Effect of biodiesel and bioethanol on exhaust emissions

ETC/ACC Technical Paper 2008/5
February 2008

Marina Kousoulidou, Giorgos Fontaras,
Giorgos Mellios, Leonidas Ntziachristos

The European Topic Centre on Air and Climate Change (ETC/ACC)
is a consortium of European institutes under contract of the European Environmental Agency
MNP UBA-D UBA-V NILU AEAT AUTh CHMI MET.NO ÖKO TNO REC

Front page picture: *Cycle from plants to emissions (some photo's by Creativ Collection).*

DISCLAIMER

LABORATORY OF APPLIED THERMODYNAMICS
MECHANICAL ENGINEERING DEPARTMENT
ARISTOTLE UNIVERSITY THESSALONIKI
P.O. BOX 458 GR 541 24 THESSALONIKI GREECE

Effect of biodiesel and bioethanol on exhaust emissions

Marina Kousoulidou
Giorgos Fontaras
Giorgos Mellios
Leonidas Ntziachristos

Report No.: 08.RE.0006.V1
Thessaloniki
February 2008

LABORATORY OF APPLIED THERMODYNAMICS
MECHANICAL ENGINEERING DEPARTMENT
ARISTOTLE UNIVERSITY THESSALONIKI
P.O.BOX 458 GR-54124 THESSALONIKI GREECE

tel: +30 2310 996047 fax: + 30 2310 996019
http://lat.eng.auth.gr/

Project Title ETC 2008 Implementation Plan / Task 2.4.2 Renewable energy	**Contract No** EEA/ADS/06/001-ACC
Report Title Effect of biodiesel and bioethanol on exhaust emissions	**Reference No** 08.RE.0006.V1
Project Manager Prof. Zissis Samaras	
Author(s) Marina Kousoulidou, Giorgos Fontaras, Giorgos Mellios, Leonidas Ntziachristos	

Summary

This report has been prepared by LAT/AUTh on behalf of the European Topic Centre on Air Emissions and Climate Change of the European Environment Agency. The objective of the report is to collect information on the effect of biofuels on tailpipe regulated and non-regulated pollutants. In principle, the report is split in two parts, one part which describes the effect of biodiesel on emissions from diesel vehicles and one part that describes the effect of bioethanol on emissions. The latter is further split into two subsections, one describing the bioethanol blend with gasoline and one with diesel. The findings of this study are summarized in a list of conclusions and recommendations at the end of the report. In summary, there have been several measurements conducted so far in characterizing the effect of biofuels on emissions. The results of the studies are often inconclusive as they present different trends for phenomenally similar testing conditions. A more detailed look on the results shows that any effects depend on biofuel properties, vehicle technology (combustion and aftertreatment system) and operation conditions. The report recommends more studies to understand the effects and aims to guide future policy development in this direction.

Keywords

Biodiesel, bioethanol, flex-fuel, E-diesel, regulated pollutants, non-regulated pollutants

Internet reference

Version / Date Version 1 / 28 Feb 2008		**Classification statement** EEA CONSULTATION ONLY	
No of Pages 50	**Price** FREE	**Declassification date** Pending EEA Comments	**Bibliography** YES

Contents

1 Introduction

Transportation accounts for about 30% of the world's secondary energy consumption and about the same in greenhouse gases. The increasing demand for transportation fuels combined with decreasing mineral oil reserves implies that the availability of petroleum is at the hands of a limited number of countries. This raises issues related to the security of energy supply. In addition, combustion of transportation fuels is one of the main sources of air pollution in urban areas.

These issues have powered the research on alternative renewable fuels such as biodiesel and bioethanol. Both fuels have attracted considerable attention during the past decade as renewable, biodegradable, and nontoxic fuels. It was not until 2003 that the European Directive 2003/30/EC set the necessary legal framework for the introduction of biofuels in the European market. Today, the European Union is on the third rank of biofuel production world-wide, behind Brazil and the United States. In Europe, Germany is the largest and France is the second largest producer of biofuels. The European Commission set the target to replace 2% of the energy used in transportation with biofuels by the end of 2005. The use of biofuels was then to grow by 0.75% annually to reach 5.75% biofuel use by 2010. However, the 2005 target was not reached (total penetration of biofuels was about 1% in 2005) and the consumption in 2010 is projected to about 4.2%, again below target. The new proposed target is now to reach 10% by 2020.

Although the EU is currently the world leader in biodiesel production, the production of the more expensive gasoline substitutes remains very low. For example, Brazil's production in 2003 was 9.9 million tons, some 20 times higher than the European production and all petrol sold in Brazil contains about 25% bioethanol. Bioethanol from maize is used in the United States since the 1980s. The US ethanol production, with corn as the primary feedstock, totaled 2.8 billion gallons in 2003 and is projected to increase to 4.5 billion gallons in 2025. In contrast, bioethanol production in EU-25 was only 446 ktons in 2003 (Table 1). Only five countries produce bioethanol in Europe. Spain is the leading bioethanol producer with 180 ktons followed by Poland, France, Sweden and the Czech Republic.

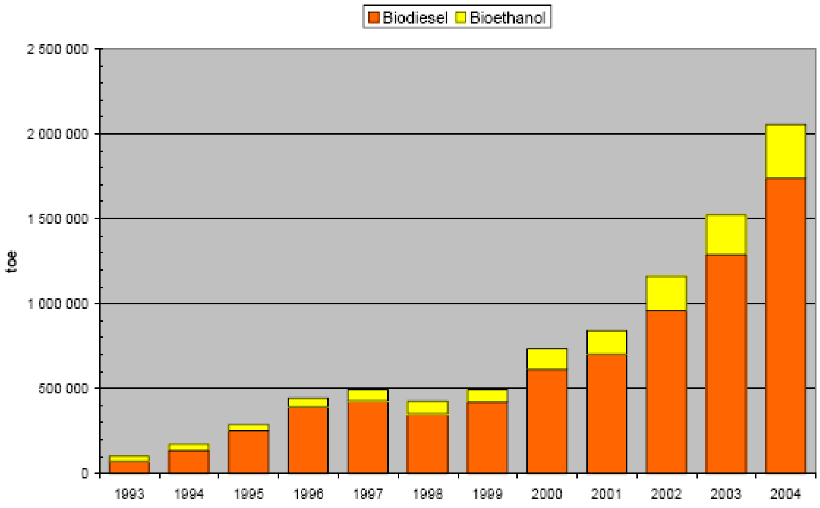


Figure 1: Biofuel production in the EU since 1993. Source: EurObserv'ER (2005)

Table 1: EU-25 Biofuel production in tonnes. Sources:EC (2004), EurObserv'ER (2007)

	Biodiesel				Bioethanol		
Country	2002	2003	2004	2005	2003	2005	2006
Germany	450 000	715 000	1 088 000	1 669 000	-	120 000	315 760
France	366 000	357 000	502 000	492 000	77 200	100 800	234 306
Italy	210 000	273 000	419 000	396 000	-	-	102 400
Czech Republic	68 800	70 000	47 000	133 000	5 000	1 120	13 200
Denmark	10 000	41 000	44 000	71 000	-	-	-
Austria	25 000	32 000	57 000	85 000	-	-	-
United Kingdom	3 000	9 000	15 000	51 000	-	-	-
Spain	-	6 000	13 000	73 000	180 000	240 000	317 000
Sweden	1 000	1 000	1 400	1 000	52 300	130 160	57 600
Poland	-	-	1 200	100 000	131 640	68 000	104 000
Hungary	-	-	2 000	2 000		11 840	4 818
Portugal	-	-	-	1 000	-	-	
Total (EU-25)	1 133 800	1 504 000	1 933 400	3 184 000	446 140	679 176	1 185 524

This study focuses on the impact of biodiesel and bioethanol on NO_x and PM exhaust emissions compared to conventional fuels.

2 Biodiesel

2.1 Chemical character

Biodiesel (fatty acid methyl esters, FAME) is usually derived from vegetable oils and animal fats by a chemical process known as transesterification, where a feedstock oil reacts with methanol and a potassium hydroxide catalyst. In addition, biodiesel may be produced by esterification of free fatty acids with low molecular weight alcohols. The feedstock can be vegetable oil, such as that derived from oil-seed crops, used frying oil or animal fat. Soy is used in US and mainly rapeseed and sunflower in Europe. Other feedstocks include coconut and palm oils.

Since the feedstock of biodiesel may vary with location, it is important to know how the various fatty acid profiles of the different sources can influence the properties of the biodiesel fuel. In turn, the properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester (Knothe and Steidley 2005; Yamane et al. 2001). Table 2 shows the fatty acid composition of some common vegetable oils used for the production of biodiesel.

Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn, by the structural features of the various fatty esters are cetane number with relation to combustion and exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity. Generally, cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation. Saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds and in a mixture they crystallize at higher temperature than the unsaturated molecules. Figure 2 shows the composition of various biodiesel feedstocks.

Table 2: Typical fatty acid composition in some vegetable oils (% wt.)

