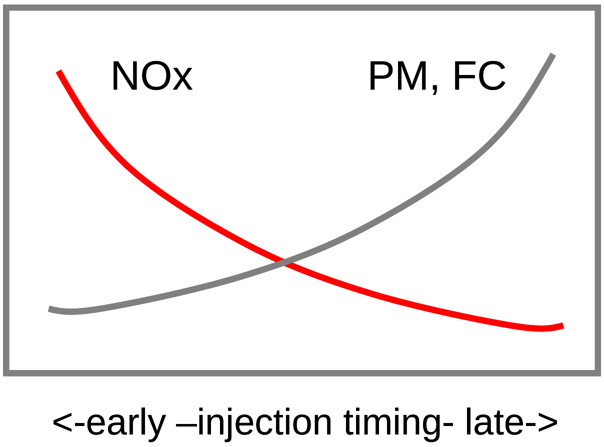


Figure 6. The conventional interrelationship between injection timing, NO_x, particle emissions and fuel consumption.

4.2 PARTICLES

The formation of particles is a very complex process. The composition of particles varies significantly depending on engine technology, fuel quality, and running conditions. The major part of diesel particles originates from the fuel, but in new engines running on high quality fuels the lubricating oil also makes, in relative terms, a significant contribution to exhaust particles.

Particle formation is at its strongest in the rich zones in the fuel jet (Figure 4). Under rich conditions, pyrolysis of the fuel results in soot formation. Soot particles formed in the fuel-rich zones can eventually be oxidized into carbon monoxide and carbon dioxide later during the combustion cycle.

Within the combustion chamber, the fuel molecules are degraded into simple hydrocarbon radicals through pyrolysis and combustion. These radicals form lightweight hydrocarbons like acetylene (C_2H_2). Acetylene again may react with other hydrocarbons forming heavier hydrocarbons, including polyaromatic hydrocarbons (PAH). Benzene rings are building blocks for PAHs. PAHs and acetylene derivates are considered to be starting points for particle formation. The PAH molecules grow by polymerization and/or absorption of acetylene and eventually transform into particles. The final formation of particles involves both physical and chemical processes, some of which are not fully known.

Particle nuclei consisting of carbon are formed. These nuclei grow both through coagulation and absorption of hydrocarbons. Water and sulphates also adhere onto the surface of the particles. The composition of PM varies greatly depending on the engine technology, test conditions, and the contents of sulphur and aromatics in the fuel. Ash also contributes to particles. An example PM composition from a post-1994 US heavy-duty diesel engine is illustrated in Figure 7. Figures 8 and 9 show different steps in the chain leading to particle formation.

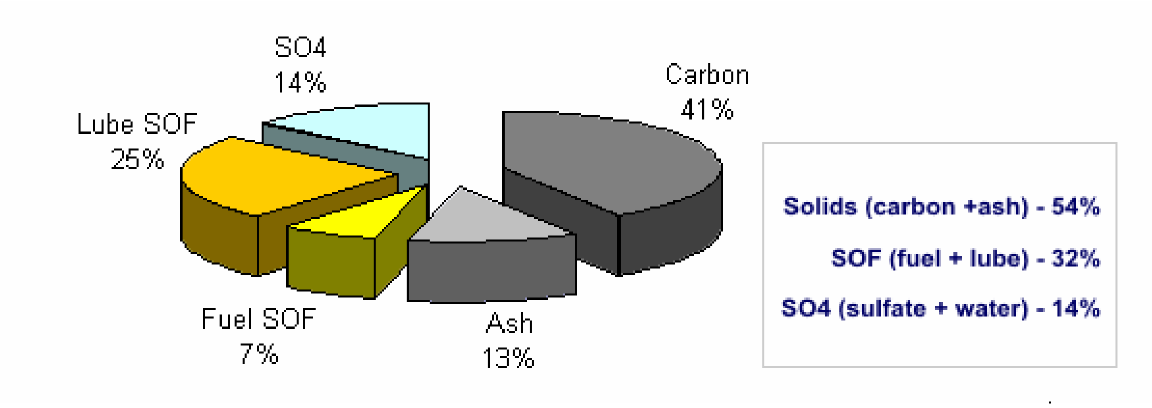


Figure 7. The composition of diesel particulate matter for a post-1994 US heavy-duty engine. (DieselNet 2002)

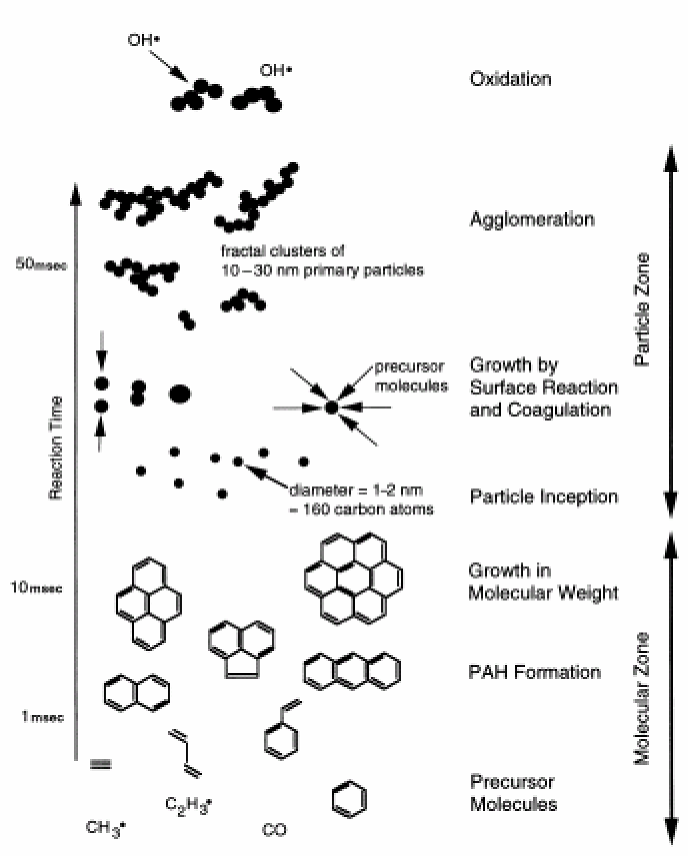


Figure 8. Particle formation. (In Sarofim 2000, based on Bockhorn et al.)

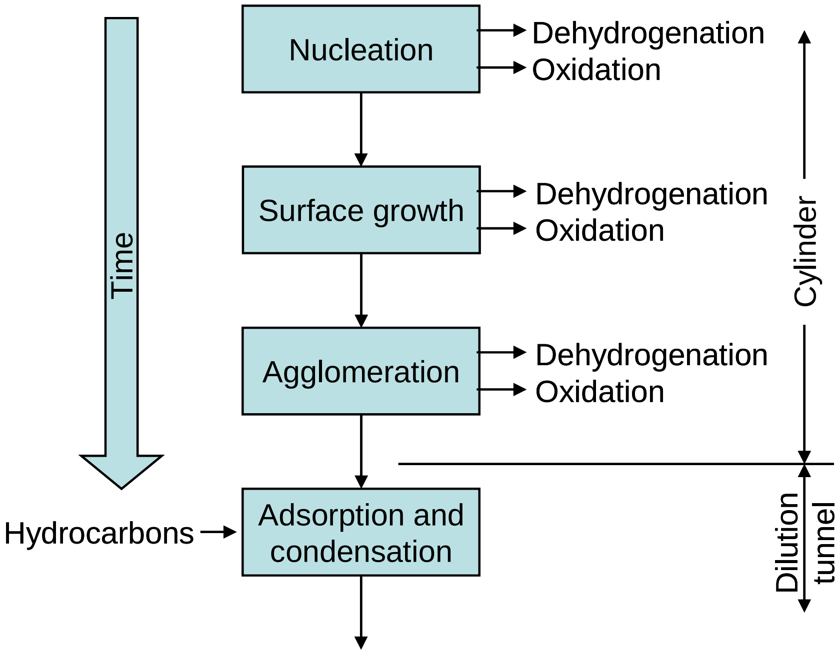


Figure 9. Particle formation. (Heywood 1988)

A number of mechanisms have been presented to explain the reductions in particle emissions when using oxygenated fuels. In general, non-aromatic fuels with simple chemical structure and short carbon-carbon chains burn cleanly with low or no soot formation. Examples of such fuels are methane (natural gas), ethanol and methanol.

A general theory is that by adding oxygen to the fuel, oxidative species will be present on the fuel side of the mixing-controlled flame. These oxidizing agents are thought to suppress soot early in its nucleation process and inhibit its peak production. The presence of oxygen reduced the formation of unsaturated cracking constituents, such as acetylene and ethylene, components which are often considered as precursors of soot and PAH. Reduction in ethylene production is thought, in turn, to suppress the formation of PAH, thus decreasing the formation of soot. (Delfort et al. 2002)

4.3 OXIDES OF NITROGEN

Factors like combustion temperature, availability of oxygen, nitrogen content of the fuel itself, and the reaction time determine NO_x emissions of combustion processes. For automotive fuels and engines the thermal process, i.e., oxidation of nitrogen of the combustion air at high temperatures is the dominating process (Zeldovich mechanism), not fuel related nitrogen. Fuel chemistry also affects combustion temperature and thus NO_x.

The increase in NO_x emissions with injection advance is related to an increase in combustion temperature. Late injection timing reduces peak temperatures and thus NO_x emissions at the cost of increased fuel consumption and particle emissions (Figure 6). As stated previously, the physical properties of the fuel may affect injection timing.

Biodiesel (FAME) is often reported to increase NO_x and reduce particle emissions. Compared with conventional diesel fuel, biodiesel has both higher density and higher viscosity, and these two factors advance injection timing in mechanically controlled injection systems. The oxygen in the biodiesel fuel is thought to add oxygen to the fuel-rich diffusion flame. These factors affect that soot formation is suppressed and NO_x formation promoted (Chang 1997). Within the diffusion flame, ethanol can be expected to work in the same way (Piel 1990). However, with ethanol, other factors dominate, so a reduction of NO_x can be expected.

The heat of evaporation and to a lesser extent specific heat capacity of the fuel also affect NO_x emissions. A stoichiometric air-gasoline mixture cools off some 20 ^{o}C when evaporated, a mixture of air and methanol some 122 ^{o}C (Menrad 1982). Reduced mixture temperature leads to reduced combustion temperature and thus reduced NO_x emissions. Due to its cooling effect, methanol has been used and is still used to increase the power output of racing engines.

It has been demonstrated that operation of diesel engines with ignition improver treated alcohol or with diesel/alcohol or diesel/water emulsions all cool down the combustion process and reduce NO_x emissions. Direct water injection (DWI) has been applied to medium-speed diesel engines for NO_x reduction. With a water to fuel ratio of 0.4 – 0.7 NO_x emissions can be reduced by some 50 – 60 %. (Wärtsilä 2005)

Fuel chemistry affects both flame temperature and ignition delay. Aromatic hydrocarbons have higher flame temperatures than paraffins and alcohols (Ekelund et al. 1989, Figure 10). Thus, blending alcohol into diesel reduces temperature both by increased heat of vaporisation and reduced flame temperature. Methane and methanol, both with one carbon atom and four hydrogen atoms, give the same flame temperature.

As mentioned in 3.2, ignition quality also depends on the chemical structure of the fuel. Ignition delay increases with declining ignition quality or cetane number. The amount of fuel burned in premixed mode is proportional to the ignition delay. Compared with mixing-controlled combustion, in which fuel burns close to stoichiometry with formation of soot, premixed combustion, due to readily available oxygen, produces more NO_x and less particles. However, as mentioned earlier, there are different views on the contribution of premixed and mixing controlled combustion to NO_x formation.

Table 2 summarizes how blending of ethanol into diesel fuel affects on NO_x emissions. Some phenomena work in opposite directions. It is impossible to indicate a general trend for blended fuels. Much depends on the ignition quality of the blend. A switch from diesel to neat ethanol would result in reduced NO_x emissions, on the condition that the ethanol is treated with additives for adequate ignition properties.

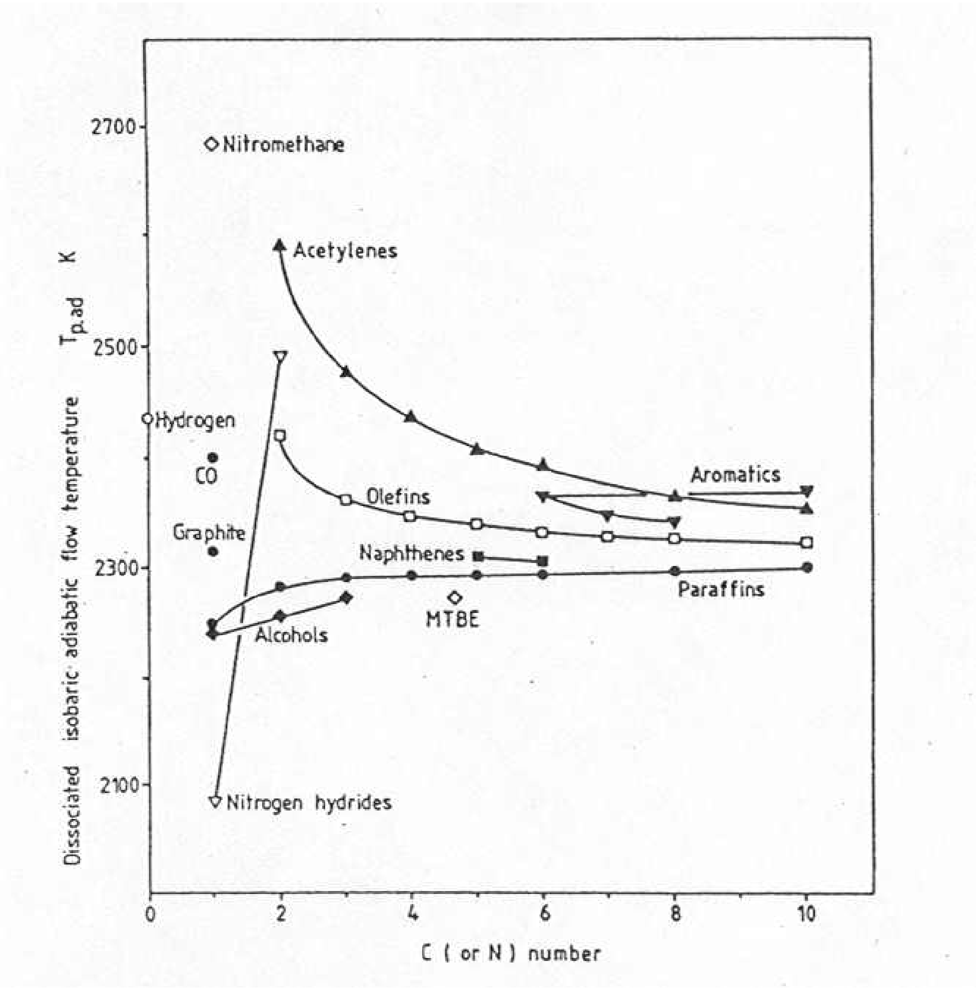


Figure 10. Flame temperatures of various fuels. (In Ekelund et al. 1989)

Table 2. The effects of blending ethanol to diesel on NO_x emissions.

Property	**Effect**	**NO_x effect**
Physical		
Reduced viscosity	Retarded start of injection	▼
Increased heat of evap.	Reduced mixture temperature	▼
Chemical		
Added fuel oxygen	Leaner mixing controlled combustion (?)	▲
Flame temperature	Reduced flame temperature	▼
Reduced ignition quality	Increased ignition delay	▲
	Overall effect	▼

4.4 CARBON DIOXIDE

Several studies on well-to-wheel carbon dioxide or greenhouse gas emissions of various fuels have been published. One recent study is by EUCAR, CONCAWE and JRC. Figure 11 shows well-to-wheel energy and greenhouse gas clusters for various fuel and power train options. Figure 11 is for passenger cars, and includes gasoline, diesel and fuel cell vehicles.

Ethanol, biodiesel (FAME), natural gas (methane), and hydrogen are the alternative fuels which have received most attention. Ethanol can be added to gasoline and with some restrictions even to diesel. Neat ethanol can fuel spark-ignited engines and, if treated with ignition improver additives, even diesel engines.

Ethanol is more energy intensive than conventional petroleum. For both gasoline and diesel, total energy use is some 250 MJ/100 km, whereas the energy use with ethanol is some 550 MJ/100 km. For conventional ethanol (crop based), there is a huge spread in equivalent CO_2 emissions, from some 50 to 200 g/km, i.e., roughly 25 -100 % of the values for gasoline and diesel. The equivalent CO_2 emission for wood based ethanol is estimated at some 35 g/km.

Figure 11 clearly demonstrates that, by default, ethanol does not reduce greenhouse gas emissions. The outcome is highly dependent on raw material and processing technology. At its best, the equivalent CO_2 emissions are only some 20 % compared with gasoline and diesel, at its worst close to 100 %. In the case of blended fuels, with ethanol concentrations typically up to 20 %, the potential for CO_2 reductions is at its highest 15 %.

Figure 11 also shows synthetic diesel produced from natural gas and DME produced from wood. As for CO_2 emissions, these two cases should in practise represent the extreme values for any synthetic fuel component. Synthetic diesel from natural gas is rather close to conventional diesel, whereas DME from wood has the potential for the lowest CO_2 emissions, with the exception of hydrogen from renewable sources or nuclear power. If synthetic fuels were to be produced from coal, this would increase CO_2 emissions significantly, as demonstrated by the example of hydrogen from coal.

When targeting a reduction in greenhouse gas emissions, the same benefit for a given amount of biofuel is obtained using the fuel neat or as a blending component. When biofuels are used as blending components (fuel components) at low concentrations many technical advantages are obtained: fuel properties are close to respective fossil fuels, technical drawbacks of biofuels diminish, and less changes or modifications are required in the distribution chain, logistics and vehicles. However, ethanol and other easily flammable components can pose safety problems already at very low concentrations.

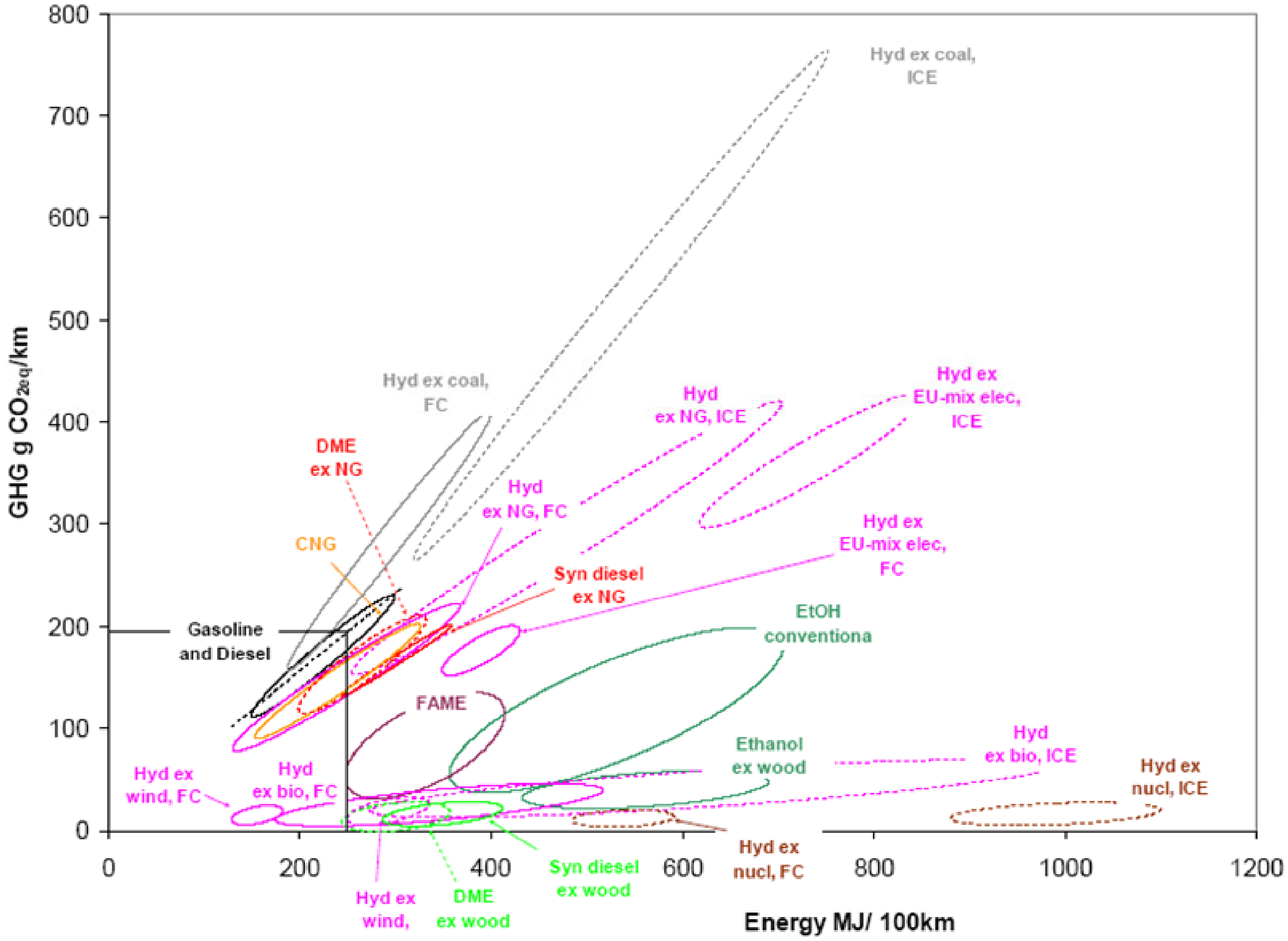


Figure 11. WTW energy and GHG emission clusters (EUCAR 2004).