Fatty acid	Structure	Formula	Cotton seed	Rape seed	Saf-flower	Soybean	Sun-flower	Peanut
Myristic	14:0	$C_{14}H_{28}O_2$	0	0	0	0	0	0
Palmitic	16:0	$C_{16}H_{32}O_2$	28.33	3.49	8.6	11.76	6.08	11.38
Stearic	18:0	$C_{18}H_{36}O_2$	0.89	0.85	1.93	3.15	3.26	2.39
Oleic	18:1	$C_{18}H_{34}O_2$	13.27	64.4	11.58	23.26	16.93	48.28
Linoleic	18:2	$C_{18}H_{30}O_2$	57.51	22.3	77.89	55.52	73.72	31.95
Linolenic	18:3	$C_{18}H_{28}O_2$	0	8.23	0	6.31	0	0.93
Arachidic	20:0	$C_{20}H_{40}O_2$	0	0	0	0	0	1.32
Behenic	22:0	$C_{22}H_{44}O_2$	0	0	0	0	0	2.52
Lignoceric	24:0	$C_{24}H_{48}O_2$	0	0	0	0	0	1.23

It therefore appears reasonable to try to enrich certain fatty esters with desirable properties in the fuel in order to improve the properties of the whole fuel. It may be possible in the future to improve the properties of biodiesel by means of genetic engineering of the parent oils, which could eventually lead to a fuel enriched with certain fatty acids, possibly oleic acid, that exhibits a combination of improved fuel properties.

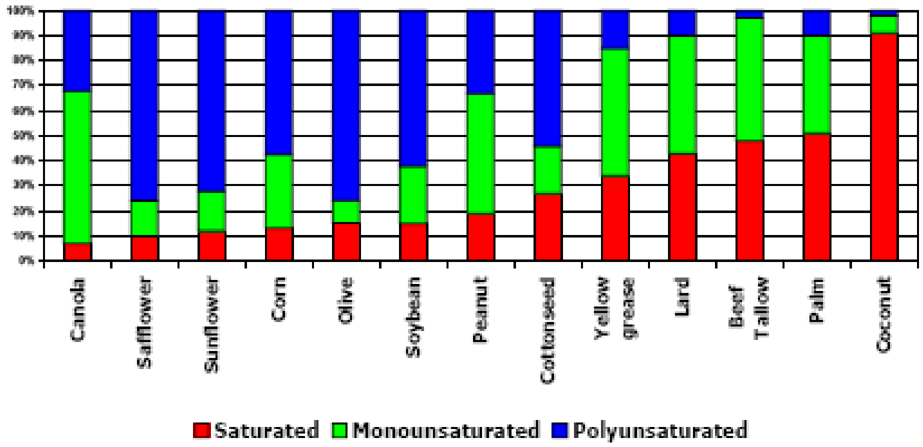


Figure 2: Composition of various biodiesel feedstocks, Source: NREL (2006)

2.2 *Physical properties*

The most important compositional difference between diesel and biodiesel is oxygen content. Biodiesel contains 10-12 wt% oxygen, which lowers energy density (Graboski and McCormick 1998). According to the formulas given in Table 2, an average of eleven percent by weight of biodiesel is oxygen.

In general, except of oxygen content, biodiesel differs than petroleum-based diesel in the following proprties:

- No sulphur or ultralow sulphur content
- No aromatic contents and no polycyclic aromatic hydrocarbons
- Higher cetane value
- Lower heating value
- Better lubricity
- Higher viscosity
- Higher flash point
- Biodegradability
- No toxicity or low toxicity

Table 3 shows the range of all main properties (density, viscosity, flash point, pour point etc.) of pure biodiesel to be used in up to B5 blends derived from rapeseed, soya, jatropha or other virgin biomass, UCO (used-cooking oil), MSW (municipal solid waste) or from any viable fuel stock, as proposed by the EN14214 standard.

Table 3: Biodiesel standards according to EN14214

Property	**Unit**	**Min**	**Max**	**Test Method**
Ester Content	% (m/m)	96.5		prEN 14103
Density @ 15°C	kg/m^3	860	900	EN ISO 3675 EN ISO 12185
Viscosity @ 40°C	Mm^2	3.5	5	EN ISO 310
Flash Point	°C	Above 101		ISO / CD 3679
Sulphur Content	mg/kg		10	
Carbon Residue (10% Bottoms)	% (m/m)		0.3	EN ISO 10370
Cetane Number		51		EN ISO 5165
Sulphated Ash Content	% (m/m)		0.02	ISO 3987
Water Content	mg/kg		500	EN ISO 12937
Total Contamination	mg/kg		24	EN 12662
Copper Strip Corrosion (3hr @ 50°C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation Stability, 110°C	h	6		pr EN 14112
Acid Value	mg KOH/g		0.5	pr EN 14104
Iodine Value			120	pr EN 14111
Linolenic acid methyl ester	% (m/m)		12	pr EN 14103
Polyunsaturated (>= 4 double bonds) methyl esters	% (m/m)		1	
Methanol Content	% (m/m)		0.2	pr EN 14110
Monoglyceride Content	% (m/m)		0.8	pr EN 14105
Diglyceride Content	% (m/m)		0.2	pr EN 14105
Triglyceride Content	% (m/m)		0.2	pr EN 14105
Free Glycerol	% (m/m)		0.02	pr EN 14105-6
Total Glycerol	% (m/m)		0.25	pr EN 14105
Alkaline Metals (Na + K)	mg/kg		5	pr EN 14108-9
Phosphorus Content	mg/kg		10	pr EN 14107

New specifications are now under proposal separately for B7 and B10 blends.

2.3 Effect of biodiesel on NO_x emissions

2.3.1 Results from experimental campaigns

Table **A. 1** summarizes all results from several experimental campaigns related to the use of biodiesel. The table shows the biodiesel blending quantity and, where available, the feedstock, the vehicle type and technology, the operating conditions, and any other remarks that are important in understanding the biodiesel effect. NOx emissions increase significantly with the use of pure biodiesel in most of the tests conducted both on heavy duty engines and passenger car emissions. The range of increase is from 5.8 to 38% with a single study showing a 25% improvement and one study showing no effect (0%) - Sharp et al. (2000), McCormick et al. (2001), Knothe and Sharp (2006), Tsolakis et al. (2007), Szybist et al. (2007), Tat (2003), Kegl (2008). Hence, use of pure biodiesel, without engine calibration may result in significant increase of NOx emission factors, hence degradation of urban air quality.

However, the effect of biodiesel may be different when looking at the use of biodiesel blends on passenger car emissions. Experiments conducted on a Euro 3 common rail passenger car at the Laboratory of Applied Thermodynamics (Fontaras et al. 2008), using biodiesel fuels of different feedstock, indicated that B10 blends show an increase in NO_x emissions in the order of 1%, on average. This is a rather marginal increase, as typical NO_x measurement confidence intervals are in the order of 2%. A recent study from the Joint Research Centre (Martini et al. 2007a) on two passenger cars does not lead to consistent conclusions: Tests on a Euro 3 common-rail equipped car with B30 over NEDC leads to -3% to 1% effect on NOx, depending on the biodesel feedstock. The same fuels, when used on a unit-injector equipped Euro 3 car, led to 0 to 6% increase in NO_x emissions. Therefore, the effect of biodiesel blends on NOx emissions from passenger cars is not straightforward as it seems to depend on feedstock, vehicle technology and operation conditions. These effects are more thoroughly discussed in the following sections.

The US studies of Schumacher et al. (1995) and McCormick et al. (2006) on heavy duty vehicles and engines also showed rather marginal and not consistent effects. Review of earlier studies by NREL on the use that B20 blends, including older technology engines, led to a -0.6%±2.0% change in NO_x emissions (with 95% confidence intervals). When focussing the study on more recent engine technologies the conclusion reverses, showing a 0.1%±2.7% increase in emissions. Similarly, an increase of 1.2%±2.9% was found when reviewing emissions from recent model heavy duty vehicles. Tests on 8 heavy duty vehicles which fulfilled post 1998 emission standards (most at 2004 certification level) by McCormick et al. (2006) showed a range of -5.8% to 6.2% effect on NOx with the use of B20, with an average value of 0.6%±1.8%.

2.3.2 Biodiesel and combustion

Since biodiesel fuels have been associated with a change of NO_x emissions, extensive studies have been made in order to understand the complex mechanism of NOx formation in the presence of biodiesel.

Biodiesel has higher values of viscosity, density and speed of sound that may cause injection and combustion variations, compared to petroleum diesel. For example, the fuel density, viscosity and compressibility have significant effects on fuel injection. The fuel quantity, injection timing and injection spray pattern in the combustion chamber are directly affected by these parameters. For example, the fuel metering in a common rail system depends on the fuel viscosity. In addition, the heating value of biodiesel is about 12% less than petroleum diesel fuel and this causes a power loss that must be compensated by increasing the fuel amount during injection. When injecting this greater quantity of fuel, some fuel injection systems start the injection earlier and hold the injection needle open for longer, changing the fuel injection timing and the start of combustion timing. The faster propagation of pressure waves caused by biodiesel's higher speed of sound and the more rapid pressure rise that results from biodiesel's greater bulk modulus may shift the injection timing settings from their optimized factory settings, leading to earlier combustion. This can result in higher combustion temperature and pressure, leading to increased NOx tailpipe emissions (Tat 2003).

Long chain saturated methyl esters have the highest cetane number while unsaturated methyl esters have the lowest. As the number of unsaturated carbon-carbon double bonds in a molecule increases, the adiabatic flame temperatures increase and therefore NOx emission increase. Cetane number variation can also be the result of biodiesel degradation (as biodiesel ages, its cetane number can increase). Figure 3 illustrates the variation in cetane number in various neat biodiesel fuels, compared with petroleum diesel. According to Knothe (2005) unsaturation in the fatty compounds causes an increase in NOx emissions. A connection between increased iodine number and increased NOx exhaust emissions is observed (Figure 4).

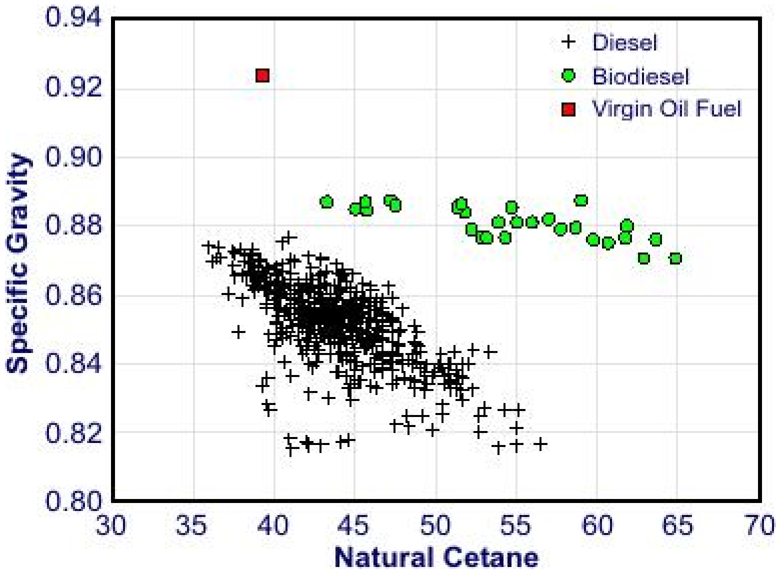


Figure 3: Cetane differences in Biodiesel and Petroleum Diesel fuels. Source: www.dieselnet.com

However, it should not be considered that the cetane number of a biodiesel blend with petroleum-diesel is the weighted average of their base constituents. The cetane number is rather a complex function of the physicochemical character of the fuel. Hence the cetane number of a biodiesel blend may be higher than the petroleum-diesel or equal to the petroleum-diesel, regardless of whether the biodiesel has a higher cetane number.

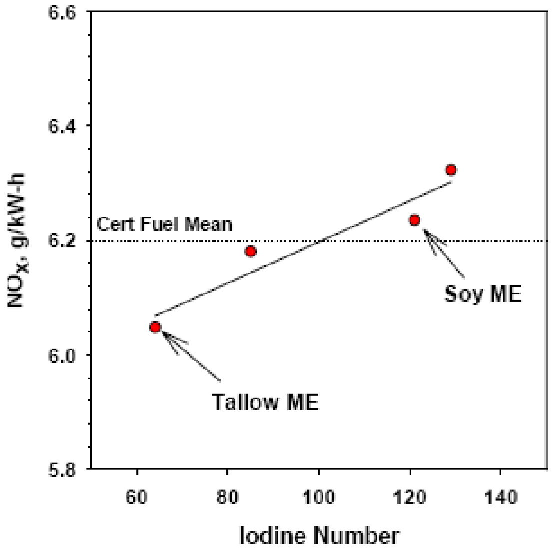


Figure 4: NOx emissions for B20 blends versus biodiesel Iodine Number. Source: McCormick, (2001)

2.3.3 Biodiesel and operation conditions

It has been observed that NOx emissions can either increase or decrease depending on the test cycle, even though this is not fundamentally understood. According to Peterson and Reece, NOx emissions from the use of biodiesel are higher than petroleum-diesel for steady state and transient engine dynamometer (FTP) tests. In contrast, NOx emissions may be lower that petroleum-diesel in the case of chassis dynamometer tests. This is attributed to the fact that the average load in a chassis dynamometer is much less than for the FTP transient and steady state engine tests. This comes to agreement with other studies (Tat 2003), demonstrating that biodiesel does not give higher NOx emissions at light load conditions. This could be the result of lower combustion temperature due to delayed injection. Therefore, retarding the timing is an effective way of reducing NOx emissions when fuelling with the biodiesel blends, even below the level of baseline diesel fuel (Marshall et al. 1995)

2.3.4 Biodiesel and engine/vehicle technology

According to several studies (EPA 2002; Sze 2007), the NOx increase appears to be higher in newer engines. A comparison between 2004 engines and pre-1998 engines showed the same results (Figure 5). On newer engines equipped with EGR, the EGR rate may decrease when biodiesel blends are used (Sze 2007). To maintain a given load, a higher volume of biodiesel must be injected into the cylinder. The increased injector opening time is interpreted as an increased load and the injection timing, rail pressure, EGR and other parameters are adjusted accordingly. This justifies the increase in NOx emissions in newer technology engines. Figure 6 demonstrates the effect of EGR on NOx emissions for different blends of biodiesel.

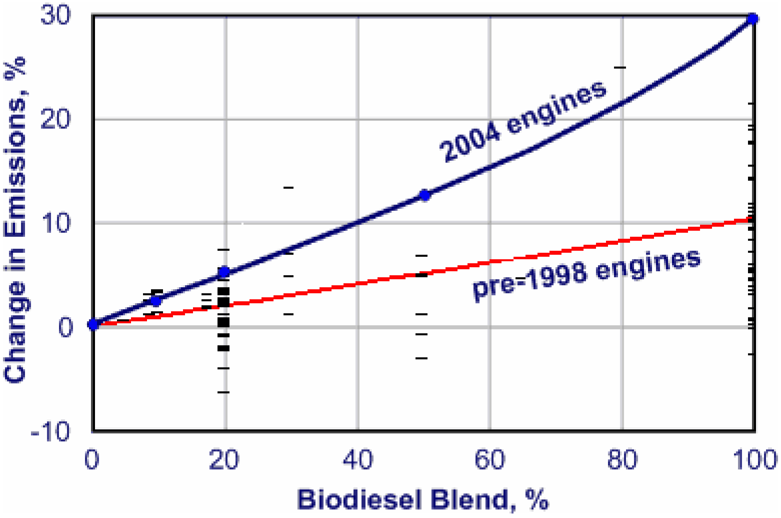


Figure 5: NOx emissions with biodiesel blends for two different engines. Source: www.dieselnet.com

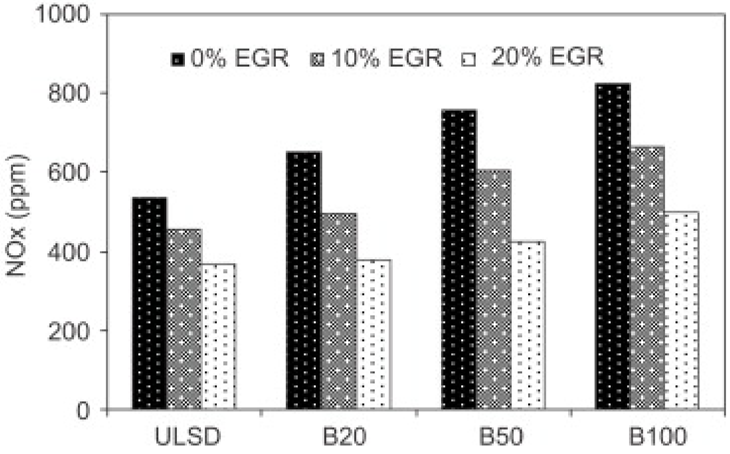


Figure 6: Effect of EGR on NOx emissions, Source: Tsolakis et al. (2007)

2.3.5 Durability Issues

Modern diesel engines are quite sensitive to fuel quality and characteristics. In particular the fuelling system of common rail engines can be affected by various factors, such as cold flow properties, concentration of unsaturated compounds, acidity and viscosity. Biodiesel is differentiated from regular diesel in certain factors that may in time have an effect on vehicle engine. Vegetable oil derived fuels can under certain circumstances lead to fuelling system malfunctions because of their reduced cold flow properties and higher viscosity, their ability to form polymers (Giannelos et al. 2005) and the fact that their application may result in injector coking formation (Pundir et al. 1994). Similar problems may appear when conventional diesel is used which is not in line with the existing fuel standards, has been derived from low quality crude or has been adulterated (Owen and Coley 1995). For this reason the application of additives (cetane improvers, cold flow improvers, oxidation stability improvers) in regular diesel or in biodiesel is a common practice (Bauer et al. 2004)

2.3.6 Conclusions on NOx tailpipe emissions from the use of biodiesel

Pure biodiesel use leads to an increase of NOx emissions from both passenger cars and heavy duty vehicles. This is mainly an effect of the higher cetane number, which leads to lower ignition delay hence combustion advance and higher combustion temperature/pressure. The unsaturated character and oxygen content of biodiesel also means higher flame temperature and oxygen presence in the flame front which also may lead to high NOx. In addition, the high oxygen content means more fuel injected, earlier injection to counterbalance the energy loss and, again, higher temperature combustion. In Euro 2 and later engines, all equipped with electronic control, more fuel injected is translated as higher load which means lower EGR rate, again a reason for higher NOx emissions. All such reasons are consistent to the up to 38% increase in NOx reported in experimental studies for pure biodiesel use.