5 PROPERTIES OF OXYGENATES

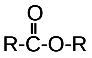
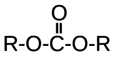
5.1 COMMON PROPERTIES OF OXYGENATES

A number of different oxygenates have been considered as components for diesel fuel or to be used as such in a compression ignition engines. These oxygenates include various alcohols, ethers, esters and carbonates (Table 3). The study at hand focuses on alcohols and ethers that have reached pilot or commercial status as blending components. The best known diesel oxygenates at the moment are esters of fatty acids, but they are out of the scope of this study. However, some summary data of the properties of other oxygenates than alcohols and ethers are given when applicable.

In general, both methanol and ethanol have been considered as transportation fuels. Ethanol and methanol are well suited for spark-ignition engines, with some exceptions like bad cold-start performance. Some heavier alcohols, like tert-butyl alcohol (TBA), would also be technically suitable for spark-ignition engines, but are not economically feasible. Ethanol is also considered as a possible oxygenate for diesel fuels.

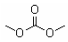
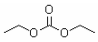
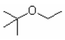
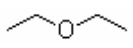
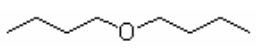
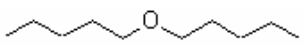
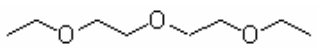
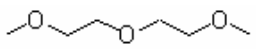
Of the ethers, potentially suitable for diesel engines are, i.a., dimethyl ether (DME), diethyl ether (DEE), dimethoxy methane (DMM), and glycol ethers (monoglyme, diglyme). Also other oxygenates, e.g. carbonates and acetates, have been studied, e.g., 2-ethyl hexyl acetate and ethylene glycol mono butyl ether acetate (Ryu 2000). Stournas (1993) studied the suitability of amides and amines processed from fatty acids. Many studies have covered a comprehensive set of oxygenates. For example, Delfort et al. (2002) studied exhaust emissions using 17 diesel oxygenates: 3 ethers, 6 acetals, 4 polyacetals and 4 carbonates. Natarjane et al. (2001) studied 71 compounds selecting two compounds as the most promising oxygenates: tripropylene-glycol-monoethyl-ether and dibutyl-maleate. A recent thesis by Nord (2005) includes a study with acetal (1,1-dietoxyethane).

Table 3. The schematic structure of oxygenates

R-OH	Alcohols
R-O-R	Ethers
R-O-R-O-R	Glymes (glycol ethers)
R-O-C-O-R	Acetals: two or more oxygen linked to a single carbon (complex ethers)
R-(O-C)$_x$-O-R-	Polyacetals (complex ethers)
 $R\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}O\text{-}R$	Esters
 $R\text{-}O\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}O\text{-}R$	Carbonates

R, hydrocarbon chain; C, carbon; O, oxygen

The following list shows a few examples of the chemical structure of oxygenates:

	DMC, dimethyl carbonate
	DEC, diethyl carbonate
	ETBE, ethyl t-butyl ether
	Ethyl ether
	Di n-butyl ether
	Di n-pentyl ether
	EXEE, 2-ethoxy ethyl ether
	Diglyme, diethylene glycol dimethyl ether

In this report, the fuel properties of ethanol are described in detail and main emphasis is given to diesel/ethanol blends (E-diesel). Other oxygenates are discussed more shortly. The properties of various possible oxygenate candidates are summarized in Table 4 and 5.

Oxygenates are generally polar compounds, whereas hydrocarbon fuels are non-polar. This may result in problems with miscibility depending on the chemical structure and oxygen content of the oxygenate. The miscibility problems are aggravated if physical properties, e.g., density, also are very different from the properties of diesel ("like dissolves like"). Thus, some oxygenates are easily miscible with diesel fuel and form stable solutions, e.g., n-pentyl ether, whereas ethanol can be blended with diesel fuel (emulsified) only with the help of additives.

Miscibility also depends on the properties of diesel fuel in question. There are differences in the polarity of hydrocarbons. Paraffins, for instance, are more non-polar than aromatics. Thus, an increase in the aromatics content of diesel fuel usually improves the solubility of oxygenates. (McCormic 2001)

Affinity of oxygenates to water is higher than that of hydrocarbon fuels. Oxygenates are therefore sensitive to water present in tank or pipelines. In addition, oxygenates tend to be hygroscopic, absorbing water from ambient air. An increase in the water content of diesel/oxygenate blends tends to increase polarity, which may lead to phase separation. Water tolerance, and miscibility in general, varies with ambient temperature. Low temperatures promote phase separation.

The fuel properties of oxygenates vary significantly with, e.g., length and type of alkyl chains. Oxygenate candidates with higher molecular weight often have higher density, higher boiling point, higher viscosity, better lubricity, lower volatility, and lower flammability than respective candidates with lower molecular weight. Therefore, they are better suited to be used as diesel fuel components.

Examples of the effects of chemical structure on vapour pressure and octane number are depicted in Figure 12. The effect of chemical structure on cetane number is typically contrary to the effect on octane number. It is well-known that cetane number of hydrocarbons, like parafins, generally increase with the increasing chain length. This applies generally also to oxygenates, as is seen for alcohols in Figure 12. Ethanol is a very problematic diesel oxygenate, as is described in Chapter 5.3, whereas higher alcohols are more suitable for diesel engines.

Pecci et al. (1993) published an extensive study on the effects of the oxygenate chemical structure on cetane number and cold properties. The following observations were reported on how the oxygenate chemical structure affected the cetane number of the blend:

- Increase with molecular weight up to hexyl ether, no further increase with heptyl and octyl ethers
- Branching of the alkyl chain strongly depresses cetane number
- Replacement of methylene groups with oxygen: the highest cetane number with three ether groups in structure
- Position of oxygen atoms shows more complex behaviour
- Cetane number of esters is low, but increases with the length of the carboxylic acid alkyl chain

The following observations were reported on low temperature behaviour (cloud point, CFPP[1]):

---

[1] Cold Filter Plugging Point

- Non-linear: dihexyl and diheptyl ethers worse than pentyl and octyl ethers
- Cold properties worsen with increased branching
- Cold properties worsen with increasing number of oxygen atoms

Pecci et al. (1993) concluded that symmetrical and asymmetrical mono-ethers seem to give the best compromise between cetane characteristics and the behaviour at low temperature. Giavazzi (1993) realized that, of these oxygenates, especially di-n-pentyl ether (DNPN) and di-n-pentoxy methane (DNPM) also benefit engine operation.

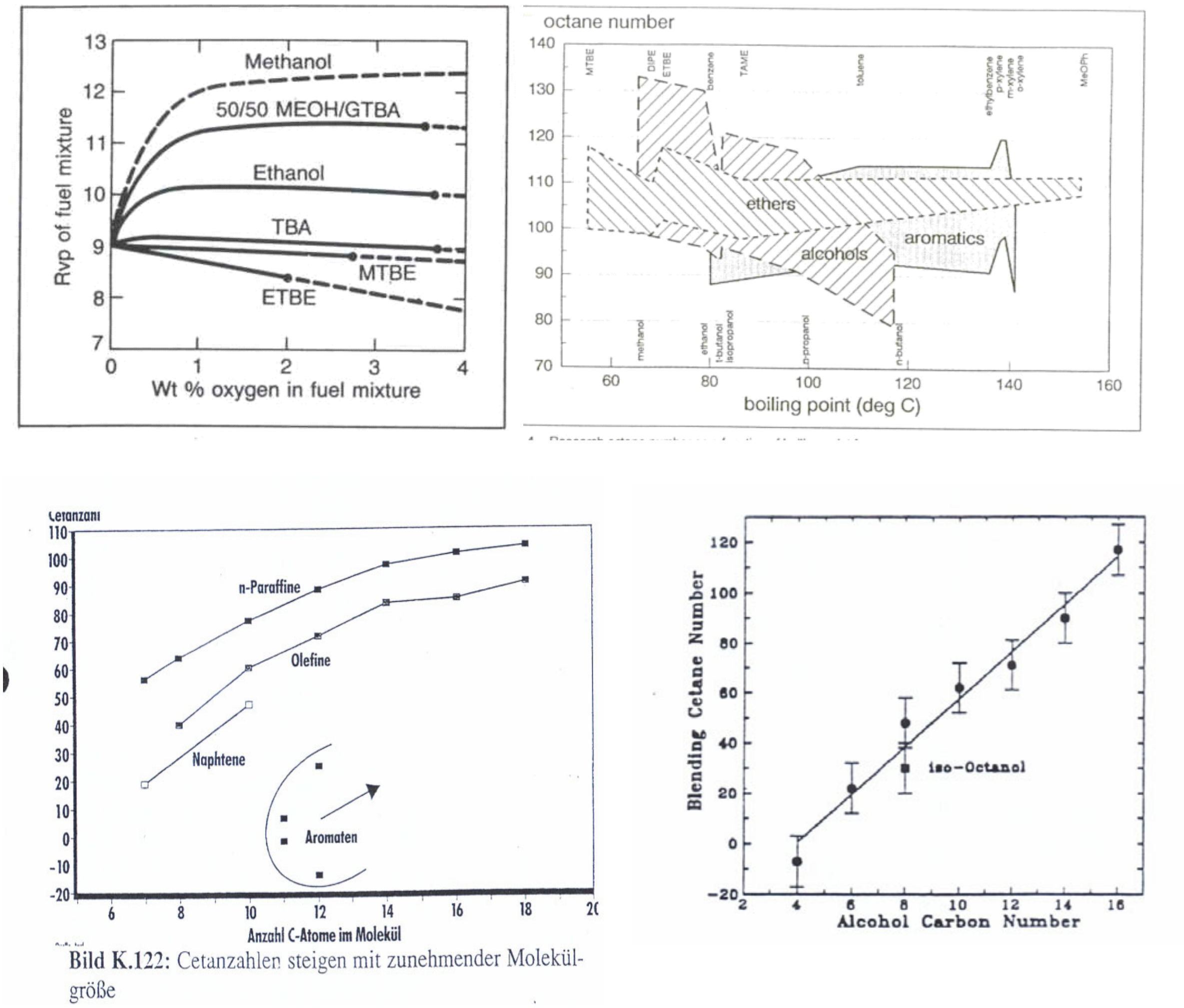


Bild K.122: Cetanzahlen steigen mit zunehmender Molekülgröße

Figure 12. a) The effect of oxygenates on vapour pressure (left-hand side). b) Research Octane Number as a function of boiling point for oxygenates and aromatics (right-hand side, high octane means low cetane). (Piel 1990, NN Oil Gas 1991). c) The effect of molecular size on cetane number. (Shell Lexikon, Stournas et al. 1993).

A summary of some properties of oxygenates in comparison with gasoline and diesel is shown in Tables 4 and 5. In literature, some fuel parameters can be found which have been obtained using untypical test methods, like ignition quality with a special IQT (Ignition Quality Tester) analyzer. Such parameters have been omitted from the Tables.

A number of extensive studies on possible diesel oxygenates have been carried out - even 71 compounds in one single study. It is not scope of this study to review the properties of all potential diesel oxygenates. However, some selected compounds are collected in Tables 4 and 5.

Table 4. Properties of gasoline, diesel, FAME, methanol, ethanol, E85 and ethanol/diesel blends. (Bertoli 1997, Murphy 1999, Piel 1990, Reynolds 2002, Waterland 2003, API Publication 4261, Clean Fuels and Electric Vehicles Report 2000, Safety Data Sheets)

	Gasoline	Diesel	FAME [a]	Methanol	Ethanol	E85[e]	E-diesel[e]
Formula	C_4-C_{12}	C_{12}-C_{20}	$C_{19}H_{34}O_2$	CH_4O	C_2H_6O	~$C_{2.7}H_7O_{0.85}$	~10% ethanol
Mol. Wt, g/mol	100-105	~200	~294	32.04	46.07	~55	~185
C/H/O, wt-%	85-88/12-15	85-88/12-15	78/12/10	38/13/50	52/13/35	58/13/29	83/13/3.4
Density, kg/m3	~750	~840	880	796	794	780	810-840
Viscosity at 40 °C, cSt (Viscosity at 20 °C, cP)	<1 (0.37-0.44)	~2-4.5 (2.6-4.1)	3.5-5	- (0.59)	- (1.19)	-	~1.9-4.1
HFRR, µm		<460	<460				>350
Boiling point, °C	30-190	170-340	300-340	64	78	30-190	109-340
Octane number, RON [b]	95-98			122-133 (BON)	121-130 (BON)	~100	
Cetane number	na	>45	>50		8		42-52
Vapour pressure RVP, actual kPa (blend kPa [d])	45-90[c]	<1	-	32 (210+)	16 (124)	40-80	16
CFPP, °C		e.g. <-25					e.g. <-25°C
Flash point, °C	<0	>56	>100	7	13		<20; 32
Autoignition temperature, °C	>340	~240		464	425		
Flammability limits, vol%	1.4-7.6	1-6		7.3-36	3.3-19	1.2-9.1	3.3-19
Flammability limits, °C	-45-(-20)	64-150		7.2-43	13-42		13-42
Heat value, MJ/kg	43	43	36	20	26	29.2	~41-42
Stoich. AFR	14.7	14.7	12.4	6.5	9.0	10.0	14.0
Flame visibility	Visible	Visible	Visible	Unvisible	Not clearly visible	Visible	Visible

na = not applicable a) Properties based on rape seed methyl ester. b) RON or MON octane numbers are not relevant for oxygenates. Thus blending octane numbers (BON) are shown here for ethanol and for ETBE. c) Raid Vapour Pressure varies in different countries and seasons d) Vapour pressure changes non-linearly when ethanol is added to gasoline, second value is blending vapour pressure e) varies depending on base diesel fuel

Table 5. Properties of selected oxygenates. (Bertoli 1997, Murphy 1999, Piel 1990, Reynolds 2002, API Publication 4261, Clean Fuels and Electric Vehicles Report 2000, Safety Data Sheets)

	ETBE	DNPE	DME	DEE	DBE	DMM	MG	DG	DMP	DBXM	EXEE	DCM	DEC
Name	Ethyl-tert-butylether	n-Pentyl ether (Dipentyl ether)	Dimethyl ether	Diethyl ether	Dibutyl ether	Dimethoxy methane (Methylal)	1,2-Dimethoxy ethane (Mono-glyme)	2-Methoxyethyl ether (Diglyme)	1,2-Dimethoxy propane, Propylen glycol dimethyl ether	Dibutoxym ethane (Butylal)	2-Ethoxyethyl ether (diethylglycol)	Dimethyl carbonate	Diethyl carbonate
Formula	$C_6H_{14}O$	$C_{10}H_{22}O$ (C5-O-C5)	C_2H_6O (C-O-C)	$C_4H_{10}O$ (C2-O-C2)	$C_8H_{18}O$ (C4-O-C4)	$C_3H_8O_2$ (C-O-C-O-C)	$C_4H_{10}O_2$ (C-O-C2-O-C)	$C_6H_{14}O_3$ (C-O-C2-O-C2-O-C)	$C_5H_{12}O_2$ (C-O-C3-O-C)	$C_9H_{20}O_2$ (C4-O-C-O-C4)	$C_8H_{18}O_3$ (C2-O-C2-O-C2-O-C2)	$C_3H_6O_3$ (C-O-CO-O-C)	$C_5H_{10}O_3$ (C2-O-CO-O-C2)
Mol. Wt, g/mol	102	158	46	74	130	76	90	134	104	160	162	90	118
C/H/O, wt-%	70/14/16	76/14/10	52/13/35	65/14/22	74/14/12	47/11/42	53/11/36	54/10/36		68/13/20	59/11/30	40/7/53	51/8/41
Density, kg/m^3	745	783	660	720	767		870	937		830	910	1069	970
Boiling point, °C	73	187	-24	35	141	42	85-93	162	96	180	189	91	127
Octane number	118 (BON)												
Cetane number		111-130	55-60		91-100		90-98	112-130		>74	113-136		
Vapour pressure, kPa	10 (27)												
Cloud point, °C		<-30								<-30	<30		<-30
Flash point, °C	<0	57	-42	-45	25	-18	<0	67-70	Na	64	71	18	33
Lower heating value, MJ/kg	36		27.6-28.8		42.8		31.6	30			33.2	13.5	
Peroxide problem	Possible	Possible	Possible	Explosions	Possible	Possible	Possible	Possible	-	-	Possible	-	-

5.2 ETHERS

5.2.1 General properties of ethers

In principle, a large number of ethers could be used as fuels or fuel components. Mono-ethers like MTBE and ETBE are widely used as blending components and octane boosters for gasoline. Ethers are in general less polar than alcohols, and therefore ethers provide better miscibility with hydrocarbon fuels than alcohols. Poly-ethers or ethers with high molecular weight are better suited to be used as diesel fuel components than mono-ethers. (Ryu 2000).

Several ethers have been evaluated as possible diesel oxygenates. Many studies have covered a comprehensive set of oxygenates, and some ethers have been mentioned as promising blending components for diesel fuel. However, these studies have often focused on exhaust emissions, especially to find the most effective oxygenates to reduce particulate matter emissions from diesel engines. The economical feasibility, safety and health aspects have been discussed only briefly, even though it is known that many ethers have problems e.g. with low flash point or toxicity. One risk with ethers is possible formation of peroxides, which may lead to explosion. Some ethers may have an anaesthetic effect.

Higher molecular weight ethers are more suitable for blending with diesel fuel. *Di-n-pentylether (DNPE)* is a well-documented diesel oxygenate with good fuel properties (Table 5, e.g. Pecci et al. 1993). If production would be economically feasible, DNPE would be an excellent oxygenate for diesel fuel.

The recent thesis by Nord (2005) includes a study on *acetal (1,1-dietoxyethane)*, which was considered a promising diesel oxygenate resulting in significant reductions of particle and NO_x emissions. However, acetal is a very light compound with a boiling point of only 103 °C and flash point of -20 °C. Acetal can be made from ethanol.

McCormick et al. (2002) mention that *2-ethoxy ethyl ether* shows interesting fuel properties and is soluble with diesel fuel, but exhibits unacceptable toxicological properties.

Diethoxy butane is mentioned as a very interesting diesel oxygenate due to good cetane number (97) and reasonable flash point (45 °C). This compound could be produced from ethanol (dehydration -> DEE -> oxidative coupling) or using fossil butadiene. (McCormick et al. 2002).

Many other ethers, like *glycol ethers* (monoglyme, diglyme) might be suitable for blending with diesel fuel. *Monoglyme* (ethylene-glycol-dimethylether) and *diglyme* (diethylene-glycol-dimethylether) were earlier known as cetane improvers. These compounds have high oxygen content, high auto-ignition tendency and high cetane number.

Natarjane et al. (2001) studied 71 compounds selecting two compounds as the most promising oxygenates: *tripropylene glycol monoethyl ether (TPGME,* $C_{10}H_{22}O_4$*)* and *dibutyl maleate (*$C_{12}H_{20}O_4$*)*. The effect of these oxygenates on soot processes have been studied later on e.g. by Mueller et al. (2003). TPGME was found to be more effective in soot reduction than dibutyl maleate.

Murphy (1999), found a few ethers like n-pentyl ether (DNPE), 2-ethoxyethyl ether (diethyl carbitol) and dibutoxy methane (butylal) potential oxygenates for blending into diesel. Murphy (2002) also reported on the properties of the following oxygenates:

- Diethyl maleate $C_8H_{12}O_4$, oxygen 37 wt-%, boiling point 223 °C, density 1 066 kg/m^3, not miscible with diesel
- Tripropylene glycol monomethyl ether $C_{10}H_{22}O_4$, oxygen 31 wt-%, boiling point 242 °C, density 968 kg/m^3, not miscible with diesel
- Dibutyl maleate $C_{12}H_{20}O_4$, oxygen 28 wt-%, boiling point 281 °C, density 987 kg/m^3, miscible with diesel
- Glycerol tributrate $C_{15}H_{26}O_6$, oxygen 32 wt-%, boiling point 307 °C, density 1 035 kg/m^3, not miscible with diesel

One interesting candidate oxygenate is Snamprogetti’s “oxy-diesel” processed via *oligomerisation of DMM*. These poly-oxy-methylenes are similar to diesel, without volatility or flash point problems. They are more biodegradable than MTBE and production costs are low. (Hart Diesel Fuel News 2001)

The reactions for poly-oxy-methylenes are:

$CH_3OH + HCHO \rightarrow CH_3OCH_2OCH_3$ (DMM) $\rightarrow$ oligomerisation $CH_3O(CH_2O)_nCH_3$,

where n = 3…6

5.2.2 Operation with pure ethers (DME, DEE, DMM)

Ethers potentially suitable as neat fuel for diesel engines are, i.a., *dimethyl ether (DME)*, *diethyl ether (DEE*) and *dimethoxy methane (DMM)*. *Diethyl ether (DEE)* is a known cold-start aid, but little is known of DEE as fuel as such for diesel engines. *Dimetoxymethane or metylal (DMM)*, processed from methanol and formaldehyde, is one possible diesel oxygenate which could be used as a fuel for diesel engines as such. Some experiments have been carried out blending DMM with diesel. (Ryu 2000, Golubkov 2005).

DME is probably the ether that has received most attention in conjunction with diesel engines. Within the IEA Implementing Agreement on Advanced Motor Fuels, two Annexes concerning DME, Annex XIV and Annex XX, were carried out. (AMF 2005)

The physical properties of DME resemble LPG, with the exception that the cetane number of DME is high. In the beginning, DME was considered as ignition improver for, e.g., methanol. However, now the focus is on the neat DME operation. DME is a gaseous fuel and therefore it requires a new fuel distribution system and even new engines. Lubricity is low, leakages and the risk for cavitation are high. Hence, the injection system has to be completely redesigned.

DME reduces particle emissions significantly, and there is also potential for NO_x reductions. Another advantage with DME is related to the processing of the fuel. The DME process is highly selective and efficient, and is in this respect superior both to the methanol synthesis and the Fischer-Tropsch synthesis for synthetic diesel. For all three alternatives, the starting point is synthesis gas either from steam reformation or gasification. - Volvo is one of the manufacturers which have been promoting DME very actively. (Landälv 2004)

5.3 ETHANOL

5.3.1 General

Ethanol has been known as an intoxicating drink since as early as 6000 – 4000 B.C. In the late 1800's, ethanol was used mainly as lamp fuel, and the first large scale use took place in early 1900's due to shortage of petroleum supplies. The first engine evaluations and automobiles ran on alcohol and/or gasoline, until in 1920's gasoline became a major motor fuel. World War I and II increased the ethanol demand, but then ethanol use decreased until the oil crisis in the 1970's. Today the reasons to use ethanol lie in energy security, but even in improvements in combustion and exhaust emissions. Nowadays also the reduction in greenhouse gas emissions is an important driving force for ethanol usage. (EIA)

Ethanol can be used as a fuel as such or blended into gasoline or diesel. In principle, ethanol is an excellent fuel for spark-ignition engines. As diesel fuel, however, ethanol has a number of shortcomings, like low ignition quality, low lubricity, poor miscibility with diesel, and low flash point.

5.3.2 Combustion properties (octane and cetane numbers), neat ethanol usage

Methanol and ethanol resemble each other, and most properties apply to both fuels. Despite of the similarities, some differences also exist, e.g., methanol is toxic, corrosive and non-biodegradable. With the exception of boiling characteristics ethanol resembles gasoline in many ways. Thus, it can be used as a gasoline component. Ethanol up to some 10% can be blended with gasoline and used without modifications in spark-ignition engines. The limit is set by the lean-out effect of ethanol (10% ethanol corresponds to 3.7% oxygen in the fuel). Special cars, so called Fuel Flexible Vehicles (FFV) have been developed for fuels containing up to 85 % alcohol[2].

The octane numbers[3] of alcohols are high, around 120-130, and they can therefore be used as octane boosters in gasoline. The high octane rating of ethanol makes it possible to increase compression ratio. Thus, higher power output can be obtained with engines optimized for ethanol use. Alcohols tend to increase Research Octane Number (RON) more than Motor Octane Number (MON), of which the latter is decisive for knocking under high-load conditions.

The difference between RON and MON is called sensitivity. The sensitivity of gasoline is typically 8 - 10 units, whereas the sensitivity of ethanol is 14 units. In addition, especially methanol is prone to early ignition induced by hot surfaces.

Ethanol differs significantly from diesel fuel. As the octane rating of ethanol is high, cetane number of neat ethanol is only approximately 8, whereas the requirement in Europe for diesel is over 51 (EN 590). Adding ethanol to diesel will reduce cetane. Therefore, cetane improver additives might be needed. The lubricity is also insufficient for high-pressure injection pumps. The low boiling point increases the risk of cavitation and high conductivity the risk of corrosion. (Peckham 2001, McCormick 2001).

If ethanol is going to be used in compression ignition engines either the engine or the fuel has to be modified. In the past, Detroit Diesel manufactured glow-plug equipped heavy-duty engines to use methanol or ethanol, but due to many problems the production was discontinued.

Treated with ignition improver and lubricity additive ethanol can be used in conventional diesel engines, although some engine modifications are still needed. In Sweden, several hundreds of city buses manufactured by Scania run on additive treated ethanol[4]. The engine modifications include, e.g., increased compression ratio, a special high-capacity fuel injection system, and a catalyst to control aldehyde emissions. The ethanol buses started service in 1985, and in 2000 there were 407 buses running on ethanol in Sweden, 250 of them in Stockholm. (Lif).

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[2] Ed75-Ed85 industry specification is ASTM D 5798 “Standard Specification for Fuel Ethanol for Automotive Spark-Ignition Engines”.

[3] Octane number is a measure of the resistance of fuel to the abnormal combustion known as “knock”. Research octane number, RON, relates to the low load operation. Motor Octane Number, MON, relates to heavy load operation.

[4] The fuel for ethanol buses in Sweden is called Etamax D (90 % of hydrated ethanol, 7 % ignition improver (Beraid 3540), denaturants (2.3 % MTBE and 0.5 % iso-butanol) and 125 ppm corrosion inhibitor additive. (Lif).

Ethanol buses are also running in Mexico, Australia and Denmark. An ignition improver additive significantly increases the cost for running heavy-duty vehicles on ethanol fuels. Thus, it would be desirable to eliminate the need for this additive.

5.3.3 Miscibility

Solubility of ethanol into diesel fuel is very low. Diesel and ethanol do not form stable blends like gasoline and ethanol. Therefore, if diesel/ethanol blends are to be used, the only practical solution is emulsions. Research and demonstrations with such fuels started already in the beginning of 80's, but due to technical problems the interest stalled. (Peckham 2002).

However, new improved additives have been developed capable of forming micro-emulsions of ethanol and diesel (see Chapter 7). Micro-emulsions consist of droplets or micelles at the size of approximately 1 µm. The micro-emulsions are chemically and thermodynamically stable, they are clear and bright blends, unlike the first emulsions, which were white ("milky"). (McCormic 2001).

Fatty acid methyl esters (FAME) are reported to act as an emulsifier for ethanol. This is an interesting option as FAME could improve lubricity of ethanol, whereas ethanol could reduce NO_x emissions and improve cold properties, both of which are shortcomings of FAME. Both components reduce particulate matter emission (McCormick 2001). There is also interest, e.g., in diesel-ethanol-water blends. However, not much data is available concerning other combinations than diesel-ethanol mixtures.

5.3.4 Oxygen content, density and energy content

The oxygen content of ethanol (C_2H_5OH) is 35%. The oxygen content of a fuel influences the stoichiometric air to fuel ratio, which is 9.0 kg air/kg fuel for ethanol and some 14.5 kg/kg for diesel fuel. In gasoline engines with fixed fuel calibration the oxygen in the fuel leads to leaner and more effective combustion up to a certain limit. Gasoline cars with a closed-loop fuel control system can compensate the leaning effect at least up to some 3.5 % oxygen content (Environment Australia 2002).

The density of ethanol is 0.79 kg/l. The energy content of ethanol is lower than for gasoline or diesel. The lower heating value of ethanol is 26.8 MJ/kg, whereas 42.5 MJ/kg is typical for diesel fuel. Compared with gasoline and diesel, the lower energy content means either increased fuel consumption for a given power output, or in the case of a diesel engine, reduced power output, if the fuelling rate is not increased.

On volumetric basis, neat ethanol contains some 40% less energy than diesel, which means some 4% less energy for a 10% blend. One report on Pure Energy's "E-diesel" (15 % ethanol, 1 – 5 % co-solvent) increased fuel consumption by 6 % (Peckham 2001). Reynolds (2002) points out that in some applications the lower energy content of E-diesel may not translate into an energy loss of a corresponding level, while in others it may. The changes in volumetric fuel consumption with varying energy content depend on both engine type and operating conditions.

5.3.5 Volatility, heat of vaporization and flame temperature

Blending vapor pressures for alcohols are significantly higher than their true vapor pressures (Figure 12). The higher is the oxygen content of alcohol, the higher the non-ideality of blending vapor pressure (Piel 1990). The vapor pressure of ethanol is low, only 16 kPa, but blending vapor pressure is up to 117 kPa when 2 – 10 % ethanol is added to gasoline. Then, with ethanol concentrations over 10 %, vapor pressure gradually declines until at some 30 – 40 % ethanol content vapor pressure is comparable with gasoline. (Environment Australia 2002, Reynolds 2002)

Vapor pressure of diesel is typically less than 0.7 kPa. The addition of ethanol will raise the vapor pressure of the blend non-linearly. Even a very low amount, 2 % or less, increases volatility significantly. This may also cause driveability and vapor-lock problems, as well as possible cavitation problems and higher evaporative emissions (Reynolds 2002). Most probably vapor recovery systems should be considered in logistics and refuelling systems to avoid evaporative emissions due to volatility of diesel/ethanol blends. In addition, the evaporative emissions from diesel cars may increase significantly, if control devices such as carbon canisters are not used when running with diesel/ethanol blends.

Permeation related problems of high volatility are discussed in Chapter 5.3.8.

High volatility of diesel/ethanol blends results in safety concerns, which are discussed under “Safety”.

Specific heat capacity, heat of vaporization and flame temperature were already touched upon in 4.3, formation of oxides of nitrogen.

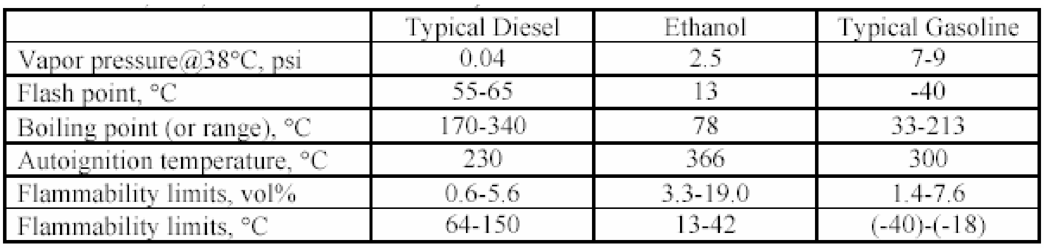
5.3.6 Safety (flame visibility, flash point, flammability)

Methanol burns with an invisible flame, and ethanol with a slightly luminous flame. A small amount of gasoline in alcohol, like in E85, improves the visibility of flame, which is a safety factor in possible accidents. There are a number of critical safety issues with ethanol, especially when E-diesel is concerned. The main concerns with E-diesel are related to safety issues and the general suitability and performance in diesel engines and vehicles. The flammability and safety properties of ethanol resemble those of gasoline. Thus, blending ethanol into diesel is somewhat similar as blending gasoline into diesel. The safety risks with E-diesel are even more pronounced in non-road applications, e.g., construction machines and indoor heaters than in on-road diesel. (Peckham 2001)

Storage and handling regulations for fuels are based on the flash point. In Europe, diesel fuel has to have a flash point higher than 55 °C. In the US, the Class II liquid requirement for flash point is higher than 38 °C. The flash point of E-diesel is lower than these limits, and E-diesel falls, thus, into the same class as gasoline. Similar procedures for safety, handling and storage are required for E-diesel as for gasoline (longer safety distances, special requirements for flame arresters on vents, etc.).

Table 6 lists some general properties and safety related issues for gasoline, diesel and ethanol. The flash point[5] of ethanol is 13 °C. The flash point does not change linearly with blending ratio: even a few percent of ethanol in diesel lowers the flash point close to 13 °C (McCormick 2001). Storage and handling regulations for fuels are based on the flash point. Ethanol and ethanol blends fall into the same class as gasoline.

Table 6. Approximate combustion safety characteristics of neat fuels. (McCormick 2001)



	Typical Diesel	Ethanol	Typical Gasoline
Vapor pressure@38°C, psi	0.04	2.5	7-9
Flash point, °C	55-65	13	-40
Boiling point (or range), °C	170-340	78	33-213
Autoignition temperature, °C	230	366	300
Flammability limits, vol%	0.6-5.6	3.3-19.0	1.4-7.6
Flammability limits, °C	64-150	13-42	(-40)-(-18)

It has been demonstrated that the safety characteristics or risks of diesel fuel containing 10 – 20 % of ethanol are identical to those of neat ethanol. In the U.S., the denaturant for fuel grade ethanol is natural gasoline, and this may also have an adverse effect on the flash point. (McCormick 2001)

A low flash point may also create safety risk within the fuel system of the engine. The flash point issue is gaining even more importance as new fuel injection equipment systems recirculate fuel raising return fuel temperature substantially. (Peckham 2002)

Flammability limits, also called explosion limits, are shown for E-diesel in Figure 13. The vapor concentration above the liquid depends on the temperature (increases with increasing temperature). Flammability limits can be expressed as flammable concentration range of vapor or as the temperatures where the vapor pressure (vapor concentration) is sufficient to support combustion. In a gasoline tank the mixture is too rich and in a diesel tank too lean to let the flame to propagate into the tank. (Peckham 2003, McCormick 2001, Peckham 2001, Weyandt 2002, Waterland 2003)

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[5] Flash point is the lowest temperature at which the vapour pressure of liquid is sufficient to produce a flammable mixture above the liquid, which ignite by a test flame in a vessel under specified conditions.

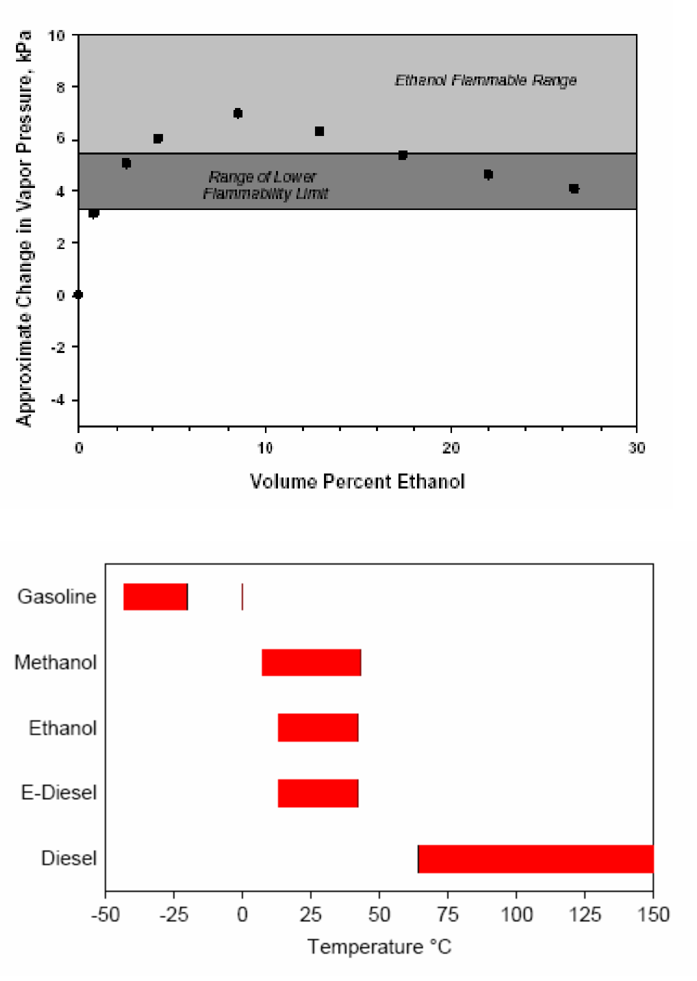

Figure 13. Flammability limits of E-diesel. (McCormick 2003, Waterland 2003)

With ethanol, the vapor in the air space in the fuel tank is flammable within a wide temperature range. In a study by Battelle, flammability limits were about 55 °F and 108 °F (13 – 42 ^{o}C) for diesel/ethanol mixtures (w/o additives) regardless of the percentage of ethanol present (Murphy/Battelle 2002). On the other hand, the low evaporation speed of ethanol keeps the alcohol concentration so low that it is not explosive in accidents (IEA/AFIS 1999). Flame-arrester devices have been developed for E-diesel refuelling, but so far the problems have not been completely solved. (Peckham 2003, McCormick 2001, Peckham 2001, Weyandt 2002, Waterland 2003)

Waterland et al. (2003) carried out a safety assessment of ethanol/diesel blends. They concluded that without modifications, risks with E-diesel are significantly greater than with diesel fuel or gasoline. It was noted that many safety actions can be adopted from experience gained with methanol fuelled heavy-duty vehicles demonstrated in 80’s and 90’s. Waterland et al. recommended that usage of ethanol/diesel blends would be limited to centrally-fueled vehicle fleets and the following actions should be taken:

- Equipping fuel storage tank vents and fill openings with flame arresters designed for ethanol
- All fuel transfer processes should include vapor recovery system
- An electrical ground connection between the vehicle and the fuelling station dispenser
- Insuring that vehicle fuel tank level detectors are of an intrinsically safe design

Safety aspects should always be kept in mind when handling E-diesel fuels. Personnel working with E-diesel blends should be trained to understand that flammability risk is higher than with standard diesel fuels.

One discussion item in conjunction with ethanol has been the risk of groundwater contamination. It has been stated that the BTEX compounds in gasoline (benzene, toluene, ethylbenzene and xylene) could travel up to 2.5 times further in groundwater in the presence of ethanol than in the absence of it due to the co-solvency effect. However, these statements of groundwater risks with ethanol have not been proven, and it has been stated that the travelling distance would not be as long as with MTBE (Environment Australia 2002).

5.3.7 Storage issues (water-tolerance, stability)

There is a lot of data on storage and stability of gasoline-ethanol blends, but less on diesel-ethanol blends. Ethanol is water-soluble and hygroscopic, and it carries therefore moisture into the fuel system. The gasoline-ethanol blends are sensitive to handling and storage practices due to the possibility of phase separation in the case of too high amount of water present. The amount of water that can be absorbed by low-concentration gasoline/ethanol blends without phase separation varies from 0.3 to 0.5 %, depending on temperature, aromatics and ethanol content. The higher the ethanol content, the greater the amount of water absorbed by the fuel without phase separation.

The additive of E-diesel should keep the mixture as an emulsion. The presence of water can lead to phase separation, but the manufacturers of emulsifiers claim that water contents up to 3 % could be tolerable (Peckham 2001). In the case of gasohol in the US, the water affinity of ethanol has led to blending the ethanol/gasoline mixtures only at product terminals. Similar procedures would possibly have to be applied for E-diesel. This means significant investments for blending systems and tanks. (McCormick 2001)

Additive manufacturers claim that E-diesels should be stable over a wide range of temperatures down to some -30 °C. In storage tanks the fuel has to be stable over long time periods, a minimum of several months is required. The oxidative and biological stability of fuel plus the stability of the additives themselves should also be known. (McCormick 2001)

5.3.8 Materials and lubricity related items

In the US, there are documented storage and handling procedures for low-concentration ethanol blends, e.g., for tanks, piping, fittings, pumps and dispensers. Some materials used in the storage systems may be unsuitable for ethanol, e.g., some single-walled fiberglass reinforced plastic tanks, some gaskets, sealants, adhesives and other materials. The unsuitable and suitable materials for high-concentration ethanol blends, such as E85, have been listed (E85 Handbook). For example, aluminum, zinc, brass, lead, and lerne (lead-tin-alloy plated steel, commonly used in fuel tanks) are incompatible with E85. Similarly, lists of compatible and incompatible non-metallic materials for E85 are available.

Permeation means how easily a fluid, or its vapor, can diffuse through a particular material. In gasoline vehicles, the enhanced control of evaporative emissions has led to fuel system materials more resistant to permeation. Ethanol can increase the permeation rate as being a polar compound and a smaller molecule than typical hydrocarbons. This and the higher vapor pressure can affect the evaporative emissions of gasoline cars. (Reynolds 2002)

Fuel lubricity is very important in diesel engine applications, because lubrication of many parts depend on the fuel for lubrication. Ethanol may decrease the lubricity of the diesel fuel, and Bosch, e.g., has experienced serious problems with injectors and injection pumps during vehicle and engine endurance tests due to low lubricity of E-diesel fuels (Peckham 2001, McCormick 2001). However, lubricity additives can improve lubricity of diesel/ethanol blends. Reports from emulsifier additive manufacturers claim that emulsifiers increase the lubricity of fuels. (McCormic 2001)

Some E-diesel durability tests have been reported. University of Illinois ran 500 hours with a Cummins B5.9 engine. E-diesel resulted in abnormal wear and corrosion in the Bosch fuel pump and the fuel injectors. Material compatibility problems occurred with an electronic sensor on the fuel pump. The pump wear was thought to be due to lower energy content of E-diesel (backlash of the timing device, high fuel rates). No contaminants in the lubricant were seen. The injector nozzle coking was reduced when compared with diesel. (McCormick 2001)

A number of field tests with E-diesel are ongoing or completed. A lot of experience has been gained in Brazil, which is one of the countries with a high interest in ethanol/diesel blends. Earlier tests in Brazil showed severe damages in fuel systems with rotary injection pumps. In-line pumps were expected to perform better. (Peckham 2002)

5.3.9 Cold properties

Cold properties of ethanol are excellent. In principle, cold flow properties should, thus, improve when blending ethanol into diesel, as long as the ethanol remains soluble. This is also the case proven by laboratory tests, with an exception for cloud point (McCormick 2001). Emulsifier manufacturers claim products to be soluble at very low temperatures.

Cloud point is not a good flow property indicator for E-diesel (Reynolds 2002): The cloud point of diesel fuel indicates the temperature, at which paraffins start to crystallize. With E-diesel, however, micro-emulsion micelles may grow resulting in a cloudy fuel, even when these micron size micelles still flow through filters. Thus, cold filter plugging point (CFPP) would be more suitable measure for E-diesel than cloud point (McCormick 2001).

5.4 OTHER ALCOHOLS

Higher alcohols are more suitable for diesel blending than ethanol. All problems that were reported for ethanol as a diesel component are easier to handle with higher alcohols. Figure 12 shows that cetane number increases with increasing chain length of the alcohol resulting in better ignition quality. Typically also miscibility with diesel improves. Lubricity is also better and flash point higher than for ethanol. However, economical feasibility of heavier alcohols has been poor so far.