Conclusions however are not straightforward for biodiesel blends. The effect of B5 blends is considered minimal, certainly within experimental uncertainty. However, the effects for B20 and B30 blends are difficult to interpret. One would tend to consider that a monotonic increase should be established for the effects of intermediate blends, considering the minimal effect of B5 and the strong increase of B100 fuels. However, the experimental results produce a more complicated picture than this. EPA considers an average effect of +2% on NOx emissions from B20 fuels. At these blending ratios, the effect is rather vehicle specific. Different studies on US heavy duty vehicles show both negative and positive effects of B20 blends with an average which is around 0%. However, late technology engines which are optimized to achieve low NOx emissions seem to lead to marginally higher NOx emissions of 0.9%±1.5% with use of B20 blends.

For passenger cars in Europe there are limited studies to reveal the effect on NOx of biodiesel blends exceeding B5-B10. LAT/AUTh studies with B10 blends led to an average increase of 0.4% on a Euro 3 common rail passenger car. A recent study from JRC on two Euro 3 passenger cars led to -3 to +6% effect of three different B30 blends over the NEDC cycle. However, the complete driving cycle is within the EGR range which determines NOx control. It would be interesting to examine the effect in higher power and load conditions.

As a result from a subset of the one mentioned in the current report, COPERT 4 introduced some correction factors for different vehicle categories with the use of B10 and B20 blends. These are 0.4-1.0% for diesel cars, 1.7-2.0% for light duty trucks and 3.0-3.5% for heavy duty trucks.

An issue which has received much attention lately is the ratio of NO2 over NOx in the exhaust. This is because NO2 is much more toxic than NO and because aftertreatment devices with oxidative catalytic activity promote the formation of NO2 over NO. As a result, a Euro 4 diesel passenger car may emit NOx with an NO2/NO ratio of over 50% while the same ratio for a Euro 1 was 5-7%. The use of biodiesel is not expected to bring significant changes in this ratio. Engine-out NO2 continues to be some 5-7% of total NOx and it is the aftertreatment device which raises this ratio to more than 70%. Therefore, even a marginal increase in engine-out NO2, supposedly originating from a direct NO2 formation mechanism, would only marginally alter the ratio in the exhaust. Of course this would need to be confirmed with some detailed experiments.

2.4 PM emissions with the use of biodiesel

2.4.1 Interest on particulate matter emissions

PM emissions are given special attention due to their environmental (Colvile et al. 2001) and health effects (Dockery and Pope 1994; Li et al. 2003). As indicated by numerous epidemiological studies, PM emissions constitute an important health risk factor for many different diseases and affect the air temperature and humidity by enhancing cloud scattering and absorption.

2.4.2 Composition of particulate matter

Particulate matter is mainly composed of elemental carbon (soot), ash and volatile compounds derived from unburned and partially burned fuel and lubricating oil and sulphate. Soot particles are formed in the combustion chamber, while the volatile compounds transform from gas phase to particle phase as the exhaust cools and dilutes with ambient air after exiting the engine exhaust pipe into the atmosphere (Munack et al. 2005). All particles emitted from diesel engines are in the respirable size range. The greatest numbers of particles tend to concentrate in the "ultrafine" range of 3–100 nm in diameter. The ultrafine range usually contains soot particles larger than 30 nm in diameter, and volatile nuclei mode particles smaller than 30 nm that form as a result of dilution and cooling of hot exhaust.

On the other hand, the greatest mass of particles resides in the accumulation mode with a diameter from 100–300 nm. These particles are soot chain agglomerates that are generated by the combustion process. The coarse mode particles are larger than 2500 nm in diameter, and are generated by the break-up of soot from the internal walls of the combustion chamber and the exhaust system. These coarse particles also slightly contribute to the mass of particles.

2.4.3 Results from experimental campaigns

Most studies link the use of biodiesel fuels with significant reduction of PM emissions for different biodiesel blends. They also indicate that the decrease of solid particulate matter increases the total particle number by up to 100%. In addition, results from numerous studies indicate that the effect of biodiesel on total particulate matter depends on the composition of diesel particulate matter, and so it is specific to the engine and the test cycle (Fontaras et al. 2007, 2008).

Most studies reported a decrease in PM emission with neat biodiesel, in some cases by as much as -77% (Knothe and Sharp 2006). The average reduction of all measurements collected in this report is in the order of -47%. According to EPA, PM reductions are in the order of 48%, coming to agreement with McCormick et al. (2001) and Yen-Cho and Chung (2002). The JRC analysis based on the results from experiments conducted on a Euro 3 common rail passenger car, reported a significant reduction of PM emissions in the order of -68%. The same analysis reports a negligible reduction in the order of 3% concerning the Euro 3 passenger car with a unit injector system.

Concerning B70 biodiesel blends, experimental studies again report significant average reductions in the order of -44%. Durbin et al. (2007) present average reductions in the order of -68%, while according to Lapuerta et al. (2008), these reductions are in the order of -32%.

Concerning B20 blends, the EPA (2002) analysis found that PM emissions were reduced by 10% using the B20 blend. Similar results are indicated by numerous studies (Yang et al. 2007). Experiments conducted by Durbin et al. (2007) indicate that concerning B20 blends, light duty vehicles present average reduction in the order of 15%, while reductions from passenger cars are in the order of 13%. According to Graboski and McCormick (1998), by using B20 blends on passenger cars, one can achieve 24% reductions.

Concerning B10 blends, according to experiments conducted by the Lab of Applied Thermodynamics (Fontaras et al. 2008) on a Euro 3 common rail passenger car the average reductions from 6 different blends were in the order of 12%. Numerous studies indicate that the average reductions of PM emissions by using biodiesel are in the order of 15%, although the range of values varies from a slight increase in the order of 1% (McCormick et al. 2001) to a significant reduction in the order of -35% (Graboski and McCormick 1998).

Increased PM emissions, however, are also possible. In the case of increased PM emissions, this is associated with an increase of the soluble organic fraction (SOF) which decreases as the load increases (Choi et al. 1997).

Table A. 2 summarizes all changes of PM emissions from the use of biodiesel fuel compared to petroleum-based diesel.

With regard to the effect of biodiesel on particle number and size distribution, little information is available up to date. In order to study the effect of biofuels on the particulate matter emissions of typical diesel cars, experiments conducted on a Euro 3 common-rail passenger car with different blends of biodiesel, showed that none of the examined biofuels seemed to dramatically change the solid particle emission rate of the car tested, given the experimental uncertainty. In addition, results showed that the exhaust particle emission rate follows a pattern determined by the driving cycle, rather than the fuel used (Fontaras et al. 2007).

There are some indications that the oxygen content of biofuels results to reduced surface concentration of solid particles, due to both a small reduction of their number and a shrinkage of their size. As a result, the exhaust gas contains less active surface for condensation, compared to fossil diesel combustion. Volatile and semi-volatile species tend to produce nuclei by homogenous nucleation, a process which is enhanced in the absence of enough solid surface for condensation. Therefore, the combination of increased semi-volatile species emitted by biodiesel and the reduction in the available surface area may promote the formation of nucleation mode particles that reside in the sub-50 nm size range. Tzamkiozis et al. (2008) observed such an increase in particle number when using 10% RME blend on a Euro 3 passenger car.

On the other hand, biofuels only contain trace sulphur. Sulphur is a well known source of volatile nanoparticles in vehicle exhaust due to the formation of sulphuric acid. The extensive use of biofuels, but even the use of conventional ultra low sulphur fuels (<10 ppm), should lead to limited exhaust gas content in sulphuric acid. However, sulphate from lube oil becomes significant in this case. For example, a mineral oil may include up to 1% wt. (10000 ppm) sulphate. Assuming an oil consumption of 1 l/1000 l fuel (which is a moderate estimate) leads to equal exhaust sulphate concentration of a 10 ppm sulphur fuel. Therefore, developing ultra-low clean fuels without decreasing the lube oil sulphur content is pointless. Currently, synthetic lube oils tend to contain less sulphur than mineral oils. However, since the sulphur level in the lube oil is not regulated, this may be proven a loophole for the control of nanoparticle emissions.

A final point which again does not only concern biofuels but PM emissions in general is the effect of the upcoming regulations on the control of solid particle number. At Euro 5 level, diesel (and gasoline direct injection) gasoline vehicles will have to comply with a particle number-based emission standard, which only counts solid particles. The rationale for addressing solid particles only was the need to develop a robust measurement protocol with little measurement variability that would allow its implementation as a type-approval procedure. The origins and the methodology of the regulation were developed with the Particle Measurement Programme. However, there has been no evidence which would suggest that volatile nanoparticles are not a health concern. On the contrary, several relevant studies (e.g. Geller et al. 2006) demonstrate that the volatile fraction is comparable if not more toxic than the solid fraction. Therefore, the use of biofuels may reduce the solid particle number. This will be perceived as an improvement over conventional fuels by the upcoming regulations. However, if this reduction is associated with an equal increase of volatile nanoparticle number, the net effect will be zero or worse for biofuels. Any interpretation of future results concerning the effect of biofuels on solid particle number should be given attention and the counter effect on total particle number should not be neglected.

2.4.4 Conclusions on PM tailpipe emissions from the use of biodiesel

In contrast to NOx emissions thare is a rather unanimous agreement on the reductions achieved on PM with the use of biodiesel. First, all reasons explained about the biodiesel effect on NOx increase (earlier injection, smaller combustion delay, higher flame temperature, etc.) lead to PM increase. In addtion, some chemical kinetics studies proposed that the C=O bond does not lead to soot formation, hence these carbon molecules do not contribute to soot production. In contrast to NOx, the positive effects on PM emissions are rather a monotonic function of blending quantity.