Recently, a new diesel fuel composition has been introduced. The fuel called Agrodiesel 15 contains 85% of Swedish Environmental Class 1 diesel fuel and the remaining 15 % are renewables consisting of 5 % RME (rapeseed methyl ester) and 10 % higher alcohols. The blend is a solution, which is stable even during long periods of storage. Stability is often problem with diesel/ethanol emulsions. Agrodiesel 15 fulfills the requirements for Swedish Environmental Class 1 diesel fuel (Petterson 2005, Golubkov 2005).

6 STANDARDS AND SPECIFICATIONS FOR ALTERNATIVE FUELS

6.1 GENERAL ON FUEL SPECIFICATIONS

Currently, various standards and specifications set rather tight limits on diesel fuel composition and properties (see also Chapter 3). It should be noted that, e.g., diesel/ethanol blends do not fulfil any current diesel specification[6] and it cannot, thus, be sold as general diesel fuel. However, diesel/ethanol blends can be used in limited fleets, in demonstration-like use. Even for limited use a specification for diesel/ethanol blends would, however, be important (McCormick 2001). Some blends have already received approvals for special applications (see National verifications and approvals in 7.2).

There is, however, an emerging need to start to include alternative fuel components in general fuel specifications. The European fuel norms EN 288 and EN 590 allow 5 % ethanol in gasoline and 5 % FAME in diesel without special labelling of the fuel pumps.

"Standardization of alternative fuels" or Annex XXVII of the IEA Implementing Agreement dealt with standardization related issues. Phase 1 covered, among other things, the following issues (AMF Annex XXVII 2004):

- Existing national and international standards for alternative fuels. National ongoing work on standardization of alternative fuels.
- Ongoing and planned/discussed international work on standardization of alternative fuels (CEN, ISO and EU).
- The participating countries opinion concerning their need for new and re-examined alternative fuel standards as well as their priority list among such standards.
- Conclusions concerning a possible common opinion between the participating countries about the need for new re-examined international alternative fuel standards and a common priority list among such standards.
- Preliminary proposals how IEA/AMF best could work on the international arena offering CEN and ISO its knowledge and competence.

Standards for alternative fuels may be required within at least three different areas (AMF Annex XXVII 2004):

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[6] There are specifications available for emulsified diesel (water-diesel) in France and Italy. Ethanol/diesel does not fulfil either these specifications.

a) for use in pure form
b) as a component in a blend (e.g., ASTM D4806)
c) for the actual blended fuel.

Examples of existing national fuel standards are:

Canada:

- CAN/CGSB-3.514-98. Fuel methanol (M85) for automotive engines. Standards Council of Canada. Internet: http://alert.scc.ca/std_e/std6928.html

France:

- NF M07-096-104, Octobre 2000, Émulsions eau dans gazole (diesel/water emulsions)

Sweden :

- SS 15 54 36, Automotive fuels – Vegetable fatty acid methyl esters – Requirements and test methods
- SS 15 54 37, Motor fuels – Fuel alcohols for high-speed diesel engines

USA:

- D4806-01a Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel.
- D5797-96 Specification for Fuel Methanol (M70-M85) for Automotive Spark-Ignition Engines.
- D5798-99 Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines.
- D6751-02 Specification for Bio diesel Fuel (B100) Blend Stock for Distillate Fuels.

The European Committee for Standardization, CEN, is developing standards for alternative fuels. CEN produces documents of four different levels (Costenoble 2004):

- European Standard (EN)
- Technical Specification (CEN/TS)
- Technical Report (CEN/TR)
- CEN Workshop Agreement (CWA)

As mentioned earlier, EN standards exist for both gasoline (EN 228) and diesel (EN 590). CEN has also developed a European standard for biodiesel, EN14213/14214. CEN Technical Committee 19 dealing with fuels issues has altogether 15 working groups on specifications (petrol, diesel, LPG and heating oil and Task Forces on ethanol, biodiesel and hydrogen), systems (including quality monitoring and safety issues), and test methods.

As for alternative fuels and alternative fuel components the coverage of CEN documentation at this moment is as follows:

- EN 228: Ethanol, up to 5 % in gasoline, Directive EC 98/70/EC
    - CWA for E85, bio-origin
- EN 590: FAME, up to 5 % in diesel
- EN 14213/14214: biodiesel
- CWA on Emulsified Diesel Fuels

In January 2003, CEN/BT agreed to create a Technical Board working group (BT/WG 149) on “Alternative fuels” and to allocate the secretariat function to SIS (Swedish Standards Institute). The aim of the more informal BT/WG 149 is to initiate a European collective view of the general strategy for improvement of standardization on alternative fuels. According to CEN/BT`s decision, BT/WG 149 shall not establish CEN publications.

CEN/BT/WG 149 states that the following standards are urgently needed (recommendation to CEN/TC 19, ENGVA News December 2004):

1. Neat FAEE and 5 % blends in diesel oil
2. E10 and E15 as ethanol/gasoline blends
3. Alcohol-diesel blends
4. GTL from natural gas
5. Fuel ethanol (E95 with additives for diesel engines)
6. Biogas

In the longer term, the following standards would be needed:

1. 30 % of FAME in diesel fuel
2. BTL diesel from gasified biomass
3. DME
4. neat methanol (M100)
5. methanol blended with gasoline (M85)
6. CNG

At the international level, fuel issues are handled by The International Organization for Standardization (ISO). For the moment, Technical committee No. 28 “Petroleum products and lubricants” (TC 28) is the most relevant TC concerning an eventually work with standardization of alternative fuels. At present, ISO/TC 28 is looking at the possibility to extend the scope of test methods for fossil fuels to Fatty acid methyl esters (FAME). (AMF Annex XXVII)

So far, diesel/ethanol blends are not covered by any universal standard or specification. However, E-diesel has been granted conditional verification as a speciality fuel (Alternative Diesel Verification) by the Californian Air Resources Board. (ARB 2003). Diesel/ethanol blends have also been approved for use in Brazil.

6.2 ETHANOL SPECIFICATIONS

Fuel ethanol is used in blends with petrol, in blends with diesel, and in ethanol fuelled vehicles (FFVs, ethanol busses). The European Union (EU) is in the process of developing a standard for fuel ethanol. Brazil and the USA have used fuel ethanol for decades, and within EU Sweden and Poland have promoted fuel ethanol use since 80's and 90's. India adopted a fuel ethanol standard in 2004. (IFQC 2004). Anhydrous ethanol is used most widely as the basis for fuel ethanol standards. (IFQC 2004).

The ASTM D4806 (US) standard gives requirements for ethanol used in gasoline, the same standard is used for ethanol in diesel (McCormick 2001). *"Specifications, Definitions, and Regulations for the Composition of Industrial, Beverage and Fuel Alcohol Products in Various Countries"* are available at *"The Online Distillery Network for Distilleries & Fuel Ethanol Plants Worldwide"* (Distillery Network, specs).

ASTM D 4806 serves as the industry standard for fuel ethanol, but some consider it as a minimum standard and others may have more stringent requirements. The Renewable Fuels Association (RFA) prepares various guidelines and recommended practices for its members, their customers, and others. RFA Publication #960501 *Fuel Ethanol Industry Guideline Specifications and Procedures (Revised May 2002)* is the primary guideline for ethanol properties for the domestic fuel industry. The RFA, through Publication #960501, recommends that all of its member companies adhere to ASTM D 4806. (Reynolds 2002).

Ethanol must be denatured when used as a fuel. In the US, the most common denaturant is gasoline. The minimum amount of denaturant is 2 %, but as gasoline is cheaper than ethanol, it is common to use 5 % of denaturant. (Reynolds 2002).

The methanol content of ethanol is limited because methanol is corrosive and less tolerant to water. Acetic acid is also corrosive. A special "pHe" test detects even the very low levels of highly acidic compounds in ethanol (a pHe of below 6.5 may mean failure in fuel pumps and injectors; pHe above 9.0 may mean deleterious effect on plastic parts). (Reynolds 2002)

Both inorganic chloride and organic chlorine are corrosive. Copper is a catalyst for oxidation and contributes to a faster rate of gum formation. (Reynolds 2002)

Both hydrated and anhydrous ethanol grades are produced. Hydrated ethanol contains 95 % ethanol and some 5 % water after distillation. Dehydration produces an anhydrous grade with an ethanol content of 99.5 %. Hydrated ethanol can be used for E85, whereas anhydrous ethanol is required for gasohol.

Table 7 shows ASTM D 4806, Swedish "Sekab" and Brazilian specification for fuel ethanol. There are also other specifications of fuel ethanol. In Sweden, there is the standard SS 155937 for fuel alcohols, in Poland the Bioethanol Standard PN-A-79521 and in India the standard "IS 15464:2004 for Anhydrous Ethanol for Use in Automotive Fuel. In addition, there are specifications such as ASTM D 5798 for E75 - E85. (IFQC 2004). The World Wide Fuel Charter (WWFC) mentions that ethanol used in gasoline shall meet ASTM D 4806 requirements, and that the blended fuel must meet all other WWFC requirements. In addition, higher ($C > 2$) alcohols are limited to max. 0.1 % (volume) and methanol is not permitted. (WWFC 2002).

Table 7. ASTM D 4806, Swedish "Sekab" and Brazilian specifications for fuel ethanol. (IFQC 2004)

	ASTM D 4806 Denatured Anhydrous Fuel Ethanol	Sweden Sekab specification	Brazilian Anhydrous Ethanol	Brazilian Hydrated ethanol
Alcohol content, vol-%			min. 99.3	min. 92.6-93.8
Ethanol, vol-%	min 92.1 1)	99.8	min. 99.3	min. 92.6
Methanol, vol-%	max 0.5			
Hydrocarbon content, vol-%			max. 3.0	max. 3.0
Evaporative residue, mg/100 ml				5
Water, wt-%		max. 0.3		
Density, g/ml		max. 0.790	max. 791.5	max. 807.6-811.0
Solvent-washed gum, mg/100 ml	max 5.0			
Water content, vol-%	max 1.0			
Denaturant content, vol-%	min 1.96 max 4.76			
Inorganic Chloride content, wt ppm (mg/L)	max 40			max. 1 (mg/kg)
Copper content, mg/kg	max 0.1		max. 0.07	
Sulphate, mg/kg				max. 4
Fe, mg/kg				max. 5
Na, mg/kg				max. 2
Acidity (as acetic acid), wt-% (mg/l)	max 0.007 (56)	max. 0.0025	max. (30)	max. (30)
Aldehydes (as acetaldehyde), wt-%		max. 0.0025		
pHe	6.5-9.0			6-8
Electrical conductivity, µS/m			max. 500	max. 500
Appearance	visibly free of suspended or precipitated contaminants (clear & bright)	Clear without particles;	Clear & free of suspended impurities	Clear & free of suspended impurities
Color		Color Hazen max. 5	Colorless or yellow	Colorless or yellow

1) After denaturing

Specifications for diesel/ethanol blends are under development. Table 8 compares the properties of E-diesel[7] with those of standard No. 2 diesel. E-diesel is currently in experimental use. It can be used legally in off-road applications, but for on-road demonstrations permission is needed from the U.S. EPA.

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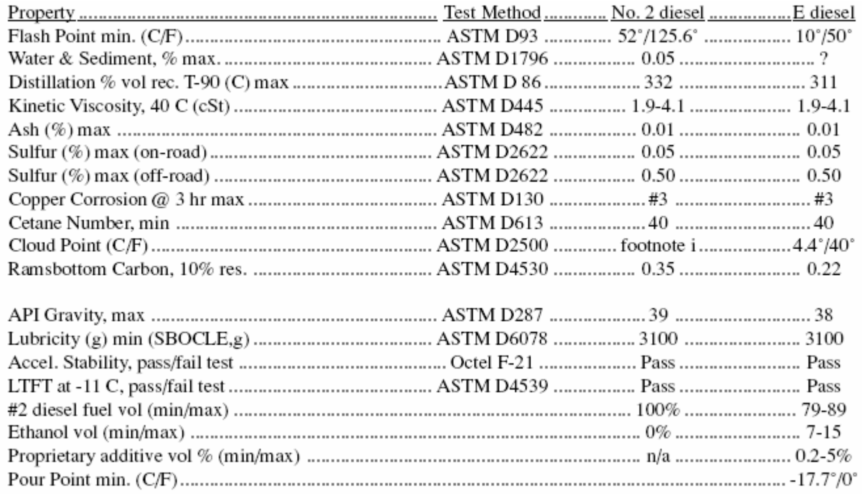
[7] US No. 2 diesel, ethanol up to 15 vol-% and additives as described in earlier Chapters

Table 8. Proposed Specification of Typical Properties (E diesel Consortium).[8]



Property	Test Method	No. 2 diesel	E diesel
Flash Point min. (C/F)	ASTM D93	52°/125.6°	10°/50°
Water & Sediment, % max.	ASTM D1796	0.05	?
Distillation % vol rec. T-90 (C) max	ASTM D 86	332	311
Kinetic Viscosity, 40 C (cSt)	ASTM D445	1.9-4.1	1.9-4.1
Ash (%) max	ASTM D482	0.01	0.01
Sulfur (%) max (on-road)	ASTM D2622	0.05	0.05
Sulfur (%) max (off-road)	ASTM D2622	0.50	0.50
Copper Corrosion @ 3 hr max	ASTM D130	#3	#3
Cetane Number, min	ASTM D613	40	40
Cloud Point (C/F)	ASTM D2500	footnote i	4.4°/40°
Ramsbottom Carbon, 10% res.	ASTM D4530	0.35	0.22
API Gravity, max	ASTM D287	39	38
Lubricity (g) min (SBOCLE,g)	ASTM D6078	3100	3100
Accel. Stability, pass/fail test	Octel F-21	Pass	Pass
LTFT at -11 C, pass/fail test	ASTM D4539	Pass	Pass
#2 diesel fuel vol (min/max)		100%	79-89
Ethanol vol (min/max)		0%	7-15
Proprietary additive vol % (min/max)		n/a	0.2-5%
Pour Point min. (C/F)			-17.7°/0°

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[8] NOTES: 1) Due to the low flash point of E diesel it should be treated as a Flammability Class 1 liquid (i.e. similar to gasoline). 2) Since ethanol has a lower BTU content than No. 2 diesel, the btu content of E diesel will be lower than No. 2 diesel. This will vary dependent upon the volume % ethanol present in the blend. The actual affect this may have on fuel economy is dependent upon the engine type and duty cycle.

7 STATUS OF DIESEL/ETHANOL BLENDS

7.1 FORMULATIONS FOR DIESEL/ETHANOL BLENDS

One option to introduce ethanol for diesel engines is to use diesel/ethanol blends with low concentration of ethanol. The alcohol diesel bi-fuel system was published first time by a German Professor H.A. Havemann et al. at the Indian Institute of Science, in the early 50's (Parivesh 2003). Research and demonstrations on such fuels were active in late 70’s and early 80’s in, e.g., the U.S., Germany, Brazil, Denmark, Sweden and South Africa. Due to technical problems the interest stalled (Peckham 2002, IFQC 2004).

Several producers and interest groups have been involved in diesel/ethanol products and additives over the years[9]. Many western companies see potential promises of ethanol-diesel blends in India and China, where 70 % of those countries’ overall transportation fuel demand is based on diesel fuel (e-mission 2002).

The critical factors of the potential commercial use of these blends include blend properties such as stability, viscosity and lubricity, safety and materials compatibility. The effect of the fuel on engine performance, durability and emissions is also of importance. With ethanol percentages of 10 % or less, operators have reported no noticeable differences in performance compared with running on diesel fuel (Hansen et al 2005).

The formulation of additives to maintain blend stability is also suggested as a critical factor in ensuring fuel compatibility with engines. Further work is required in confirming the long-term effects on engine durability, and ensuring safety in handling and storing ethanol/diesel blends. From a safety point of view, the low flammability limits of diesel/ethanol blends have to be taken into account in fuel handling. According to the NFPA in the USA, ethanol–diesel blends should be treated as Class I liquids as they have flashpoints below 37.8 °C, in contrast to diesel fuel being Class II liquid. Therefore, for example, fuel tanks might be necessary to be equipped with flame arresters. (Hansen et al 2005).

A Swedish brochure on the Etamix D3 diesel/ethanol blend claims that the blend containing 10 % ethanol derivative has a flash point higher than 30 °C (Class 2b) and can be handled in existing diesel fuel systems. (Etamix D3).

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[9] See http://E-diesel.org/index.htm “E diesel Consortium“, which is a group of stakeholders interested in developing a pathway for the commercialization of E diesel fuels. Renewable Fuels Foundation (RFF) is the research and education arm of the Renewable Fuels Association (RFA), the national trade association for the U.S. fuel ethanol industry. E diesel Consortium is a committee of the RFF.

Ethanol is not miscible with diesel, even though a small amount of ethanol is dissolved in diesel at room temperature. The properties of diesel fuel affect miscibility of ethanol, e.g., lowering aromatic content of diesel fuel reduces solubility of ethanol. Diesel/ethanol emulsions obtained with emulsifiers or without additives are “milky” mixtures, where ethanol is as small droplets in diesel. This kind of mixture tends to be rather unstable, and phase separation occurs easily during storage (McCormic 2001).

Micro-emulsions of ethanol and diesel can be obtained using additives containing surfactants or co-solvents. Microemulsions consist of droplets or micelles at the size of about 1 µm. The microemulsions are chemically and thermodynamically stable, they are clear and bright blends, unlike the emulsions (McCormic 2001).

Fatty acid methyl esters (FAME) are reported to act as an emulsifier for ethanol, which is an interesting option as FAME could improve lubricity of ethanol, whereas ethanol could reduce NO_x emissions and improve cold properties, which are shortcomings of FAME. Both components reduce particulate matter emission (McCormick 2001). VTT’s studies confirmed that blending RME into diesel/ethanol blends improves fuel performance (Nylund 2000). There is also interest in, e.g., diesel-ethanol-water blends. However, not much data is available concerning other combinations than diesel/ethanol mixtures.

Hansen (2005) and McCormic (2001) have reviewed chemical compounds and additives that have been studied for diesel ethanol blends. Here, only additives that are commercially available or have been demonstrated in larger field tests are discussed. The most common blends are listed in Table 9.

Australian APACE Research has developed the **Dalco** additive, which is an emulsifier agent (Queensland Government). A trial in Sweden on ethanol diesel blends was carried out in 1993 using the Dalco additive. At that time, 15 % hydrous ethanol, 3 % emulsifier (Dalco) and 82 % diesel was blended by Sekab and Aspen Petroleum in Sweden. (E-diesel brochure, e).

Akzo Nobel developed the Beraid® ED additive. A mixture of 5 – 15 % anhydrous bioethanol, Beraid® ED additive and diesel fuel was given the name E-diesel. The Beraid® ED additive enables splash-blending of ethanol and diesel, even at low temperatures. The amount of additive needed varies from 0.5 to 5 % depending mainly on the properties of base fuel. For example, 2 % has been used in field test with Danish diesel fuel. The Beraid® ED additive also contains lubricity and cetane improver components. (E-diesel brochures a-e).

A Brazilian emulsifier, **AEP-102**, is derived from soy. A plant (ECOMAT), producing 14 000 ton/y of AEP additive, was inaugurated in 2001. A mixture of 86 % diesel, 11 % anhydrous alcohol and 2.6 % AEP-102 additive has been tested in urban buses in Curitiba and in São Paolo. A reduction in smoke emission and fuel consumption has been observed, but even some problems with rotary-type injection pumps. Stability of mixture is a problem. The mixture is estimated to be 14 % more expensive than diesel fuel (Santos et al. 2000). The mixture of diesel, ethanol and AEP-102 additive is called MAD-8 (Figure 14, Azevedo et al. 2002).

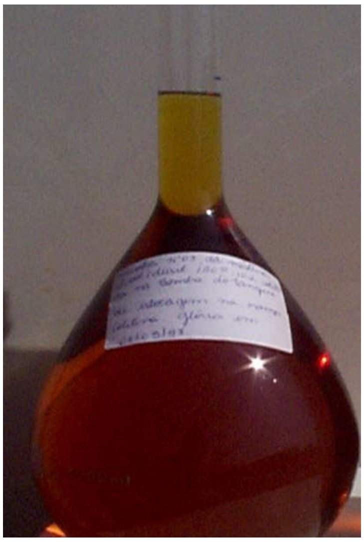


Figure 14. MAD-8 diesel/ethanol blend. (Azevedo et al. 2002)

One of the diesel ethanol emulsions tested is Swedish **Etamix D3** containing ethanol, solubility agent and lubricity agent. This fuel has been tested, e.g., by Wettenberg et al. (2003). According to the Etamix D3 brochure, this fuel contains 10 % ethanol derivative and 90 % Swedish Environmental Class 1 fuel (Etamix D3 brochure, SEKAB Svensk Etanolkemi AB). However, Etamix D3 is no longer listed as an available product on the website of Sekab AB. See comment on flash point earlier in the text.