The only occasions where biodiesel use may lead to increased PM emissions is in engines which emit a high soluble fraction and high lube oil consumption. In such cases biodiesel may dissolve lube oil which is then exhausted. Also, the heavy oil fraction of biodiesel may be exhausted uncombusted to the tailpipe. However, as late technology engines have a rather low fraction of soluble PM (10-30%), any effect of biodiesel on its increase is masked by the corresponding decrease in soot emissions and, hence, they have an overall positive effect in reducing PM.

Based on a smaller dataset than the one considered in this study, COPERT 4 also introduced some corrections depending on vehicle category for both B10 and B20 blends. The ranges are correspondingly -13% to -20% for passenger cars, -15% to -20% for light duty vehicles and -10% to -15% for heavy duty vehicles.

2.5 Unregulated emissions

The impact of several non-regulated emissions such as Polycyclic Aromatic Compounds (PACs) on human health has raised great concerns. It has been found that these may be mutagenic and carcinogenic (Munack et al. 2005). They can be formed in the engine or can be found in diesel fuel. Concerning the use of biodiesel, emissions of PAH and nitro-PAH were found by several authors to be significantly lower than those observed with petroleum-based diesel (Sharp et al. 2000). This trend appears to be consistent on both light- and heavy-duty engines and on different test cycles. The main problem is that while regulated emissions of biodiesel blends are reasonably well documented in several studies, non-regulated emissions, on the contrary, lack extensive research. According to the EPA analysis concerning the biodiesel effect on several substances classified as toxic air pollutants, including acetaldehyde, benzene, 1,3-butadiene, n-hexane, toluene and others, significant reductions were observed by increasing biodiesel content in blend. More specific, the non-regulated emissions from the use of biodiesel-both for B20 blend and neat biodiesel were significantly lower compared to those from petroleum-based diesel. According to the joint research of the U.S Dept. of Agriculture and the Dept. of Energy, the reduction of non-regulated emissions is in the order of 1-5% concerning sulphur oxides-SO_2, hydrogen fluorides-HF and methane-CH_4.

According to experiments conducted in a six cylinder heavy-duty diesel engine (typical of the Brazilian fleet of urban buses, in a steady-state condition under 1500 rpm), fuelled with pure diesel and biodiesel blends (B2, B5 and B20), significant reductions were presented (Correa and Arbilla 2006). The average reduction of MAHs was 4.2% (B5), 8.2% (B5), and 21.1% (B20). The average reduction for PAHs was 2.7% (B2), 6.3% (B5), and 17.2% (B20).

In contrary, the JRC study indicates that the experiments conducted in a light duty vehicle, fuelled with for B30 blends and neat biodiesel showed a significant increase of PAHs emissions in the order of 163% for the urban driving cycle and an increase in the order of 16% for the extra-urban driving cycle. Concerning the experiments conducted with neat biodiesel, the corresponding increase was in the order of 150% for the urban driving cycle and in the order of 10% for the extra-urban driving cycle.

Table 4 summarizes all changes of non-regulated emissions from the use of biodiesel fuel compared to petroleum-based diesel.

2.6 Waste cooking oil as a biodiesel source

Recently, waste cooking oil has been considered as a feedstock for biodiesel production. In general, waste oils, used cooking oil, and animal fats, are important for low cost biodiesel production (Yang et al. 2007). Huge quantities of waste cooking oil are available throughout the world. In the United States, the Energy Information Administration estimates 100 million gallons per day (Radich 2006). In several countries, large amounts of waste cooking oil are illegally dumped into rivers and landfills, causing environmental pollution. Recycling waste cooking oil as fuel in diesel engines would reduce such environmental degradation (Pugazhvadivu and Jeyachandran 2005b).

For waste oil to become useful for diesel combustion, further to purification, transesterification significantly reduces viscosity and enhances its physical properties for combustion. It has been reported that the methyl ester processed from waste cooking oil for use in diesel engines offers lower smoke levels and higher thermal efficiencies than clean vegetable oils and waste cooking oil (Kumar et al. 2003).

Table 4: Effect of biodiesel on non-regulated emissions, compared to neat diesel.

Emissions	Source	B2	B5	B20	B30	B100	Vehicle	Driving Cycle
Sulphates	(EPA 2002)			-20%		-100%	HDV	FTP
PAHs	(EPA 2002)			-13%		-80%	HDV	FTP
	(Martini et al. 2007a)				163%	150%	LDV	Urban cycle
					16%	10%	LDV	Extra-Urban
	(Correa and Arbilla 2006)	-2.7%	-6.3%	-17.2%			Urban Bus	FTP
nPAH	(EPA 2002)			-50%		-90%	HDV	FTP
O3 pot of speciated HC	(EPA 2002)			-10%		-50%	HDV	FTP
MAHs	(Correa and Arbilla 2006)	-4.2%	-8.2%	-21.1%			Urban Bus	FTP

Although the viscosity of waste cooking oils can be reduced by the transesterification process, diesel-engine performance and exhaust emission testing over the long term is needed for further application. Use of waste cooking oil in a diesel engine for extended periods may result in severe engine deposits, piston-ring sticking, injector coking and thickening of the lubricating oil. In addition, the high viscosity waste cooking oil reduces fuel atomization, increases fuel spray penetration and produces higher smoke emission (Altin et al. 2001; Pugazhvadivu and Jeyachandran 2005a). Cetinkaya et al. (2005) investigated the engine performance and the road performance of biodiesel fuel originated from used cooking oil in a Renault Mégane vehicle and a 75 kW Renault Mégane Diesel engine in winter conditions for 7500 km road tests in urban and long distance traffic. The results indicated that the torque and brake power output obtained during the use of waste cooking oil biodiesel were 3–5% less then those of diesel fuel. The engine exhaust gas temperature at each engine speed of biodiesel was less than the neat diesel fuel. After the first period, as a result of winter conditions and insufficient combustion, carbonization of the injectors was observed with biodiesel usage.

According to Lapuerta et al. (2008), experiments conducted on a four-cylinder, four-stroke, turbocharged, intercooled, direct injection diesel engine, showed that the use of B20 blends derived from waste cooking oils results in significant reduction concerning PM emissions, similar to biodiesel of different origin. The study of Yang et al. (2007) measured NOx and PM emissions and also PAHs in diluted exhaust. Diesel and the B20 blended fuel (20% methyl ester of waste cooking oil and 80% diesel) were separately used in two brand-new modern diesel engines of identical type for durability test (80,000 km). For this study, the engines were mounted and operated on an engine dynamometer. Emissions of NOx, PM and PAHs were measured at 20,000-km intervals. The results of the durability runs, using B20 fuel, showed average emission factors over time of 4.27 and 0.087 g bhp h^{-1} for NOx and PM, respectively. At 0 km, the emission factors of PM for B20 were lower than those for diesel. After running for 20,000 km and longer, B20 emission levels were higher than diesel. The viscosity of B20 (3.53 cst) is higher than that of diesel (3.15 cst) and results show that higher B20 viscosity is a factor causing higher emission after extended miles of engine operation. In general, air-pollutant emissions would increase as mileage accumulated (however, statistically not significantly).

The average total PAH emission factors were 1097 and 1437 μg bhp h^{-1} for B20 and diesel, respectively. For most ringed-PAHs and total-PAHs, B20 has lower PAH emission levels than that of diesel fuel. For both B20 and diesel, total PAH emission levels decreased as the driving mileage accumulated. However, particulate PAH emissions increased for B20 as the mileage increased. Statistical analysis results show that B20 would cause higher particulate PAH emission significantly (p=0.026) with long-term driving.

It therefore seems that waste cooking oil may also be used as a biodiesel after this has been converted by means of esterification and complies with the EN14124 norm. Long-term effects on combustion and emissions may require more attention that biodiesel from other sources.

3 Bioethanol

3.1 Bioethanol production

Like biodiesel, bioethanol is a liquid biofuel. It is made from starch plants (corn, wheat and cassava), sugar plants (beet and cane) and cellulose plants. The production of bioethanol first uses enzyme amylases to convert a feedstock crop into fermentable sugars. Yeast is then added to the mash to ferment the sugars to alcohol and carbon dioxide, the liquid fraction being distilled to produce ethanol.

According to Balat et al. (2008), one major problem with bioethanol production is the availability of raw materials for the production. The availability of feedstocks for bioethanol can vary considerably from season to season and depend on geographic locations. Therefore, the choice of crop used to produce bioethanol depends on the prevailing soil and climatic conditions. For example, in Brazil, sugar cane is the preferred feedstock due to its very high sugar content and fuel yield. In the North America, over 50 production plants produce fuel ethanol from starch crops such as corn. Most European ethanol is produced using sugarbeet and grains. However, it should be kept in mind that the price of the raw materials is also highly volatile and this can affect the production costs of bioethanol.

3.2 Bioethanol use

In Europe, the use of bioethanol as a blend in petrol is increasing. Both France and Spain have established fuel ethanol industries where ethanol is not used directly but is transformed into ETBE (Ethyl Tert-Butyl Ether). ETBE is produced by mixing ethanol and isobutylene and reacting them with heat over a catalyst. The promise of ETBE is that it eliminates many of the historical impediments to the greater use of ethanol, such as increased volatility of gasoline and incompatibility with gasoline pipelines. In 2003, the largest consumers were Spain at 200 mil. lt, Sweden at 180 mil., and France at 100 mil.. Sweden uses ethanol in both E5 and E85. Poland was closely behind, producing and consuming 80 mil. lt of bioethanol.

Bioethanol can be used as a fuel in a number of different ways:

- As a blend with gasoline (from 5% to 85%). As a 5% blend it can be used in all petrol engines. As a low percentage alcohol-petrol blend ('E10' is 10% ethanol, also known as 'gasohol') ethanol can also be used with no or little modification. However, higher E85 blends require several modifications.
- As a direct substitute for petrol in cars with appropriately modified engines.
- As a blend with diesel in diesel engines, also known as "E-diesel" fuel blends
- As a blend with biodiesel in diesel engines, also known as "BE-diesel" fuel blends

The suitability of ethanol as vehicle fuel is demonstrated by its use as a high performance motor-racing fuel (and is used at Le Mans).

The following sections include a brief analysis of the vehicle types that can operate on ethanol blends and associate these to tailpipe emissions and performance. Table A. 3 and Table A. 4 demonstrate the available data concerning NOx and PM emissions for different ethanol-gasoline, ethanol-diesel and ethanol-biodiesel blends.

3.3 *"Flex-Fuel" or "Flexi-Fuel" Vehicles*

In Europe, Ford, Volvo and Saab now produce 'Flex-Fuel' Vehicles (FFVs) that run on any percentage petrol-ethanol blend (up to E85) or on neat gasoline. The engine management system automatically detects what type of fuel is being used and accordingly adjusts the timing. This makes these vehicles fuel-flexible. Over 15,000 flex-fuel versions of the Ford Focus have already been sold in Sweden, where there are more than 800 filling stations with E85 bioethanol fuel.

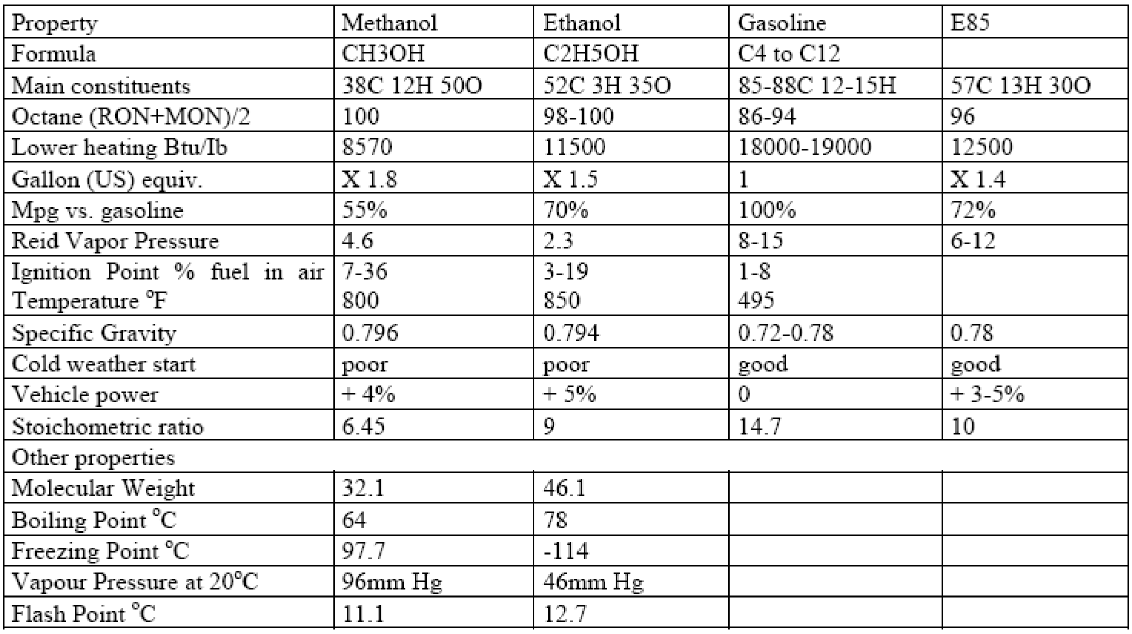
There are some modifications required on gasoline cars to run on bioethanol (for blends higher than E5). Alcohol fuels degrade certain types of rubber and accelerate the corrosion of several metals. Therefore some engine components that come in contact with ethanol may need to be replaced with a non degradable material. Compared to gasoline, biofuel has a higher natural octane number that enables its use at high compression ratio, thus increasing engine efficiency. However, it has a lower energy density than gasoline and this requires an adjustment of the ignition timing in a conventional gasoline engine and fitting a larger tank to achieve the same useful distance. Pure bioethanol is difficult to vaporise at low temperatures. Use of E95-E100 may provide difficulties in starting up vehicles in cold weather. For this reason, the fuel is usually blended with a small amount of petrol to improve ignition (E85 is a common high percentage blend). Table 5 demonstrates the properties of methanol, ethanol, gasoline and E85. Also, Figure 7 demonstrates how the ethanol concentration influences the octane number, the heating value etc. One should notice that not all properties are linear functions of ethanol blending.

One of the primary arguments of ethanol enrichment advocates is the claimed reduction in air pollutant emissions relative to petrol fuel. Since ethanol is an 'oxygenate' and introduces greater oxygen-to-fuel mixture, an improvement of combustion efficiency is expected. However, the true picture is far more complex than what this argument might suggest. The following sections discuss the main results from a considerable number of studies of vehicle tailpipe emissions in the peer-reviewed and technical literature.

3.3.1 NOx emissions

The main conclusion from all studies collected on the use of E10 blends, is that no consistent change can be seen concerning NOx emissions. In general, some studies indicate that E10 blends generally cause higher emissions of nitrogen oxides compare to neat petrol (CARB 1998; Koshland et al. 1998; NRC 1999; Reuter et al. 1992; Hsieh et al. 2002), some studies indicate mixed results (He et al. 2003b; Knapp et al. 1998) and some show no change or marginally lower emissions (Egeback et al. 2005; Reading et al. 2002). The average increase of NOx emissions is in the order of 1%, with a range from -10% to 7%, as shown from various experiments conducted on passenger cars (Karlsson 2006; Reading et al. 2002; TNO 2004). Another recent report released through the GAVE project (DeServes 2005) compared emissions of four different ethanol blends (E5, E10, E70, E85) from three Euro 4 flexifuel passenger cars. The tests were performed on a range of different driving cycles, including NEDC and Artemis urban, road and motorway cycles. No consistent change was found in NOx emissions from E5 and E10 blends. According to the same project, NEDC tests conducted at -7ºC did not show higher emissions compared to those at 22ºC, indicating that the temperature has no impact on NOx emissions.

Table 5: Properties of methanol, ethanol, gasoline and E85. Source: Jankowski and Sandel (2003)



Property	Methanol	Ethanol	Gasoline	E85
Formula	CH3OH	C2H5OH	C4 to C12	
Main constituents	38C 12H 50O	52C 3H 35O	85-88C 12-15H	57C 13H 30O
Octane (RON+MON)/2	100	98-100	86-94	96
Lower heating Btu/Ib	8570	11500	18000-19000	12500
Gallon (US) equiv.	X 1.8	X 1.5	1	X 1.4
Mpg vs. gasoline	55%	70%	100%	72%
Reid Vapor Pressure	4.6	2.3	8-15	6-12
Ignition Point % fuel in air Temperature °F	7-36 800	3-19 850	1-8 495	
Specific Gravity	0.796	0.794	0.72-0.78	0.78
Cold weather start	poor	poor	good	good
Vehicle power	+ 4%	+ 5%	0	+ 3-5%
Stoichometric ratio	6.45	9	14.7	10
Other properties				
Molecular Weight	32.1	46.1		
Boiling Point °C	64	78		
Freezing Point °C	97.7	-114		
Vapour Pressure at 20°C	96mm Hg	46mm Hg		
Flash Point °C	11.1	12.7		

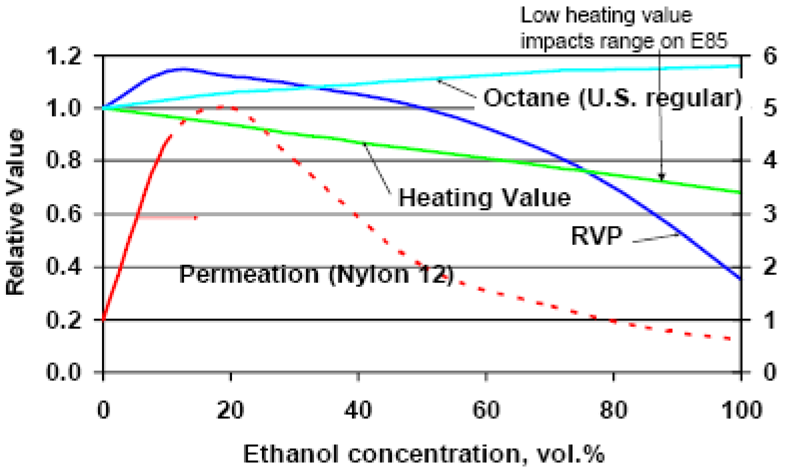


Figure 7: Typical ethanol impacts on fuel properties. Source: Herwick (2006)

The average increase of NOx emissions is in the order of 25% with the use of E20 blends in passenger cars, ranging from -17% to +79% (Egeback et al. 2005; Karlsson 2006; Zervas et al. 2003). However the experiments conducted by Orbital (2004) provide data as a function of the mileage of the cars tested. Results show that as mileage increases, NOx emissions also increase compared to neat gasoline. For example, at 6,400 km the average increase of NOx emissions was ~19%, ranging from -17% to 52%. At 40,000 km, the average increase was about 30%, ranging from 2% to 78%, and at 80,000 km, the average increase was in the order of 38%, ranging from 5% to 79%.