The one diesel/ethanol blend that can be considered as a truly commercial product is **“O_2 diesel”** containing 91.5 % diesel, 7.5 % fuel-grade ethanol and 1 % emulsifier (Octel Octimax). This product was developed by AAE Technologies (UK, founded 1997), who signed a marketing agreement with Octel Starreon in 2000. “O_2 diesel” is a stable solution of diesel and ethanol, and can be produced by splash-blending. The blend gives significant emission benefits when compared with diesel fuel (Figure 15), and no harmful effects have been observed in the field tests. This product has been widely tested, e.g., in the USA and Brazil, and it has several certifications and approvals, as is mentioned in 6.3.2. (O_2 diesel brochure)

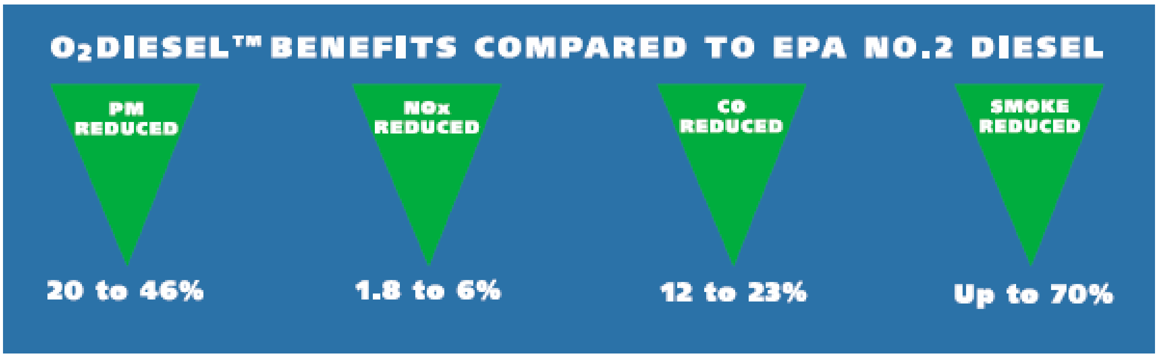


Figure 15. The emission benefits obtained with “O_2 diesel”. (http://www.o2diesel.com/)

Another potential diesel/ethanol blend is E-diesel manufactured by **PureEnergy** Corporation (PEC). This blend contains 15 % anhydrous ethanol and 1 – 5 % “Puranol” co-solvent. This fuel can also be splash-blended in a similar way as “O_2-diesel”. E-diesel is stable down to 21 °F (-6 ^{o}C).

The amount of additive needed depends on temperature and humidity. Various emission and field tests have been carried out with E-diesel. Significant reductions, even 41 % in particulate matter emission and 27 % in carbon monoxide emissions with a blend containing 15 % ethanol have been observed compared with diesel fuel. (Puranol brochure).

GE Betz is an additive manufacturer who has a product for diesel/ethanol blends. This additive is, however, petroleum based, whereas additives manufactured by O_2 diesel and PureEnergy originate from renewable materials. (Hansen 2004).

The German company BASF has a concept called Dasol A-8 with 8 % ethanol and 2.6 % solubilizer. In addition, the blend contains cetane and lubricity additives plus a highly reactive polyisobutene for detergency and corrosion inhibition. Dasol was tested in 80 cars in Brazil. Testing was limited to cars with in-line injection pumps. (Peckham 2002).

Table 9. The most common diesel/ethanol blends.

Company/ Producer	Sekab / Aspen Petroleum	O_2Diesel (AAE Technologies/ Octel Starregon)	Pure Energy	Akzo Nobel	Sekab
Product/ denotation	Dalco	O_2Diesel™	E-diesel	e-diesel	Etamix D3
Type of					
Diesel	Swedish ”MK 1”	Number 2 diesel	Number 2 diesel	Diesel fuel	Swedish ”MK1”
Alcohol	Fuel ethanol	Fuel ethanol	Ethanol	Anhydrous ethanol	Ethanol derivative
Additive	Dalco additive	AAE 07+ cetane improver	Puranol additive	Beraid ED10	Not specified
Blending	mixing 20 h at 70°C, emulsion	splash blending, microemulsion	splash blending, microemulsion	splash blending, microemulsion	splash blending, microemulsion
Composition					
Diesel	82 %	92	80–84%	>80%	90%
Ethanol	15%	7.7% vol	15%	15%	10% (derivative)
Additives	3%	Less than 1 %	1.5-2%	0.5-5% (e.g. 2%)	Not specified

7.2 NATIONAL VERIFICATIONS AND APPROVALS

There are many concerns about diesel/ethanol blends related to safety, stability, water tolerance, lubricity and cetane number. Some studies also report about problems with elastomers and other materials in the fuel systems when using ethanol blends. In addition, ethanol/diesel blends have shown vapor-lock problems and power loss. Lubricity of ethanol is poor and it may affect fuel-lubricant interactions resulting in wear in pumps, injectors and cylinder liners. The high volatility may lead to cavitation in pumps and injectors, resulting in both component wear and hot restart problems.

Due to concerns of safety, liability, and materials and component compatibility it will be difficult to obtain warranties from engine/vehicle manufacturers for diesel/ethanol blends. On the US markets, new fuels should pass the ***EPA fuel registration requirements***, Tier 1 and Tier 2 emission and health effects testing – a time consuming and expensive process (McCormick 2001). Small companies do not need to fulfill the Tier 1 and 2 testing requirements, so there are several small companies such as O_2Diesel (formerly AAE Technologies and Octel-Starreon), Pure Energy and AGP Corn Processing and Corn Plus registered by the US EPA in ethanol/diesel fuel business. (Peckham 2001).

In December 2004, a presentation of current status of E-diesel in California was held (Peeples 2004). According to Peeples, the achieved milestones and the ongoing program show how a long-distance path has to be completed before the final approval can be obtained for new fuels on market.

Achievements:

- "Alternative Diesel Verification" status from CARB for E diesel® product – Sept. 23, 2003. www.arb.ca.gov/fuels/diesel/altdiesel/092303o2dsl.pdf
- Designated as a "Developmental Engine Fuel" by the Division of Measurement Standards of Calif. Dept. of Agriculture (pending ASTM specification) – Sept. 2003.
- O_2Diesel™ reviewed by California State Fire Marshal according to agency policies & regulations – Sept. 2003.
- Launch of fleet programs, in addition to demonstrations, in compliance with regulations.
- Launch of CARB "Diesel Emissions Control Strategy" (DECS) Levels 1, 2, & 3 verification testing (2004)

Technical Agenda 2004:

- "Ethanol-Blended Diesel Fuel Handbook" (DOE Argonne National Laboratories) – release pending
- Uniform Safety and Handling procedures – Evaluation begun in 2001/02 at SwRI
- Greenhouse gas impact analysis by Argonne National Labs
- Health effects testing required per Section 211(b) of the CAA – Tier 1 complete
- John Deere cooperative test program – SwRI durability phase of testing now underway

Recent development of O_2Diesel^{TM} has been progressive. In March 2005, it was reported that Brazil's National Petroleum Agency ("ANP") has approved O_2Diesel^{TM} as an alternative diesel fuel for use in bus, truck and off-road fleets. The ANP approval follows eight months of thorough evaluation of the emission and performance data from O_2Diesel^{TM} tests in the US and Brazil.

Without ANP’s approval, fuel that does not conform to the specifications for standard diesel fuel cannot be sold in Brazil, and O_2Diesel^{TM} is presently the only ANP-approved alternative diesel fuel. O_2Diesel^{TM} plans to start its captive fleet test program in the city of Rio de Janeiro, in April 2005. (www.o2diesel.net)

7.3 ENGINE MANUFACTURERS VIEW

Currently, no engine manufacturers have indicated they will extend warranty coverage to their equipment when operating on E-diesel. They believe there are simply too many unanswered questions as well as the potential for liability exposure due to the increased flammability range of E-diesel. Engine manufacturers will not be prepared to extend warranty coverage, or even adopt a position of neutrality, until the open technical issues surrounding E-diesel are resolved.

The auto- and engine manufacturers’ views on fuel quality issues are summarized in the Word Wide Fuel Charter (WWFC). WWFC divides the markets in four categories, depending on the emission regulations in place. WWFC is rather restrictive regarding alternative fuel components. In Category 4, which is the most stringent category (US California LEV-II, US EPA Tier 2, Euro 4), e.g. FAME in diesel fuel is not approved. The requirement for methanol and ethanol in diesel fuel through Category 1 to 5 is “non detectable”.

The low flashpoint level of E-diesel is likely to generate risks to engines, vehicles and fuel distribution facilities, which raise serious safety concerns for fuel handling, storage and use (danger of explosion). Vehicle and engine manufacturers are concerned that E-diesel may damage vehicle parts, especially fuel injectors, and cause other types of vehicle failure due to low lubricity. The fuel’s compatibility with the vehicle in other ways, its effect on vehicle emissions and its health effects remain unknown. Since ethanol has lower energy content than diesel fuel, its presence in the fuel will reduce fuel economy. Therefore, until the many safety, performance and health concerns are resolved and sufficient peer-reviewed research is conducted in these important areas, manufacturers do not support adding ethanol to any category of diesel fuel (WWFC 2002). E.g. Cummins recommends against the use of diesel/ethanol blends (Cummins 2004: Diesohol – Comments to Discussion Paper May 2004).

Reynolds (2002) states: The various agencies world-wide need to initiate a dialogue with the auto manufacturers concerning the World-Wide Fuel Charter and global fuels harmonization initiatives. The auto manufacturers need to be made acutely aware of various policies and initiatives that would result in changes to existing and future transportation fuels. When the WWFC is in contrast with public policy objectives, those issues need to be thoroughly discussed to determine if more suitable specifications and text can be utilized. Similarly, this will give the automakers an avenue to explain, in detail, why certain aspects of the WWFC seem to contradict some energy related public policy objectives.

8 PRACTICAL EXPERIENCES WITH OXYGENATED DIESEL FUELS

8.1 GENERAL

The reports on field tests with oxygenated diesel fuels are rather scarce, especially reports on recent tests. Most of the available test results identified fuel economy and cost as the only appreciable differences between E-diesel and conventional diesel fuel. For mileage comparison, 10 % and 7 % reductions in fuel economy corresponded with 15 % and 10 % blends of ethanol and diesel fuel, respectively. Ethanol-diesel blends were found to be slightly more expensive than diesel fuel, due to the limited production of the special blending additive. Diesel/ethanol blends, when commercially available, are expected to cost a few percent more per gallon than conventional diesel fuel. (Reardon 2001)

8.2 ETHANOL BLENDS

8.2.1 Engine tests for performance and emissions

Performance

Hansen et al (2000) measured a 7 – 10 % decrease in power at rated speed with a 15 % ethanol-diesel blend run in a Cummins 5.9 litre engine. Kass et al. (2001) checked the torque output from the same model engine with two blends containing 10 % and 15 % ethanol, respectively, and reported an approximate 8 % reduction for both fuel blends.

The specific fuel consumption (SFC in kg/kWh) increases with increasing concentrations of ethanol in the blend because of the reduced energy content. However, specific energy consumption (SEC in MJ/kWh) is approximately the same as for diesel fuel or has been shown to be slightly better. Hansen et al (2001) reported a 2 – 3 % higher brake thermal efficiency with ethanol based blends.

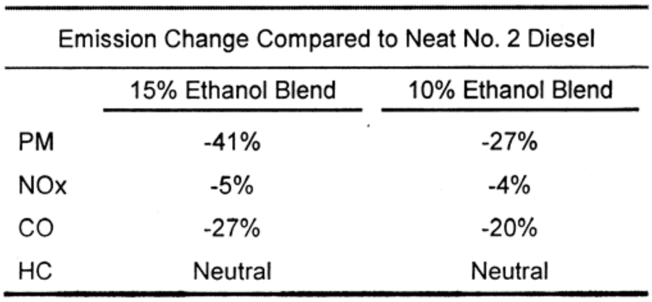
Bilgin et al (2002) evaluated experimentally the performance of a variable compression ratio compression-ignition engine operating with ethanol-diesel fuel blends. Blends having 2, 4, and 6 % of ethanol on a volume basis were used, as well as diesel fuel alone. The experiments were performed for the compression ratios of 19, 21 and 23. The experimental results indicated the 4 % ethanol blend to increase power output and efficiency of the engine while it decreased specific fuel consumption for various compression ratios. The best efficiency was attained at the compression ratio of 21 with an increment ratio of 3.5 %.

Emissions

According to Reardon (2001), ethanol-diesel blends significantly reduce particulate emissions in diesel engine exhaust by 20 percent or more, even in the newer diesel engines designed to meet today's stringent air emission standards.

Emissions tests conducted at the Southwest Research Institute with a series 60 Detroit Diesel heavy-duty diesel engine showed clear reduction in exhaust emissions with oxygenated fuels. A 15 % ethanol-diesel blend had been tested in three demonstration projects in over one million miles. The greatest reduction was achieved in PM emissions, by 41 %. NO_x was reduced by 5 % and CO by 27 %. Neutral emissions were found in the case of total HC (Table 10). (Ahmed 2001)

Table 10. Average percentage change for the transient emissions. (Ahmed 2001)



Emission Change Compared to Neat No. 2 Diesel

	15% Ethanol Blend	10% Ethanol Blend
PM	-41%	-27%
NOx	-5%	-4%
CO	-27%	-20%
HC	Neutral	Neutral

Emissions tests conducted specifically with ethanol-diesel blends confirm the effect of a substantial reduction in PM (Kass et al., 2001; Satge de Caro et al., 2001). The effect on carbon monoxide (CO), total hydrocarbon (THC) and oxides of nitrogen (NO_x) are less clear (Kass et al 2001).

The results of Spreen (1999) and Kass et al. (2001) showed a consistent reduction in PM of 20 – 27 % and 30 – 41 % for 10 % and 15 % ethanol blends, respectively. Reductions in NO_x varied from zero to 4 – 5 %. Both decreases and increases in CO emissions occurred, while THC increased substantially, but both were still well below the regulated emissions limit. Further factors that need to be considered are the effect of ethanol-diesel blends on exhaust gas recirculation systems (EGR). Kass et al. (2001) stated that the higher CO and THC emissions suggest that fuel blends might offer a means to enhance advanced emission control systems that require regeneration, such as NO_x adsorbers, by supplying a reducing agent.

Ahmed (2001) reports the ethanol-diesel blend to be tested in light-duty diesel engine at Argonne National Laboratories and Autoresearch Laboratories in Illinois in 2000. The test engine was Volkswagen's 1.9-liter TDI diesel engine with direct fuel injection and EGR. Two compositions of blends were used; 10 % and 15 % ethanol. Reduction ranges of 22 - 75 % for PM and 60 - 84 % for NO_x were achieved.

Wetterberg et al. (2003) tested several types of diesel fuels – including diesel-ethanol blend – in different, large off-road engines in Umeå, Sweden. The engines were not tuned in order to optimise them for the different fuels. As a result, the THC emissions were the highest with diesel-ethanol blend while the other fuels followed in the order: basic diesel oil, diesel-RME (Rapeseed Methyl Esther) blend, and Fischer-Tropsch fuel. Emissions of PM were significantly higher with basic diesel oil than with other fuels, but this result was not so evident as the THC results. Between those fuels, other consistent differences in regulated emissions were not observed.

He et al. (2003) researched the smoke and NO_x emissions of ethanol blended fuel in DI diesel engine using pure diesel fuel (E0) and two diesel-ethanol blends containing 10 % (E10) and 30 % (E30) ethanol. Unregulated emissions, including formaldehyde, acetaldehyde and unburned ethanol, were also investigated. The results indicated that the increase of ethanol in the blends reduces smoke significantly especially at medium and high loads (Figure 16), but increases NO_X emissions, acetaldehyde and unburned ethanol in the exhaust gases (Figure 17).

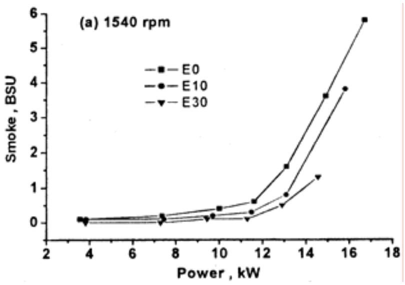


Figure 16. Bosch smoke index as a function of engine power. (He et al. 2003)

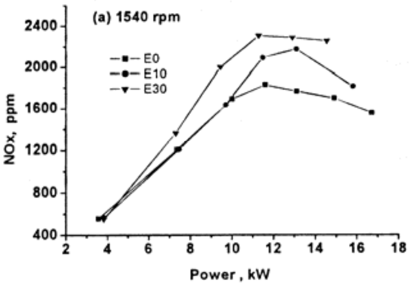


Figure 17. NO_x emissions as a function of engine power (He et al. 2003)

Compared with the gasoline engine fuelled by ethanol blended gasoline and equipped with a three-way catalytic converter, the tailpipe emissions of acetaldehyde and unburned ethanol are higher in diesel engine. He et al. (2003) also recorded the in-cylinder combustion process by using high speed CCD camera. Increasing ethanol content in the blends decreased flame luminosity, concluding the soot formation in fuel-rich regions can be suppressed by ethanol.

Mohammadi et al (2004) performed experiments with 15 % ethanol-diesel fuel using single cylinder naturally aspirated DI diesel engine equipped with high pressure common rail injection and a cold EGR system. Weak sooting tendency of ethanol-blend fuel enabled to use high EGR-rates for significant NO_x reduction. At an EGR rate of 20 %, having almost equal NO_x emissions levels, the PM level of ethanol blended fuel was 60 % lower than that of diesel fuel. Their results also indicated that low levels of PM and NO_x emissions are achievable without noticeable penalty in fuel consumption. Effects of fuel and EGR-rate on NO_X-PM trade off are presented in Figure 18.

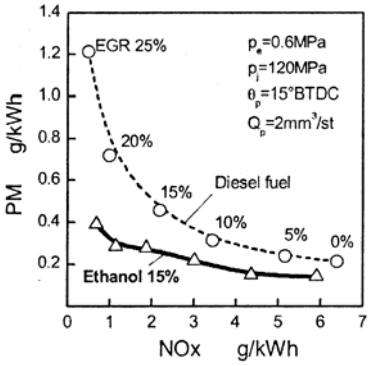


Figure 18. Effects of EGR-rate on NO_x-PM trade off of ethanol blended fuel at high engine load. (Mohammadi et al 2004)

On September 23, 2003, the first diesel-ethanol blend (O_2Diesel^{TM}) was verified as an alternative fuel by Californian Air Resources Board (ARB 2003). According to the verification letter, 1.6 % reduction in NO_x emissions and 20 % reduction in PM emissions were achieved. Additionally, in Canadian testing by Emissions Testing Centre (ETC), 46 % PM reductions were achieved in DT-466 engine equipped with an oxidation catalyst (DOC). (e-mission, 2004)

Figure 19 shows the reduction in PM emissions as a function of fuel oxygen content. The Figure is based on data from AAE, PEC and BetzDearborn. The engines used for testing were a 1991 DDC Series 60 engine and a Cummins ISB engine. (McCormic 2001)

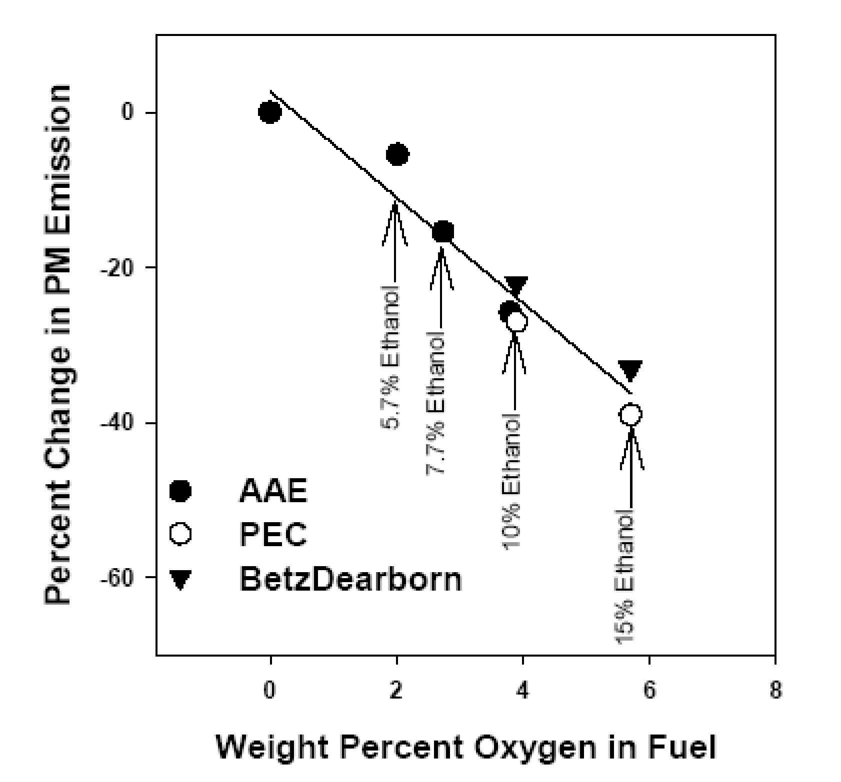


Figure 19. The effect of fuel oxygen content on PM emissions. (McCormic 2001)

Blends with biodiesel

Shi et al. (2005) prepared a mixture of 20 vol.-% ethanol in methyl soyate, and added this mixture to diesel fuel in 15 and 20 vol.-% blends. A blend containing only 20 % methyl soyate in diesel fuel was also tested. These blends, without any other additives, were found to be stable for up to 3 months. Diesel engine performance and emission characteristics were investigated and compared with diesel fuel. PM emissions were detected to decrease (a maximum reduction of 48 %) with increasing oxygenate content in the fuels, but NO_x emissions increased by 25 – 32 %, on average. All the oxygenate fuels produced moderately lowered CO emissions relative to diesel fuel. The methyl soyate blend emitted less THC emissions compared with diesel fuel. On the other hand, blends containing ethanol produced much higher THC emissions than diesel fuel. In this case, ethanol content may be the essential factor in the THC emission.

Engine durability

A laboratory-based 500 h durability test was performed by Hansen et al. (2000) with a Cummins ISB 235 engine running on a 15 % ethanol-diesel blend. With the exception of the fuel injection system, no abnormal deterioration in engine condition was detected based on detailed engine component measurements and examination. Calibration checks of both the injection pump and injectors showed that they were within normal tolerances.

VTT's IEA AMF Annex X "Fuel Characterisation"

Many standardized tests for evaluating fuel properties have originally been designed for screening straight-run hydrocarbon products. In the case of fuels blended with new components or treated with additives, the traditional test methods may give misleading results. The objective of Annex X, which was active in 1996 – 1997, was to evaluate the correlation between the results of standardized testing and of the real-life serviceability of new diesel fuel qualities. Combustion properties, properties affecting exhaust emissions, low-temperature performance and diesel fuel lubricity were studied. (Nylund 2000)

The test fuel matrix comprised of typical conventional hydrocarbon diesel fuels, low-emission hydrocarbon fuels, rapeseed and tall oil esters and two ethanol-blended diesel fuels. One blend contained 15 % ethanol (EtOH15), the other 10 % ethanol and additionally some 4 % RME (EtRE). The fuels were also treated with ignition improver additive. Combustion and emission tests were carried out with a heavy-duty bus engine (Volvo THD 103 KB) and a diesel passenger car. A farm tractor engine was used for cold-start testing.

The traditional cetane number measurement described well ignition delay of the heavy-duty engine at low and medium loads, but was more suitable for hydrocarbon fuels than for alternative diesel fuels. Cetane number measurement overestimated the effect of cetane improver, especially for biodiesels. Figure 20 shows the cetane number of the test fuels. The cetane number of the untreated fuels varied from some 40 to 55. The addition of cetane improver increased the cetane number by 2 to 15 units, depending on the fuel. The fuels containing esters had the strongest response to the additive, the ASTM 2D fuel the weakest. The CFR test engine run somewhat irregularly on the ethanol blended fuels.

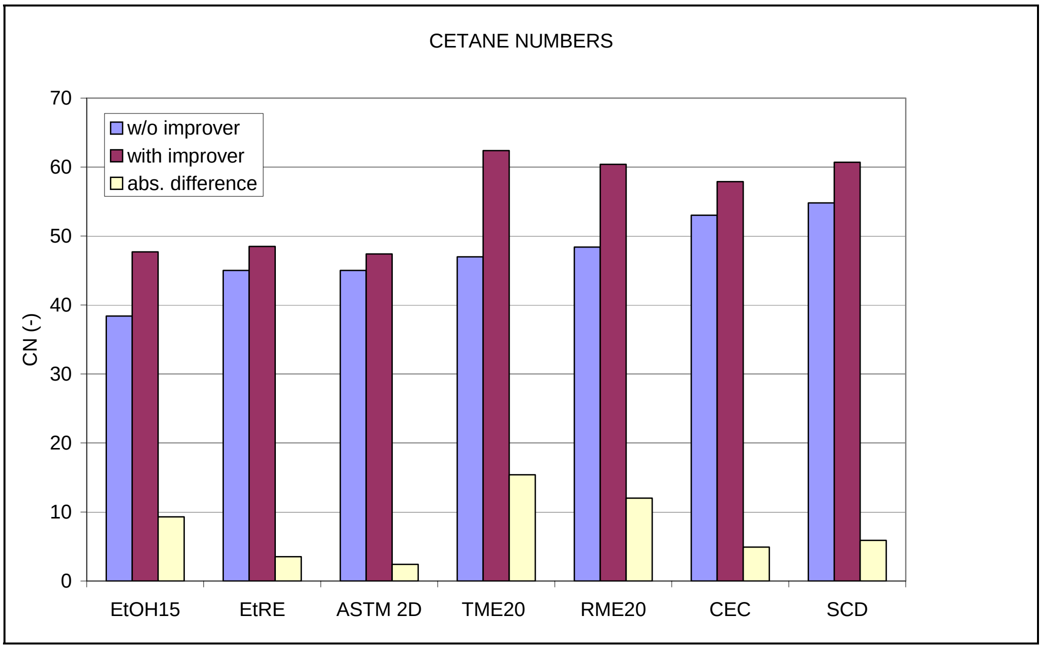
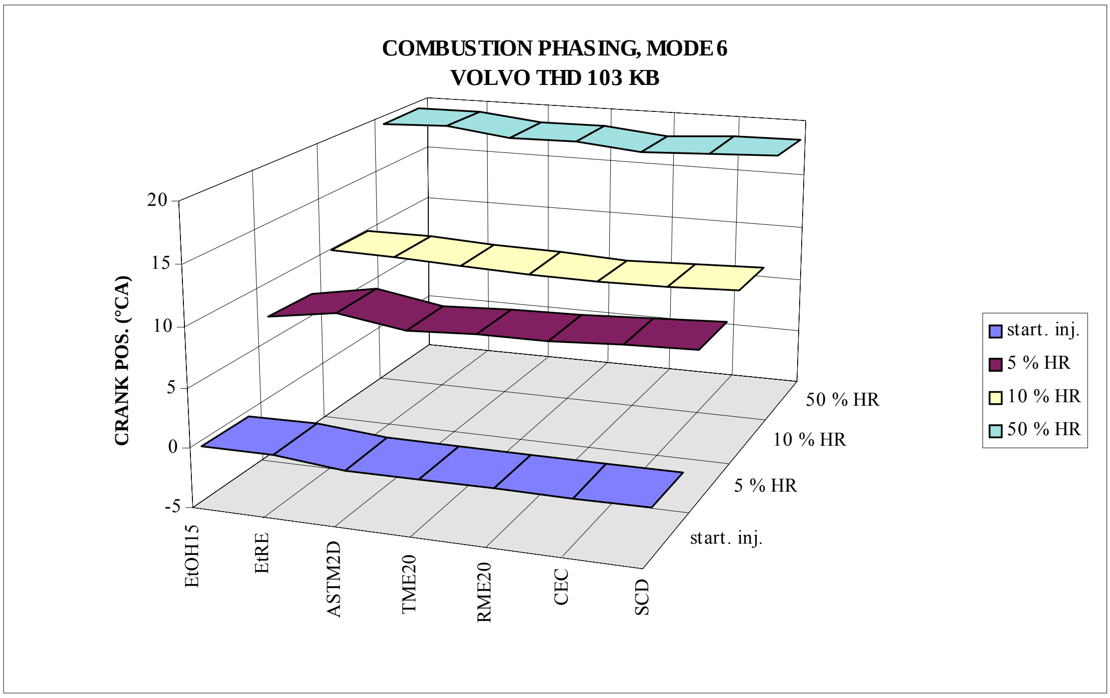


Figure 20. Cetane numbers for the test fuels of IEA AMF Annex X (CEC= European reference diesel fuel). (Nylund 2000)

The bus engine was instrumented with a cylinder pressure measurement system to study combustion phasing. The engine was run according to the ECE 49 steady-state duty cycle. The combustion parameters at different loads varied considerably. At high loads, where the temperature of cylinder is high, the ignition properties of the fuel are not as critical as at low loads. The start of injection and heat release parameters (5, 10 and 50 % HR) at low load mode 2 and high load mode 6 of the ECE R49 test are shown in Figure 21.



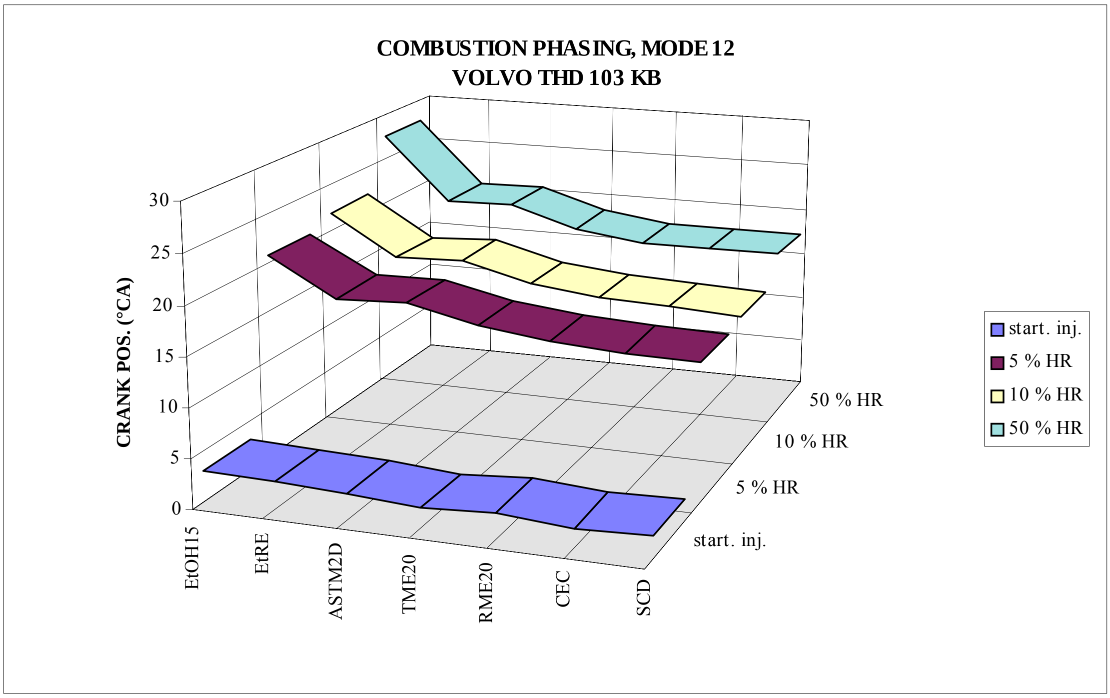


Figure 21. Start of injection, 5, 10 and 50 % heat release at high load mode 6 and low load mode 12 of ECE R49 test. The test fuels are presented in increasing order of cetane number. (Nylund 2000)

The fuels are presented in Figure 21 in increasing order of cetane number. This Figure is for fuels without ignition improver additive. To a certain extent cetane number correlated to the combustion parameters. The Figure shows that ignition delay is the longest with ethanol and low cetane fuels, whereas the duration of combustion is shorter with low cetane fuels. The abnormally long ignition delay with the 15 % ethanol blend in low-load mode 2 results in retarded combustion (lower part of the Figure). RME in combination with ethanol acts as a cetane booster, and the ethanol/RME mix gives combustion phasing comparable to the ASTM 2D diesel fuel. At high load (mode 6), the fuel effects are rather small (upper part of the Figure).

Figure 22 shows the ECE R49 weighted emission results for the various fuels. Compared with the other fuels, both ethanol blends reduced NO_x and PM emissions. However, for the 15 % ethanol blend an increase in aggregate CO and HC emissions can be seen. Figure 23 presents mode-by-mode emissions for reference diesel and the two ethanol blends. In the low-load modes, especially in mode 12, the 15 % ethanol blend results in significantly elevated CO and HC emissions.

The 15 % ethanol blend without ignition improver additive did not work properly in the bus engine. The ignition properties of the blend improved significantly when ignition improver additive was used.

The addition of some 4 % RME to the blend also improved both combustion characteristics and emission performance. RME also improved lubricity of both conventional diesel fuels and the ethanol blend.

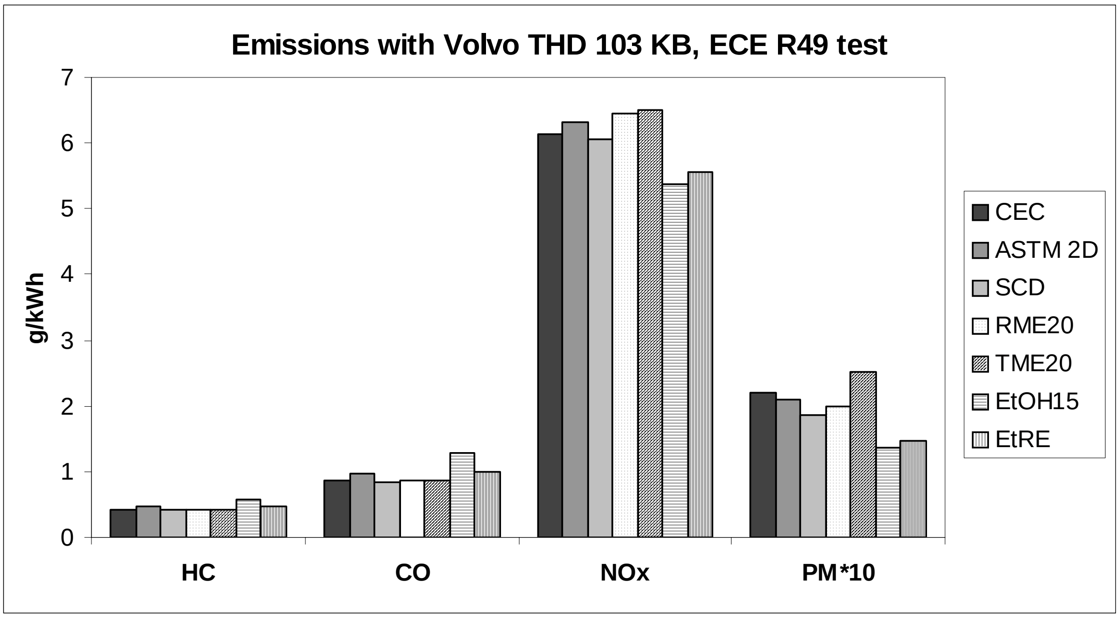


Figure 22. ECE R49 results for the bus engine (fuels without cetane improver). (Nylund 2000)

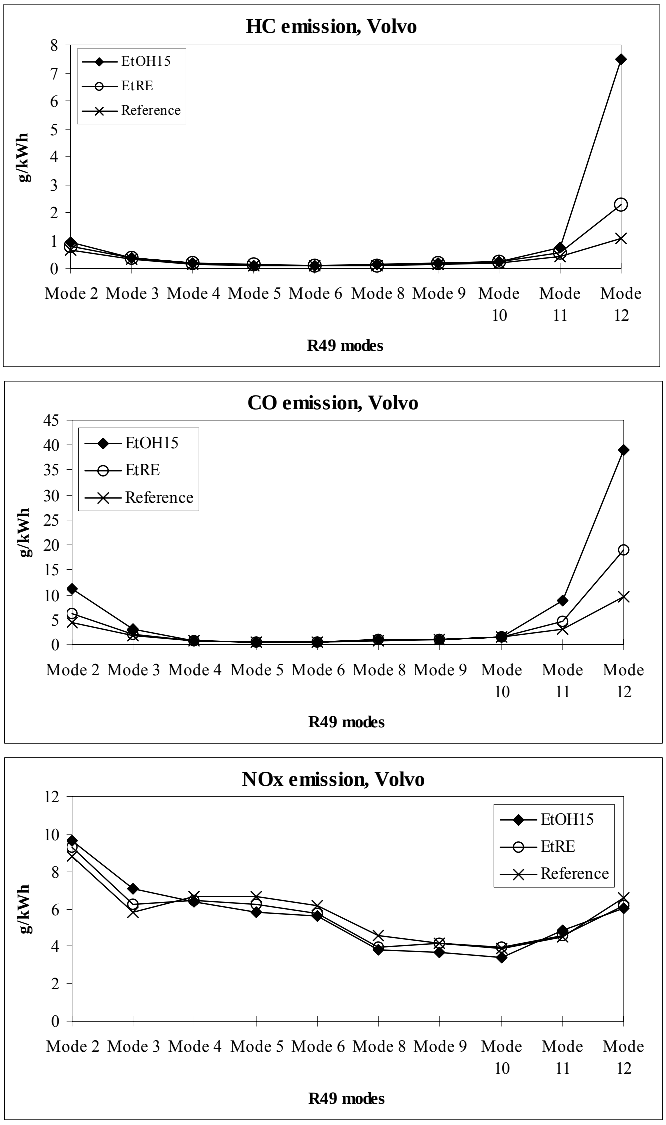


Figure 23. Mode-by-mode emissions for the reference fuel and the ethanol blends. (Nylund 2000)

8.2.2 Trucks

In 2001, a 3-year test and demonstration concluded that diesel/ethanol blend performed as well as conventional diesel fuel with no fuel-related or other unusual maintenance problems after nearly 400,000 miles of use in each of two over-the-road diesel trucks. This field demonstration was designed to test the fuel under typical driving. For the test, two different ethanol-diesel blends were used in trucks equipped with Mack E-7 diesel engines. Diesel fuel was mixed with 15 % and 10 % anhydrous ethanol, and a special blending additive developed by Pure Energy Corporation of New York. Oil analyses, taken at each oil change were normal. (Reardon, 2001)

Over-the-road tests by ADM, Bloomington, IL, US on two trucks operating with 15 % diesel/ethanol blend have resulted in an accumulation of over 400,000 km on each vehicle with no abnormal deterioration in condition. (Marek and Evanoff, 2001).

8.2.3 Buses

The Chicago Transit Authority (CTA) in the US monitored the condition and overall performance of a fleet of 30 buses, of which 15 were operated with the 15 % ethanol blend and 15 were the control and run on diesel. After 434,500 km accumulated by the 15 buses running on the blend, no abnormal maintenance or fuel-related problems were encountered. (Marek and Evanoff, 2001)

Until February 2002, four Lincoln city buses were the longest-running public transit vehicles in the USA fuelled by ethanol-diesel blend. The buses could be run with this blend exactly same performance and same fuel mileage as a diesel would after 19 months. (e-mission, 2002)

Sunoco, the Ontario oil refiner, participated in Ottawa bus trials in February 2002. The intention was to select and operate the group of 10 diesel buses with a 7.7 vol.-% ethanol blend, especially during the entire Ottawa winter time. The project was funded by the Canadian government as well as AAE Technologies, Sunoco, and Commercial Alcohols. The plan involved to that project when completed was to publicize the results widely and bring the ethanol-diesel blends in the mainstream as fast as possible. (e-mission, 2002)

During the winter time in Winnipeg 2002, a 6-month cold weather testing of the ethanol-diesel blend was carried out by 10 buses. The main reason for testing that blend under extreme conditions (ambient temperature down to -30 ºC) was to confirm that the fuel can be blended, delivered, stored, dispensed, and vehicles operate successfully in a cold climate, just like conventional fuel. (e-mission, 2002)

As a result, with DDC Series 50 four-stroke engines, no difference in maintenance performance was detected. On the other hand, there were some operational problems in buses equipped with older two-stroke engines. The reliability, mainly in terms of non-starting and low-power, decreased with ethanol blended fuel. The testing is planned to be expanded. (e-mission, 2003)

Fresno Area Express (FAX) chose 31 of its older buses to be fuelled by 7.7 % ethanol-diesel blend. After couple of month's experience, any power loss or maintenance issues related to fuel were not found as a problem. (e-mission, 2004)

According to Wang et al. (2003), the most noteworthy benefits of ethanol-diesel blends use lie with petroleum reductions and reductions in urban PM_{10} and CO emissions by bus operations.

8.2.4 Off-road machinery

In-field studies of a tractor and combine running on 10 % ethanol yielded increases in fuel consumed of 4 – 5 % compared with the same model tractor and combine operating with diesel fuel, which was approximately equivalent to the reduction in energy content. The operators did not notice any significant differences when operating their machines in the field. (Hansen et al., 2001)

(Hansen et al., 2001) conducted a farm demonstration project with four John Deere and two Caterpillar tractors, one of each vehicle type running on a 10 % ethanol-diesel blend and the others on diesel. One of the objectives was to monitor the durability of the vehicles. The tractors operated 700 - 1000 h with no abnormal deterioration in engine condition, based on oil analyses.

In February 2002 John Deere announced 2 years of extensive engine and emissions testing. Estimated to cost over $1.22 million and take 24 months of complete, the highly structured program includes a broad testing range, covering emissions, materials and system components, vehicle performance, engine durability, and fuel system and emissions durability. (e-mission, 2002)

8.2.5 General use

In Sweden, field testing was carried out with the Dalco additive in 1993. A fleet of 21 vehicles, buses and trucks, were running without problems. The emulsion resulted in 15 – 56 % lower particulate matter emissions compared with diesel fuel. The major problem in using the Dalco additive is the difficult blending procedure. The components were mixed for 20 hours at 70 °C, but the emulsion was not even then stable. (E-diesel brochure (e)). In Brazil, field tests were carried out with a blend of diesel fuel and 20 % hydrated alcohol using the Dalco additive (also corrosion inhibitor and cetane improver was used). Due to serious problems, e.g., with injection pump, this alternative was abandoned (Santos 2000).

Notable trials on Beraid® ED –based E-diesel have been conducted in Scandinavia and Thailand. In Denmark, two Scania tank trucks were running on E-diesel from 2001 to 2002 (Figure 24, Löfvenberg 2002). No harmful effects of E-diesel on the engine over a distance of 124 000 km were observed. Emission tests showed CO and PM emission reductions by some 30 % for E-diesel compared with Danish diesel fuel (“Miljödiesel 50”). (E-diesel brochures (a-d)). Further tests started in Stockholm in 2002 (E-diesel brochures (e)). A field test in Thailand was expected to finish in 2004 (IFQC 2004).

Figure 24. Danish tank trucks on E-diesel (Löfvenberg 2002, www.akzonobel.com).

8.3 OTHERS

Huang et al. (2004) carried out a study of the performance and emissions of the diesel-methanol blend in a compression ignition engine. The thermal efficiency of the engine increased and the diesel equivalent BSFC decreased with increase in the methanol mass fraction of the diesel-methanol blends. As reasons for that were listed an increased fraction of premixed combustion phase, oxygen enrichment, and improvement in the diffusive combustion phase. A marked reduction in the exhaust CO and smoke could be achieved when operating with the diesel-methanol blend. Methanol addition to diesel fuel was found to have a strong effect on the NO_x concentration, increasing it at high engine loads rather than at low loads.