The experiments conducted with E70 and E85 blends (DeServes 2005) indicated that the NOx emissions in Artemis cycles (Artemis-Urban and Artemis-Road) were 60% and 67% lower with the E70 and E85 blends respectively, over the E5 emissions. However, those were single tests from a single study and therefore it is difficult to conclude whether this is a consistent effect.

All studies report a very high variation in NOx emissions with the use of bioethanol blends, ranging from significant improvements (up to 67%) to equally significant degradation (+79%). The variations in published results are not directly associated with ethanol content or vehicle class. However, one needs to consider that, in contrast to a diesel engine, the gasoline engine emission performance is dominated by the operation of the three way catalyst. Small variations of the combustion stoichiometry may have important effects on the catalyst efficiency. In particular for NOx, if the ethanol oxygen content in the fuel is not properly compensated for by the engine, this will lead to a lean exhaust, which completely inhibits the reducing efficiency of the catalyst and will lead to higher NOx emissions. In contrast, over-compensation will lead to the opposite result. In addition, use of an additive package to change certain properties of the blend, may influence the emission performance of the vehicle. According to Gautam and Martin (2000), longer-chain alcohol additives result in an increase of NOx emissions.

3.3.2 PM emissions

Exhaust PM emissions from gasoline passenger cars are only a fraction of diesel ones (1-3 mg/km, compared to 25-50 mg/km). In any case, measurements conducted to evaluate the impact of ethanol-petrol blends on PM emissions showed that E10 leads to reductions of some 50%, with a range from -33% to -59% Reading et al. (2002) compared to neat gasoline. The tests on the three cars conducted by DeServes (2005) showed an inconsistent effect of bioethanol. On two of the cars, PM emissions were increased by up to 100% and on the third car, emissions were reduced by 80% over the E5 fuel. In all cases, emissions were below 2 mg/km and it is therefore difficult to conclude whether any differences were due to real fuel effects or the experimental uncertainty of this sensitive measurement.

3.3.3 Non-regulated emissions

Most studies indicate that emissions of benzene, toluene, ethyl benzene are slightly decreased when using ethanol blends. However, aldehydes show a significant increase.

Use of E5 blends in passenger cars over the NEDC (Delgado and Izquierdo 2003) led to a decrease of benzene and toluene emissions by 13% and 32% respectively. The reductions were 16% and 27% respectively, over the urban part and 30% and 100% over the extra urban part. The ethylbenzene emissions showed an increase of 45% in the urban phase, a decrease of 100% in the extra-urban phase and an increase of 39% in total. It should be noted that the measured values of all these components were very small, especially for benzene, and the differences are subject to experimental uncertainty. In addition, differences on an absolute scale are less important. The formaldehyde, acetaldehyde and metacroleine emissions decreased when ethanol was added to the petrol. In the urban phase and in the total of the driving cycle the formaldehyde emissions decreased by 68%, the acetaldehyde emissions decreased by 36% and the metacroleine emissions decreased by 100% (Delgado and Izquierdo 2003).

When using E10 blends, experiments conducted by Apace (1998) on a 1999-vehicle fleet indicated that the use of E10 blends in passenger cars results in a 19% decrease of 1,3 butadiene, 27% decrease of benzene, 30% decrease of toluene and a 27% decrease of xylenes. On the other hand, formaldhehyde and acetaldehyde were found to increase by 25% and 189%, respectively. According to (Apace 1998; Reuter et al. 1992; Zervas et al. 2003) E10 causes a significant increase in emissions of acetaldehyde (ethanal), with levels increasing by about 100–200% and in some cases by up to 700% (Knapp et al. 1998).

In addition, according to an extensive investigation that was carried out in Sweden, where 12 passenger cars were tested with E23 blends, when comparing the use of the 23% ethanol blend in gasoline with the use of neat gasoline, the emissions of acetaldehydes increased, while emissions of polycyclic aromatic hydrocarbons (PAHs) - especially benzopyrene - decreased.

For blends of over 70% in ethanol, acetaldehyde emissions can increase by as much as 500% according to Reading et al. (2002) with an error in the order of ±300%. According to DeServes (2005), the emissions of acetaldehyde show a clear fuel dependence with largely increased emissions for the high ethanol fuels, E70 and E85. As compared to the cold-start NEDC emissions, the aldehyde emissions in the Artemis cycles are considerably lower, approximately 90%, ranging from -80 to -100%. The difference in acetaldehyde emissions between the NEDC and the Artemis cycles is attributed to the cold start in the NEDC.

3.3.4 Evaporative emissions

- Policy context

The EU Directive 2003/17/EC, in addition to provisions on gasoline and diesel fuel maximum sulphur content in 2005 and beyond, requires the European Commission to review a number of other fuel specifications for possible amendments. One specific requirement is to assess the current gasoline summer vapour pressure limits with respect to ethanol directly blended into gasoline. The fuel Directive 98/70/EC defines gasoline volatility classes and their vapour pressure limits. Each European country applies one or more volatility classes depending on its climate and on the season, and all gasoline, including gasoline/ethanol blends, must comply with the relevant Dry Vapour Pressure Equivalent (DVPE) limits. A vapour pressure waiver for gasoline/ethanol blends has been proposed in order to facilitate the spread of ethanol usage and consequently to increase its market penetration. Ethanol is normally distributed separately to gasoline, and only blended at the terminal into road tankers for final distribution. However, there is concern about the possible consequences of the increased vapour pressure of the ethanol/gasoline blends on evaporative emissions from gasoline cars.

- Effect of ethanol on evaporative emissions

The blending of ethanol up to E30 into gasoline results in an increase in vapour pressure, as was shown in Figure 7, and thus increases evaporative emissions. The increase of DVPE is roughly constant at ~7 kPa for ethanol contents between 2 % and 10 %, a range where a high plateau of DVPE is observed. Results from a major test programme specifically designed to investigate the influence of gasoline vapour pressure and ethanol content on evaporative emissions from modern European passenger cars confirmed that vapour pressure is a key fuel variable for evaporative emissions (Martini et al. 2007b). In general, increasing fuel vapour pressure above that of the 60 kPa DVPE reference fuel used for system development increased evaporative emissions. However, the effect of vapour pressure is strongly non-linear, as expected for a process in which a vapour breakthrough through the canister effect may occur. The ethanol blends with final DVPE around 75 kPa gave considerably higher evaporative emissions than the other lower volatility fuels in most of the vehicles. Differences between fuels with DVPE in the range 60-70 kPa were small.

However, due to the combination of DVPE variations, ethanol content and significant canister weight changes, the influence of individual parameters could not be reliably estimated. The results obtained in a few tests where extra purging of the canister was carried out suggest that differences in evaporative emissions on fuels in this volatility range could be reduced if a more extensive canister conditioning procedure was adopted. The engineering margin built into the system may also explain the reduced fuel effect. The evaporative emission control system is designed for the DVPE of the reference fuel (60 kPa) used in the homologation test but, as for other emission control devices, the manufacturer introduces a certain margin to take into account the production variability.

Ethanol might influence evaporative emissions also via different mechanisms than the increased vapour pressure of ethanol/gasoline blends (CARB 1999). Ethanol is known to increase the fuel permeation rate through the elastomeric materials (rubber and plastic parts) that make up the vehicle’s fuel and fuel vapour systems. Results from a large-scale study on fuel permeation showed that non-ethanol hydrocarbon permeation emissions generally increased when the ethanol containing fuels were tested (CRC 2004).

- Effect of ethanol on canister efficiency

One of the potential issues associated with the use of ethanol/gasoline blends is the effect of ethanol on canister efficiency (Grisanti et al. 1995). The working capacity of a canister is typically around 50% of its total equilibrium adsorption capacity and it is heavily dependant on several parameters like canister design and purge conditions. During normal operation a “heel” of material that cannot be easily desorbed builds up within the carbon bed reducing the working capacity of the canister. The magnitude of the heel depends also on the carbon properties. Larger hydrocarbon molecules are less easily desorbed than smaller ones, so over time the average molecular weight of the heel increases. Ethanol is a polar molecule and it is known to be less easily desorbed from activated carbon; therefore the use of a fuel containing ethanol could significantly increase the heel and reduce canister working capacity. This would result in an increase of evaporative emissions.

- VOC speciation data

Speciated hydrocarbon emissions from evaporative emissions tests generally show relatively high levels of light hydrocarbons (C3 – C5) and low levels of ethanol. Light hydrocarbons are the main contributors to evaporative emissions because of their low boiling point and their higher diffusion rate in the carbon bed.