The Swedish fuel called Agrodiesel 15 contains 85 % of Swedish Environmental Class 1 diesel fuel and the remaining 15 % is renewables consisting of 5 % RME (rapeseed methyl ester) and 10 % heavy alcohols. The blend is a stable solution, which fulfills the requirements for Swedish Environmental Class 1 diesel fuel (Petterson 2005, Golubkov 2005). Heavy-duty engine tests with Agrodiesel 15 have shown e.g. lower particle and PAH emissions than Swedish Environmental Class 1 diesel fuel. A long-term test of 500 hours showed no excessive wear and no engine failures during the test. A field test of one year with buses has also been carried out in co-operation with Västerås Lokaltraffik. Agrodiesel 15 performed well without any engine failures., Oil analyses and engine inspections revealed no problems. Drivers felt that odour of Agrodiesel 15 was stronger than from hydrocarbon diesel, and some comments stated that the buses had slightly less power with Agrodiesel 15. (Petterson 2005).

Keyu at al. (2002) carried out the experiments with a single cylinder diesel engine and a light duty diesel vehicle using a blend of dimethyl carbonate (DMC) and diesel fuel. Due to the lower calorific value of the blended fuel, tests with the single cylinder diesel engine indicated an increase in fuel consumption at fixed engine power, and tests with the diesel vehicle indicated a reduction in power at fixed fuel pump setting. The single cylinder diesel engine tests showed a significant reduction in exhaust submicron particles with an increase in DMC -% in fuel (Figure 25). Reduction of NO_x was also observed. The diesel vehicle tests indicated a significant reduction in smoke and CO, with an increase in both HC and NO_x emissions per measured maximum power.

Huang et al. (2003) investigated the combustion characteristics and heat release of a direct injection (DI) compression ignition engine fuelled with diesel-dimethyl carbonate (DMC) blends. The premixed combustion was prolonged and the duration of the diffusive combustion was shortened with increase in the DMC addition. The maximums of the cylinder pressure, the rate of pressure rise and the rate of heat release increased with increase in the DMC addition, especially at medium and high loads. The diesel equivalent BSFC, CO and smoke emissions decreased with increase in the DMC addition but no significant effect on NO_x was observed.

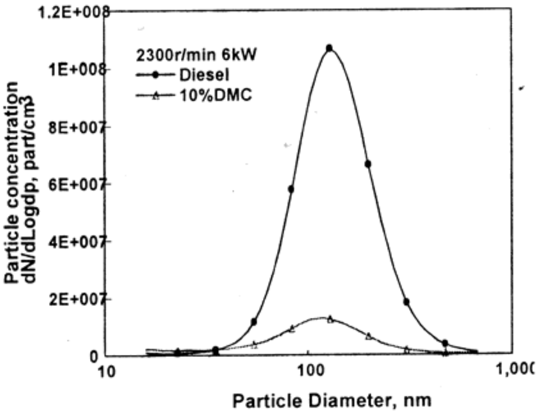


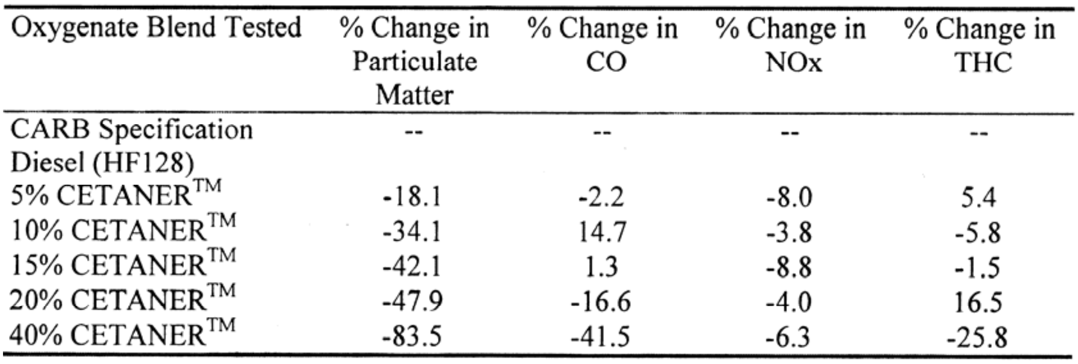
Figure 25. Effect of DMC on particle number size distribution under loaded conditions. (Keyu at al. 2002)

Blending dimethyl ether (DME) in diesel fuel is one option to utilize DME in diesel engines without drastic redesign of fuel pumps and fuel injectors. It should be noted, however, that even modest addition of DME significantly reduces the viscosity of the fuel mixture. Already a 25 wt-% addition of DME into diesel fuel reduces fuel viscosity below the ASTM specification. (Chapman et al. 2003)

Hess et al. (2000) studied experimentally the effects of the addition of CETANER^{TM} (developed by Air Products and Chemicals, Inc.) into diesel fuel at various blend levels of 5 – 40 % by mass. The test engine was Cummins ISB 5.9 litre turbocharged DI diesel engine. The advantages of CETANER^{TM} are: derived from a non-petroleum feedstock, cetane number greater than 100, and cost comparable to diesel fuel. It can be manufactured from coal-derived syngas through a two-stage process: liquid phase dimethyl ether (DME) synthesis, and chemistry to form long chain linear ethers from DME. With a 40 % CETANER^{TM} –blend, an even 83 % reduction in PM, 6.3 % reduction in NO_x, 26 % reduction in THC, and 42 % reduction in CO emissions was observed. At above 15 % CETANER^{TM} addition, the engine was unable to reach peak power output, so de-rating is required without engine modifications. Still, at 15 % CETANER^{TM} addition, reductions of 42 %, 8.8 %, 1.5 % and 1.3 % in emissions of PM, NO_x, THC and CO were observed, respectively (Table 11).

Zhu et al. (2003) tested experimentally three different diesel fuels for their emission characterizations in vehicle exhaust on a light duty diesel truck. One of these fuels was oxygenate (diethylene glycol dimethyl ether, DEDM) blended diesel fuel. Addition of the DEDM-oxygenate (14.4 vol.-%) led to reductions in PM, THC and CO emissions. The largest emissions reduction was observed for PM, since it was reduced by 20-40 %. There was no clear evidence of reductions in NO_x emissions. According to this study, the amount of toxic compounds in exhaust emissions, such as benzene, butadiene, formaldehyde or PAHs, did not increase as a result of blending diesel fuel with DEDM.

Table 11. Emissions results from the AVL 8-mode test protocol. (Hess et al. 2000)



Oxygenate Blend Tested	% Change in Particulate Matter	% Change in CO	% Change in NOx	% Change in THC
CARB Specification Diesel (HF128)	--	--	--	--
5% CETANER^{TM}	-18.1	-2.2	-8.0	5.4
10% CETANER^{TM}	-34.1	14.7	-3.8	-5.8
15% CETANER^{TM}	-42.1	1.3	-8.8	-1.5
20% CETANER^{TM}	-47.9	-16.6	-4.0	16.5
40% CETANER^{TM}	-83.5	-41.5	-6.3	-25.8

Lin and Huang (2003) investigated the effect of the proportion of ethylene glycol mono-acetate added to fuel oil on engine performance and emission characteristics in marine diesel engines. Ethylene glycol mono-acetate was mixed with diesel fuel in various proportions to prepare oxygenated diesel fuel. A four-cylinder diesel engine was used to test the engine performance and emission characteristics. Based on the experimental results, ethylene glycol mono-acetate addition into the diesel oil increased BSFC, with lowered NO_X, CO and CO_2 emissions.

9 SUMMARY

In Milan in 2002, the Executive Committee of the Implementing Agreement on Advanced Motor Fuels took a decision to start a new Annex on diesel oxygenates, Annex XXVI "Evaluation of practical experiences of ongoing projects around the world using alcohols/ethers as oxygenates in diesel fuel". The original project plan by Befri Konsult stated that the main objective was to get a truthful picture of the performance of such diesel blends containing alcohols or ethers that have reached pilot or commercial status. TEC TransEnergy Consulting Ltd of Finland was asked to assist Befri Konsult in preparing the final report of Annex XXVI. Compared with the original project plan, a more detailed chapter on fuel properties, including limitations of blending low-boiling components into diesel fuel, was added to the final report.

Overall, the relative share of diesel of the total fuel consumption by all highway vehicles has been steadily increasing. For evident reasons, when planning the implementation of alternative fuels or, e.g., biocomponents, diesel vehicles and diesel fuel cannot be overlooked, as diesel by volume in most cases is very close to gasoline. In addition, the greater part of the commercial vehicle operations rely on diesel vehicles. In Europe, there is a Directive (2003/30/EC) in place calling for a 2 % fuel replacement by biofuels (energy base) in 2005 and a 5.75 % replacement in 2010. So far the target values are indicative, not mandatory.

Oxygenates blended into diesel fuel can serve at least two purposes. Components based on renewable feedstocks make it possible to introduce a renewable component into diesel fuel. Such components could be bio-ethanol, biodiesel or synthetic components made from biomass via gasification and synthesis gas. Secondly, oxygenates blended into diesel fuel might help to reduce emissions. Especially for heavy-duty vehicles, the most critical emission components are particles and oxides of nitrogen. Several studies have shown that oxygenated fuel components help to bring down particle emissions.

By default, ethanol does not reduce greenhouse gas emissions. The outcome is highly dependent on raw material and processing technology. At its best, the equivalent CO_2 emissions are only some 20 % compared with gasoline and diesel, at its worst close to 100 %.

A number of different oxygenates have been considered as components for diesel fuel or to be used as such in a compression ignition engines. These oxygenates include various alcohols, ethers, esters and carbonates. Biodiesel, i.e., esters of vegetable oils also contain oxygen. However, the study at hand focuses on alcohols and ethers as blending components for diesel. Of the ethers, potentially suitable for diesel engines are, i.a., DME (dimethyl ether), diethyl ether (DEE), dimethoxy methane (DMM), and glycol ethers (monoglyme, diglyme). As for practical experiences, the greater part of actual field testing has taken place on diesel/ethanol blends (E-diesel).

There are a number of fuel properties, both physical and chemical, which are crucial for the proper operation of a diesel engine. National and regional regulations and standards control diesel fuel quality. Fuel quality requirements are in place partly to secure the operability and integrity of vehicles and engines, partly to control exhaust emissions.

Ethanol differs significantly from diesel fuel. As the octane rating of ethanol is high, cetane number of neat ethanol is only approximately 8, whereas the requirement in Europe for diesel is 51 or more (EN 590). Adding ethanol to diesel will reduce cetane. Therefore, cetane improver additives might be needed. Fuel lubricity is very important in diesel engine applications, because lubrication of many parts depend on the fuel for lubrication. Ethanol may decrease the lubricity of the diesel fuel, and Bosch, e.g., has experienced serious problems with injectors and injection pumps during vehicle and engine endurance tests due to low lubricity of E-diesel fuels (i.e., diesel/ethanol blends). The low boiling point increases the risk of cavitation and high conductivity the risk of corrosion.

Ethanol is not miscible with diesel, even though a small amount of ethanol is dissolved in diesel at room temperature. The properties of diesel fuel affect miscibility of ethanol, e.g., lowering aromatic content of diesel fuel reduces solubility of ethanol. Diesel/ethanol emulsions obtained with emulsifiers or without additives are “milky” mixtures, where ethanol is as small droplets in diesel. This kind of mixture tends to be rather unstable, and phase separation occurs easily during storage. Micro-emulsions of ethanol and diesel can be obtained using additives containing surfactants or co-solvents. Microemulsions consist of droplets or micelles at the size of about 1 µm. The microemulsions are chemically and thermodynamically stable, they are clear and bright blends, unlike the emulsions.

Storage and handling regulations for fuels are based on the flash point. In Europe, diesel fuel has to have a flash point higher than 55 °C. In the US, the Class II liquid requirement for flash point is higher than 38 °C. The problem with, e.g., ethanol blended into diesel is that ethanol lowers the flash point of the blend significantly even at low concentrations. Regarding safety, diesel-ethanol blends fall into the same category as gasoline. Similar procedures for safety, handling and storage are required for diesel-ethanol blends as for gasoline.

Currently, various standards and specifications set rather tight limits on diesel fuel composition and properties. It should be noted that, e.g., E-diesel does not fulfil any current diesel specification and it cannot, thus, be sold as general diesel fuel. Some blends have already received approvals for special applications.

Several producers and interest groups have been involved in diesel/ethanol products and additives over the years. The critical factors of the potential commercial use of these blends include blend properties such as stability, viscosity and lubricity, safety and materials compatibility. The effect of the fuel on engine performance, durability and emissions is also of importance. With ethanol percentages of 10 % or less, operators have reported no noticeable differences in performance compared with running on diesel fuel.

The formulation of additives to maintain blend stability is also suggested as a critical factor in ensuring fuel compatibility with engines. Further work is required in confirming the long-term effects on engine durability, and ensuring safety in handling and storing ethanol/diesel blends. Fatty acid methyl esters (FAME) are reported to act as an emulsifier for ethanol, which is an interesting option as FAME could improve lubricity of ethanol. From a safety point of view, the low flammability limits of diesel/ethanol blends have to be taken into account in fuel handling.

Companies that are or have been involved in diesel/ethanol blends are e.g. Sekab, Aspen Petroleum, O_2Diesel, Pure Energy, Akzo Nobel and GE Betz. The list of various additives or components for diesel/ethanol blends include names like Dalco, Beraid, AEP-102, Puranol and Dasol A-8.

Earlier, there were a lot of activities with E-diesel in Sweden. Now it looks like the interest has lessened somewhat. For the time being, California and Brazil are leading the development of E-diesel. On September 23, 2003, the first diesel-ethanol blend (O_2Diesel^{TM}) was verified as an alternative fuel by Californian Air Resources Board. In March 2005, it was reported that Brazil's National Petroleum Agency ("ANP") has approved O_2Diesel^{TM} as an alternative diesel fuel for use in bus, truck and off-road fleets. The ANP approval follows eight months of thorough evaluation of the emission and performance data from O_2Diesel^{TM} tests in the US and Brazil.

Currently, no engine manufacturers have indicated they will extend warranty coverage to their equipment when operating with E-diesel. They believe there are simply too many unanswered questions as well as the potential for liability exposure due to the increased flammability range of E-diesel. Engine manufacturers will not be prepared to extend warranty coverage, or even adopt a position of neutrality, until the open technical issues surrounding E-diesel are resolved. The auto- and engine manufacturers' views on fuel quality issues are summarized in the Word Wide Fuel Charter (WWFC).

The reports on field tests with oxygenated diesel fuels are rather scarce, especially reports on recent tests. There are, however, some reports available on engine tests and tests with trucks, buses and even off-road equipment. Most of the available test results identified fuel economy and cost as the only appreciable differences between E-diesel and conventional diesel fuel. For mileage comparison, 10 % and 7 % reductions in fuel economy corresponded with 15 % and 10 % blends of ethanol and diesel fuel, respectively. Ethanol-diesel blends were found to be slightly more expensive than diesel fuel, due to the limited production of the special blending additive. Diesel/ethanol blends, when commercially available, are expected to cost a few percent more per gallon than conventional diesel fuel. The price per energy content is also higher.

Hansen et al. measured a 7 – 10 % decrease in power at rated speed with a 15 % ethanol-diesel blend run in a Cummins 5.9 litre engine. Kass et al. checked the torque output from the same model engine with two blends containing 10 % and 15 % ethanol, respectively, and reported an approximate 8 % reduction for both fuel blends. The specific fuel consumption (SFC in kg/kWh) increases with increasing concentrations of ethanol in the blend because of the reduced energy content. However, specific energy consumption (SEC in MJ/kWh) is approximately the same as for diesel fuel or has been shown to be slightly better. Hansen et al reported a 2 – 3 % higher brake thermal efficiency with ethanol based blends.

Most emissions tests with heavy-duty engines confirm the effect of a substantial reduction in PM when running with E-diesel. The typical range for PM reduction is 20 – 40 %. Most studies also report reduced NO_x emissions. For a light-duty engine, Ahmed found reduction ranges of 22 - 75 % for PM and 60 - 84 % for NO_x.

A laboratory-based 500 h durability test was performed by Hansen et al. with a Cummins ISB 235 engine running on a 15 % ethanol-diesel blend. With the exception of the fuel injection system, no abnormal deterioration in engine condition was detected based on detailed engine component measurements and examination. Calibration checks of both the injection pump and injectors showed that they were within normal tolerances.

Within VTT’s Annex X, “Characterisation of new fuel qualities”, combustion properties, properties affecting exhaust emissions, low-temperature performance and diesel fuel lubricity were studied with several fuels. Measured in a bus engine, ignition delay is the longest with ethanol and low cetane fuels, whereas the duration of combustion is shorter with low cetane fuels. The 15 % ethanol blend resulted in abnormally long ignition delay in low-load modes, and in retarded combustion as a consequence. RME in combination with ethanol acts as a cetane booster, and the ethanol/RME mix gives combustion phasing comparable to the ASTM 2D diesel fuel. At high load, the fuel effects are rather small.

In US in 2001, a 3-year test and demonstration concluded that diesel/ethanol blend performed as well as conventional diesel fuel with no fuel-related or other unusual maintenance problems after nearly 400,000 miles of use in each of two over-the-road diesel trucks. In another over-the-road tests two trucks operating with 15 % diesel/ethanol blend accumulated over 400,000 km on each vehicle with no abnormal deterioration in condition.

Several transit companies have tested E-diesel. The Chicago Transit Authority monitored the condition and overall performance of a fleet of 30 buses, of which 15 were operated with the 15 % ethanol blend and 15 were the control and run on diesel. No abnormal maintenance or fuel-related problems were encountered. Until February 2002, four Lincoln city buses were the longest-running public transit vehicles in the USA fuelled by ethanol-diesel blend. With this blend, the buses could be run exactly at the same performance and same fuel mileage as a diesel would after 19 months.

Studies in Winnipeg 2002 focused on testing E-diesel under extreme conditions (ambient temperature down to -30 ºC). With DDC Series 50 four-stroke engines, no difference in maintenance performance was detected. On the other hand, there were some operational problems in buses equipped with older two-stroke engines. The reliability, mainly in terms of non-starting and low-power, decreased with ethanol blended fuel.

In tests with farm tractors and combines running on 10 % ethanol, operators did not notice any significant differences when operating their machines in the field. John Deere is one of the off-road machinery manufacturers interested in E-diesel. In February 2002, John Deere announced 2 years of extensive engine and emissions testing.

In early field tests in Sweden, a fleet of buses and trucks was running without problems with the Dalco additive. The major problem in using the Dalco additive was the difficult blending procedure. Notable trials on Beraid® ED –based E-diesel have been conducted in Scandinavia and Thailand.

Higher alcohols are more suitable for diesel blending than ethanol. Cetane number increases with increasing chain length of alcohol, miscibility with diesel improves, lubricity is better and flash point higher than for ethanol. However, economical feasibility of heavier alcohols has been poor so far. Recently, a new diesel fuel composition was introduced. Agrodiesel 15 contains 85 % of Swedish Environmental Class 1 diesel fuel and the remaining 15 % are renewables consisting of 5 % RME (rapeseed methyl ester) and 10 % heavy alcohols. According to the producer Agrodiesel 15 fulfills the requirements for diesel fuel.

Most tests with other oxygenates than ethanol have been conducted with laboratory engines or single vehicles. So far, no really comprehensive field tests with blended fuels have been carried out. Several ethers have been evaluated as possible diesel oxygenates. Poly-ethers or ethers with high molecular weight are better suited to be used as diesel fuel components than mono-ethers. However, many oxygenates have problems with low flash point or toxicity problems. One risk with ethers is possible formation of peroxides, which may lead to explosion. Some ethers may have an anaesthetic effect. Only a few ethers, like n-pentyl ether (DNPE), are potential blending components in practise. High price might also be a limitation.

At the moment, the development of E-diesel is fast in California and Brazil. Although no universal approvals to replace diesel with E-diesel exist, approvals for E-diesel for special services have been granted. The auto industry, on the other hand, has a very restrictive attitude towards E-diesel. The critical factors of the potential commercial use of these blends include blend properties such as stability, viscosity and lubricity, safety and materials compatibility. Solubility of ethanol and fuel stability were earlier problems associated with E-diesel. However, microemulsions obtained by using additives containing surfactants or co-solvents have solved most mixing and stability problems and make splash blending possible. Further work is required in confirming the long-term effects on engine durability, and ensuring safety in handling and storing ethanol/diesel blends. The safety risk caused by the low flash-point of E-diesel is still an issue. From a safety point of view E-diesel must in principle be treated as gasoline, and this can cause problems in systems accustomed to diesel fuel.

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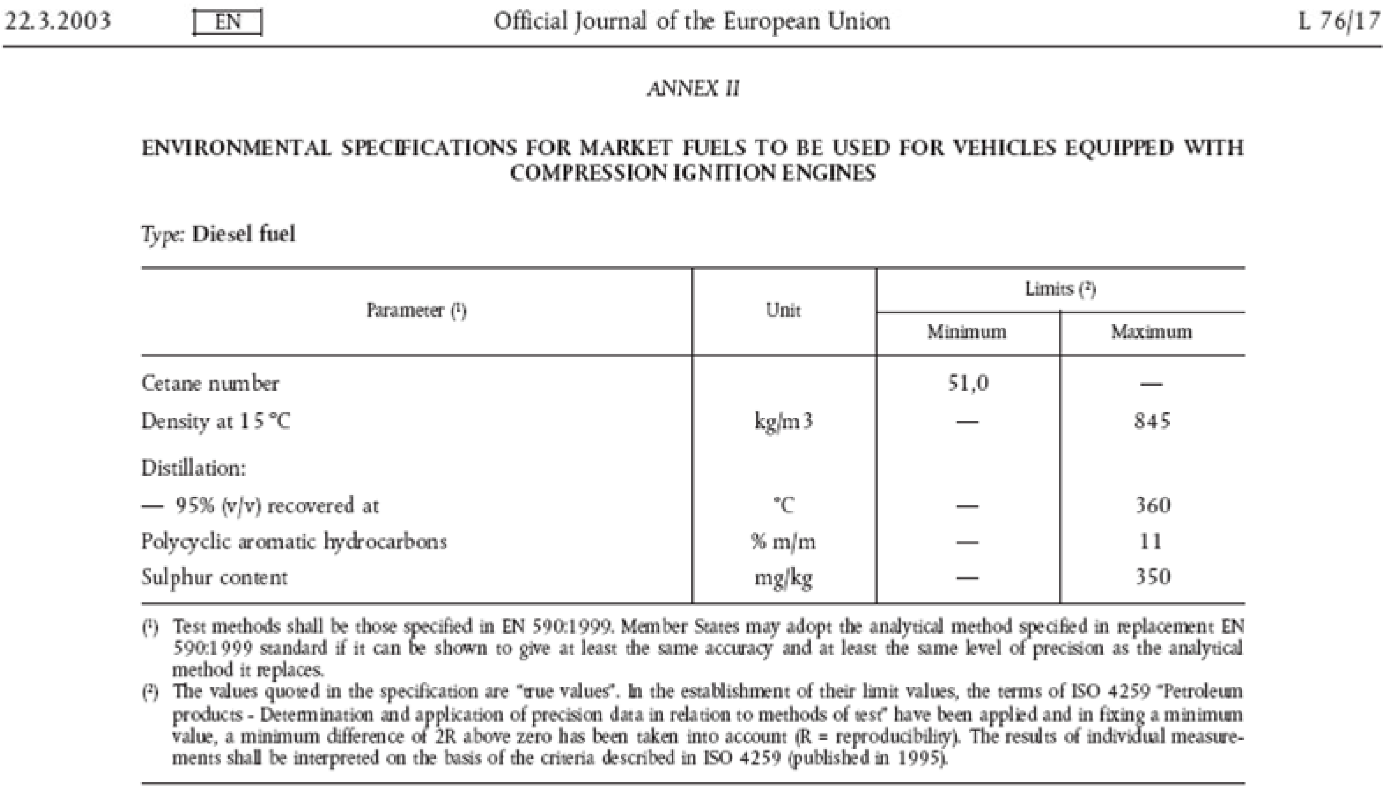
APPENDIX 1: DIESEL FUEL SPECIFICATIONS

Directive 2003/17/EC



22.3.2003 EN Official Journal of the European Union L 76/17

ANNEX II

ENVIRONMENTAL SPECIFICATIONS FOR MARKET FUELS TO BE USED FOR VEHICLES EQUIPPED WITH COMPRESSION IGNITION ENGINES

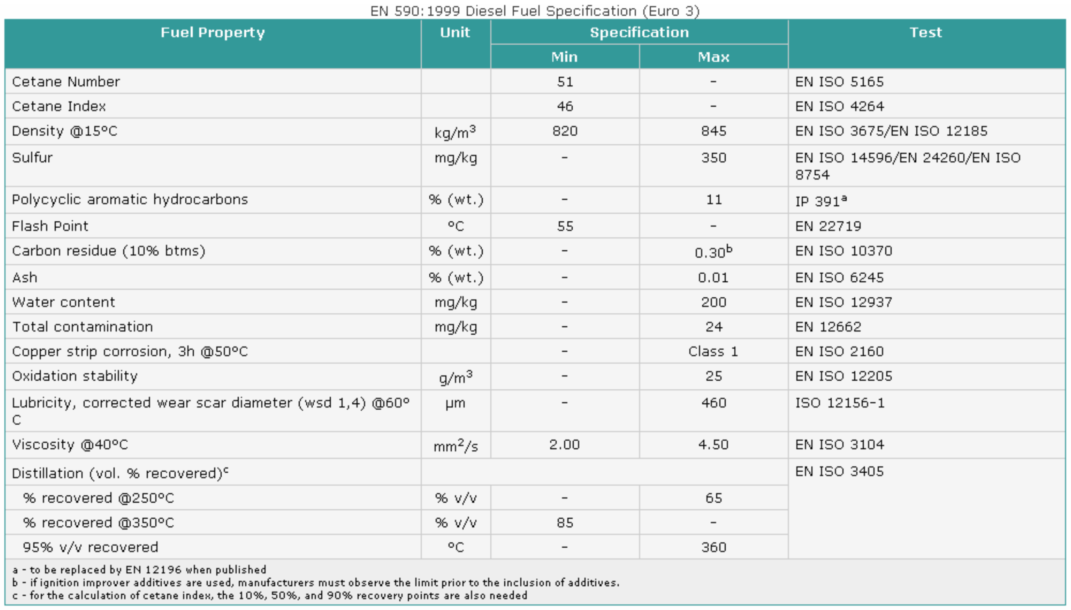
Type: **Diesel fuel**

Parameter (¹)	Unit	Limits (²)	
		Minimum	Maximum
Cetane number		51,0	—
Density at 15 °C	kg/m3	—	845
Distillation:			
— 95% (v/v) recovered at	°C	—	360
Polycyclic aromatic hydrocarbons	% m/m	—	11
Sulphur content	mg/kg	—	350

(¹) Test methods shall be those specified in EN 590:1999. Member States may adopt the analytical method specified in replacement EN 590:1999 standard if it can be shown to give at least the same accuracy and at least the same level of precision as the analytical method it replaces.

(²) The values quoted in the specification are "true values". In the establishment of their limit values, the terms of ISO 4259 "Petroleum products - Determination and application of precision data in relation to methods of test" have been applied and in fixing a minimum value, a minimum difference of 2R above zero has been taken into account (R = reproducibility). The results of individual measurements shall be interpreted on the basis of the criteria described in ISO 4259 (published in 1995).

EN 590/1999 (Source DieselNet.com)



EN 590:1999 Diesel Fuel Specification (Euro 3)

Fuel Property	Unit	Specification		Test
		Min	Max	
Cetane Number		51	-	EN ISO 5165
Cetane Index		46	-	EN ISO 4264
Density @15°C	kg/m^3	820	845	EN ISO 3675/EN ISO 12185
Sulfur	mg/kg	-	350	EN ISO 14596/EN 24260/EN ISO 8754
Polycyclic aromatic hydrocarbons	% (wt.)	-	11	IP 391[a]
Flash Point	°C	55	-	EN 22719
Carbon residue (10% btms)	% (wt.)	-	0.30[b]	EN ISO 10370
Ash	% (wt.)	-	0.01	EN ISO 6245
Water content	mg/kg	-	200	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper strip corrosion, 3h @50°C		-	Class 1	EN ISO 2160
Oxidation stability	g/m^3	-	25	EN ISO 12205
Lubricity, corrected wear scar diameter (wsd 1,4) @60° C	µm	-	460	ISO 12156-1
Viscosity @40°C	mm^2/s	2.00	4.50	EN ISO 3104
Distillation (vol. % recovered)[c]				EN ISO 3405
% recovered @250°C	% v/v	-	65	
% recovered @350°C	% v/v	85	-	
95% v/v recovered	°C	-	360	

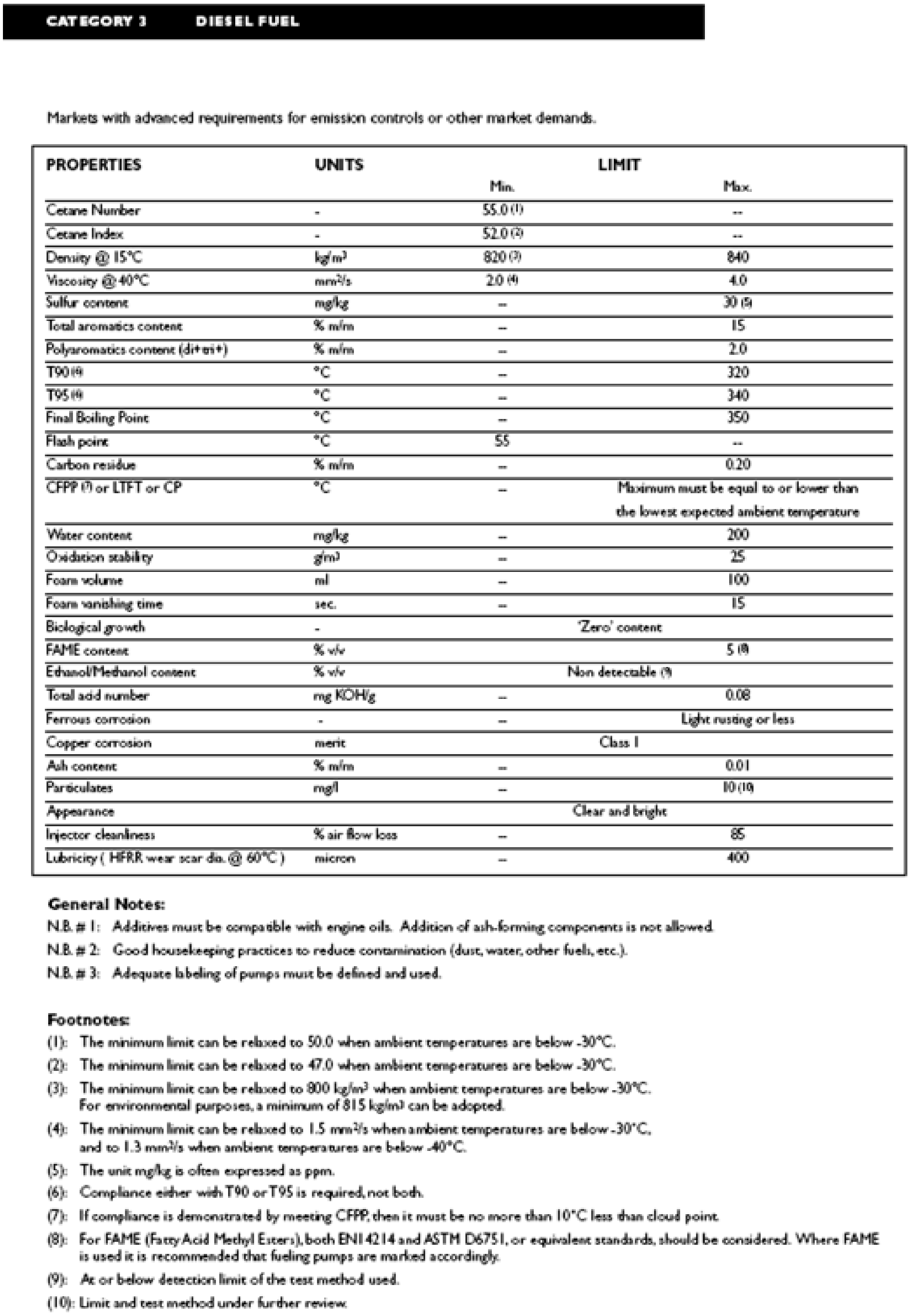
a - to be replaced by EN 12196 when published
b - if ignition improver additives are used, manufacturers must observe the limit prior to the inclusion of additives.
c - for the calculation of cetane index, the 10%, 50%, and 90% recovery points are also needed

EN 590 :2004.

Property	**Unit**	**Specification**	
		Min	**Max**
Cetane Number		51.0	-
Cetane Index		46.0	-
Density at 15°C	kg/m^3	820	845
Polycyclic aromatic hydrocarbons	% (m/m)	-	11
Sulfur	mg/kg	-	50.0 (10.0*)
Flash Point	°C	55	-
Carbon residue (10% dist. residue)	% (m/m)	-	0.30
Ash	% (m/m)	-	0.01
Water content	mg/kg	-	200
Total contamination	mg/kg	-	24
Copper strip corrosion (3h at 50°C)		Class 1	
Oxidation stability	g/m^3	-	25
Lubricity, corrected wear scar diameter (wsd 1,4) at 60°C	µm	-	460
Viscosity at 40°C	mm^2/s	2.00	4.50
Distillation (vol. % recovered)			
recovered at 250°C	% (V/V)	-	65
recovered at 350°C	% (V/V)	85	-
95% (V/V) recovered at	°C	-	360
95% (V/V) recovered at	°C	-	360
Fatty acid methyl ester (FAME) content	% (V/V)	-	5

*) From 1 January 2005, “sulfur-free” fuel (10 ppm S, both diesel and gasoline) must be available “on an appropriately balanced geographical basis”.

Word-Wide Fuel Charter 2002



CATEGORY 3 DIESEL FUEL

Markets with advanced requirements for emission controls or other market demands.

PROPERTIES	UNITS	LIMIT	
		Min.	Max.
Cetane Number	-	55.0 (1)	--
Cetane Index	-	52.0 (2)	--
Density @ 15°C	kg/m³	820 (3)	840
Viscosity @ 40°C	mm²/s	2.0 (4)	4.0
Sulfur content	mg/kg	--	30 (5)
Total aromatics content	% m/m	--	15
Polyaromatics content (di+tri+)	% m/m	--	2.0
T90 (6)	°C	--	320
T95 (6)	°C	--	340
Final Boiling Point	°C	--	350
Flash point	°C	55	--
Carbon residue	% m/m	--	0.20
CFPP (7) or LTFT or CP	°C	--	Maximum must be equal to or lower than the lowest expected ambient temperature
Water content	mg/kg	--	200
Oxidation stability	g/m³	--	25
Foam volume	ml	--	100
Foam vanishing time	sec.	--	15
Biological growth	-	'Zero' content	
FAME content	% v/v		5 (8)
Ethanol/Methanol content	% v/v	Non detectable (9)	
Total acid number	mg KOH/g	--	0.08
Ferrous corrosion	-	--	Light rusting or less
Copper corrosion	merit	Class I	
Ash content	% m/m	--	0.01
Particulates	mg/l	--	10 (10)
Appearance		Clear and bright	
Injector cleanliness	% air flow loss	--	85
Lubricity (HFRR wear scar dia. @ 60°C)	micron	--	400

General Notes:

N.B. # 1: Additives must be compatible with engine oils. Addition of ash-forming components is not allowed.

N.B. # 2: Good housekeeping practices to reduce contamination (dust, water, other fuels, etc.).

N.B. # 3: Adequate labeling of pumps must be defined and used.

Footnotes:

(1): The minimum limit can be relaxed to 50.0 when ambient temperatures are below -30°C.

(2): The minimum limit can be relaxed to 47.0 when ambient temperatures are below -30°C.

(3): The minimum limit can be relaxed to 800 kg/m³ when ambient temperatures are below -30°C. For environmental purposes, a minimum of 815 kg/m³ can be adopted.

(4): The minimum limit can be relaxed to 1.5 mm²/s when ambient temperatures are below -30°C, and to 1.3 mm²/s when ambient temperatures are below -40°C.

(5): The unit mg/kg is often expressed as ppm.

(6): Compliance either with T90 or T95 is required, not both.

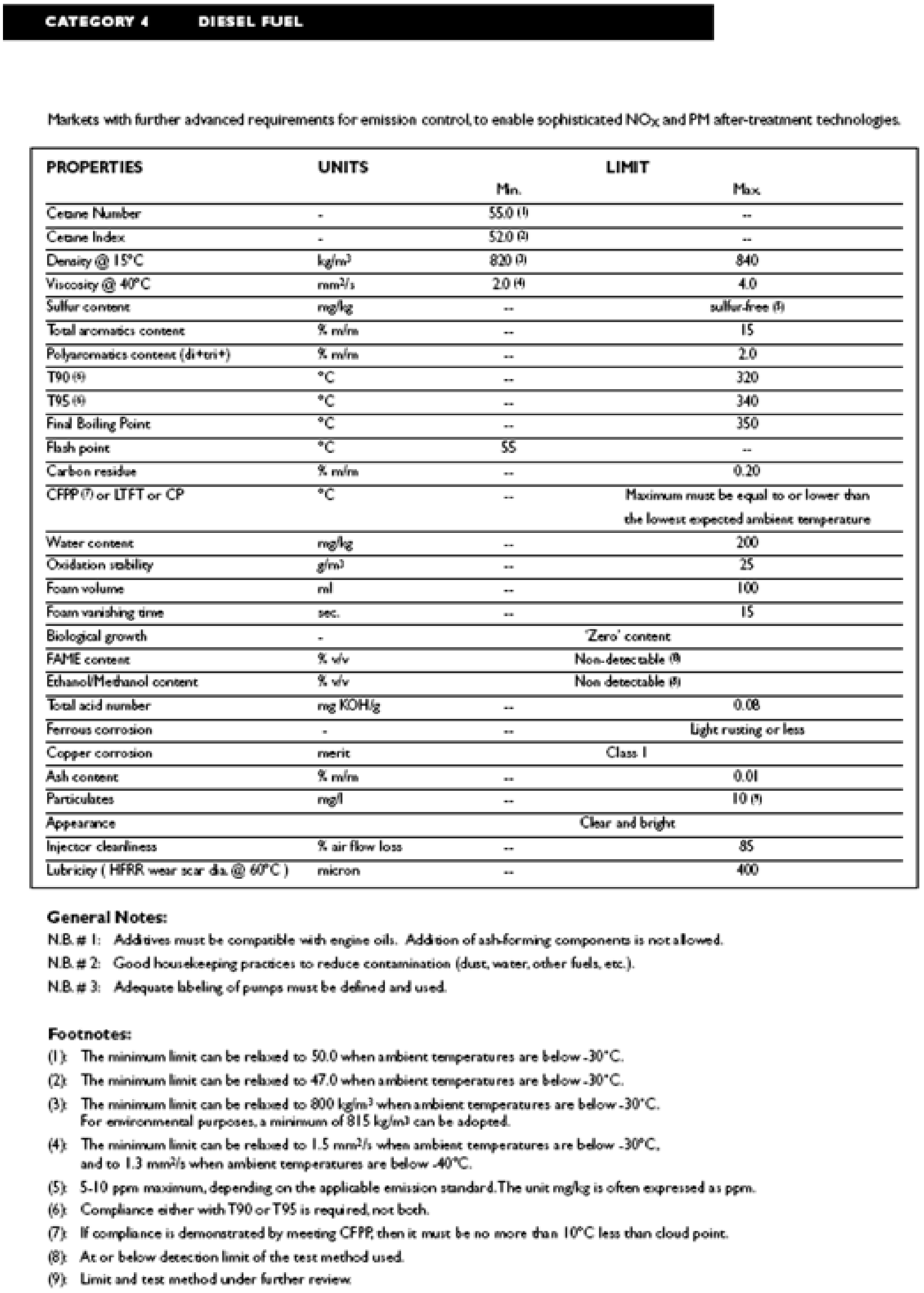
(7): If compliance is demonstrated by meeting CFPP, then it must be no more than 10°C less than cloud point.

(8): For FAME (Fatty Acid Methyl Esters), both EN14214 and ASTM D6751, or equivalent standards, should be considered. Where FAME is used it is recommended that fueling pumps are marked accordingly.

(9): At or below detection limit of the test method used.

(10): Limit and test method under further review.

Word-Wide Fuel Charter 2002



CATEGORY 4 DIESEL FUEL

Markets with further advanced requirements for emission control, to enable sophisticated NO_X and PM after-treatment technologies.

PROPERTIES	UNITS	LIMIT	
		Min.	Max.
Cetane Number	-	55.0 (1)	--
Cetane Index	-	52.0 (2)	--
Density @ 15°C	kg/m^3	820 (3)	840
Viscosity @ 40°C	mm^2/s	2.0 (4)	4.0
Sulfur content	mg/kg	--	sulfur-free (5)
Total aromatics content	% m/m	--	15
Polyaromatics content (di+tri+)	% m/m	--	2.0
T90 (6)	°C	--	320
T95 (6)	°C	--	340
Final Boiling Point	°C	--	350
Flash point	°C	55	--
Carbon residue	% m/m	--	0.20
CFPP (7) or LTFT or CP	°C	--	Maximum must be equal to or lower than the lowest expected ambient temperature
Water content	mg/kg	--	200
Oxidation stability	g/m^3	--	25
Foam volume	ml	--	100
Foam vanishing time	sec.	--	15
Biological growth	-	'Zero' content	
FAME content	% v/v	Non-detectable (8)	
Ethanol/Methanol content	% v/v	Non detectable (8)	
Total acid number	mg KOH/g	--	0.08
Ferrous corrosion	-	--	Light rusting or less
Copper corrosion	merit	Class I	
Ash content	% m/m	--	0.01
Particulates	mg/l	--	10 (9)
Appearance		Clear and bright	
Injector cleanliness	% air flow loss	--	85
Lubricity (HFRR wear scar dia. @ 60°C)	micron	--	400

General Notes:

N.B. # 1: Additives must be compatible with engine oils. Addition of ash-forming components is not allowed.

N.B. # 2: Good housekeeping practices to reduce contamination (dust, water, other fuels, etc.).

N.B. # 3: Adequate labeling of pumps must be defined and used.

Footnotes:

(1): The minimum limit can be relaxed to 50.0 when ambient temperatures are below -30°C.

(2): The minimum limit can be relaxed to 47.0 when ambient temperatures are below -30°C.

(3): The minimum limit can be relaxed to 800 kg/m^3 when ambient temperatures are below -30°C.
For environmental purposes, a minimum of 815 kg/m^3 can be adopted.

(4): The minimum limit can be relaxed to 1.5 mm^2/s when ambient temperatures are below -30°C,
and to 1.3 mm^2/s when ambient temperatures are below -40°C.

(5): 5-10 ppm maximum, depending on the applicable emission standard. The unit mg/kg is often expressed as ppm.

(6): Compliance either with T90 or T95 is required, not both.

(7): If compliance is demonstrated by meeting CFPP, then it must be no more than 10°C less than cloud point.

(8): At or below detection limit of the test method used.

(9): Limit and test method under further review.