Ethanol is present in low concentrations in the evaporative emissions when ethanol containing fuels are used. Moreover, once ethanol has been used, it appears in the fuel vapour even if pure hydrocarbon fuels are used. In this case the most likely source of ethanol is the canister heel, i.e. ethanol can not be completely desorbed during the purging operations prior to fuel change. The low levels of ethanol seem also to confirm that it is efficiently adsorbed by the canister and that the contribution of ethanol breathing losses to the total evaporative emission is quite low.

Heavier hydrocarbons like aromatics are found in significant concentrations. These hydrocarbons are less likely to be emitted through the canister vent as their concentration in the gasoline vapours above the liquid surface in the tank is expected to be low due to the high boiling point. In this case the main source of emissions is likely to be fuel permeation (Lockhart et al. 2001).

3.4 "E-Diesel"

Since ethanol is a widely available oxygenate with a long history of use in gasoline blends, it has also been considered as a potential oxygenate for diesel fuel blending. In this effort, numerous techniques have been examined in order to evaluate whether it is possible to use blends of diesel and ethanol in compression ignition engines. Some of these techniques include alcohol fumigation, dual injection, alcohol-diesel fuel emulsions, and alcohol-diesel fuel blends. Among these techniques, blends are the most promising since they are stable and can be used in engines with relatively no modifications. Blends of ethanol with diesel fuel are often referred to as "E-Diesel".

The addition of ethanol to diesel fuel simultaneously decreases cetane number, heating value, aromatics fractions and kinematic viscosity and changes distillation temperatures (He et al. 2003a). Most importantly, E diesel blends have a much lower flash point than diesel fuel and higher vapour formation potential in confined spaces (Peckham 2001).

The solubility of ethanol in diesel is affected mainly by temperature, hydrocarbon composition of diesel and water content in the blend (Ecklund et al. 1984). For example, blends with 20% ethanol and 50% ethanol will separate at about 0°C and 23°C, respectively (Murayama et al. 1982). In order to keep the blends homogenous and stable, an additive is used and an ignition improver, which can enhance cetane number of the blends and bring favourable effects on the physicochemical properties related to ignition and combustion (He et al. 2003a). In addition, additives can prevent the ethanol and diesel from separating at very low temperatures or if water contamination occurs. Two common types of additives are surfactants and co-solvents. Surfactants are molecules with a polar end and a non-polar end. The polar end is attracted to the ethanol molecules while the non-polar end to the hydrocarbon molecules in the diesel fuel. Co-solvents have intermediate polarity between ethanol and diesel fuel and act as a bridging agent to produce a homogeneous blend. Both surfactants and co-solvents allow ethanol and diesel fuel to be splash blended.

The comparison of the emissions from E Diesel and diesel fuel is complicated and results vary widely according to the conditions under which the fuel is used (speed, load, test cycle, engine size, engine design etc). Since the blending of ethanol and diesel fuels results in a decrease of the cetane number and alteration of the physiochemical properties, an additive package is usually used for compensating the fuel characteristics deterioration. The variation of cetane number and physiochemical properties of each individual blend can also influence the emissions.

3.4.1 NOx emissions with the use of E-Diesel fuel

According to experiments conducted by (Corkwell et al. 2003; Reuter et al. 1992) on different passenger cars under various operation conditions with E10 blends, NOx emissions showed an average increase in the order of 12%, ranging from a 2% decrease to a 25% increase compared to neat diesel. Based on all available data collected though in this study, regardless of the cetane number of the end fuel, the average effect was a more moderate 1% increase in NOx emissions with E-Diesel.

By comparing neat diesel emissions with E-Diesel emissions at the same cetane level, measurements by Corkwell et al. (2003) conducted on passenger cars indicate that when a cetane improver is used to match the cetane number of the neat diesel, a 2% reduction in NOx may be expected. Schuetzle et al. (2002) conducted experiments on a pair of vehicles equipped with 2.3 lt turbo-charged engines, and emission measurements were performed on a chassis dynamometer with two different E10 diesels, following the European EUDC cycles. The E blend with no cetane improver reduced NOx emissions by 6%. The E blend with a cetane improver reduced NOx emissions by 7%. Therefore the exact effect depends on both the fuel and the additive package.

The engine speed and load condition can also influence NOx emissions from passenger cars. Cole et al. (2001) conducted measurements with ethanol-diesel blends with 10% ethanol and additives under a matrix of conditions that included 26 independent combinations of engine speed and engine load. The experiments were conducted in a 1.9 l., turbo-charged, direct injection engine which was installed on a dynamometer. Under the highest speed and lightest load condition, E Diesel resulted in NOx reductions in the order of 49%. Equal reductions were also achieved at 1500 rpm and all loads. Under conditions of low speed with low load and high speed with high load, NOx emissions increased up to 51%. On average, for all different combinations of speed and load, NOx emissions increased by 1%. Finally, experiments conducted by He et al. (2003a) on a direct injection diesel engine indicated that at high loads, the ethanol-diesel blends result in a 2% decrease of NOx emissions.

With respect to heavy duty vehicles, use of E10 ethanol-diesel blend was shown to reduce NOx emissions in the order of 1.8% compared to neat diesel (Fanick and Williamson 2002; Kass et al. 2001; Merrit 2005; Schuetzle et al. 2002), with a range of -6% to +5%. The results from experiments conducted in DDC 12.7 l. heavy-duty diesel engine Spreen (1999) showed reductions in NOx emissions from zero to -5%. These observations come to agreement with Lofvenberg (2002), whose experiments on a 11 lt heavy-duty engine indicated that by using E diesel blend (E10) and a cetane improver, one can achieve a 5% reduction of NOx. Experiments (Merrit 2005) conducted on three different Tier II non-road engines at 3 different blend levels of ethanol and using three different additive packages indicated that by increasing the ethanol content, NOx emissions were reduced with ethanol use on two of the engines, with reductions ranging from -5% to -9%. On the third engine they were increased by +2%.

Similar to passenger cars, different effects may be observed for different load/speed conditions on heavy duty engines as well. Kass et al. (2001) investigated diesel fuel blends containing 10 % vol. of ethanol in a 5.9 l Cummins B series engine. In the case of NOx emissions, the diesel fuel and E Diesel fuel performed similarly under the range of conditions tested. At the extremes, the E-diesel fuel led to a variation of NOx emissions within the range -6% to 9%, compared to the neat diesel.

3.4.2 PM emissions

The addition of ethanol in diesel fuel results in significant reductions of PM emissions. The average reduction from all measurements collected on the use of E10 on passenger cars is in the order of -5%, ranging from -67% to +65%. Corkwell et al. (2003) found reductions of -13% on average, ranging from -16% to -25%, when using E10 on a 1.9 l. turbo-charged passenger car tested over the FTP cycle. When using cetane improvers to fix the cetane number of E10 to that of neat diesel, Corkwell et al. (2003) found that PM decreases by -25% on average. According to experiments conducted by Spreen (1999) on a diesel engine, results showed a consistent PM reduction of -23% and -35% for E10 and E15 blends respectively. Cole et al. (2001) studied the PM variation with load and speed from a 1.9 l engine and observed a range of -72% to +65%, compared to neat diesel. The greatest reductions were achieved at highest engine loads under all speeds and also under lowest engine loads at the highest speeds.

PM emissions from heavy duty engines decrease by, on average, -23% when using E10, ranging from -44% to +6% for all tests collected (Fanick and Williamson 2002; Kass et al. 2001; Lofvenberg 2002). The study of Schuetzle et al. (2002) on the two engines mentioned in the previous section led to reductions of -18% without the cetane improver and -34% with the cetane improver. The study of Merrit (2005) on the three Tier II non-road diesel engines provided reductions from -13% to -30%. The PM results from the study of Kass et al. (2001) on a 5.9 l Cummins B series engine using E10, showed that generally, E Diesel results in reductions in PM emissions relative to diesel fuel. Only under the lowest speed condition did E Diesel show an increase in PM emissions in the order of 6%. The PM reduction ranged from -13% to -44% and tended to be the strongest under mid-range speed conditions.

3.5 BE-Diesel (Biodiesel-Ethanol-Diesel)

The main disadvantage of E–diesel fuel blends is that ethanol is immiscible in diesel over a wide range of temperatures (Gerdes and Suppes 2001). Studies have revealed that biodiesel can be used successfully as an amphiphile to stabilize ethanol in diesel and the biodiesel–ethanol–diesel (BE–diesel) blend fuel can be stable well below sub-zero temperatures

(Fernando and Hanna 2004). It has been therefore suggested that the biodiesel and ethanol blends can be an optimized oxygenated agent for diesel fuels (McCormick and Parish 2001). According to Cardone et al. (2002), the disadvantages of BE-Diesel compared to fossil diesel is the lower heating value of BE–diesel which might be responsible for the lower engine power, lower exhaust temperature, lower torque, and higher SFC than those of fossil diesel. These are all similar properties to conventional biodiesel.

A number of studies have found that ethanol-blend and biodiesel-blend would substantially reduce PM emissions, but produce higher levels of NOx concentrations compared with fossil diesel (Ali et al. 1995; Starr 1997).

Pang et al. (2006) used a 5% ethanol, 20% biodiesel and 75% diesel blend on a Cummins-4B diesel engine and found that PM emissions were reduced by 22–40% compared to neat diesel. Shi et al. (2005) and Ali et al. (1995) tested four and twelve different blends of biodiesel, ethanol and diesel, respectively in diesel engine to investigate the regulated emission and the performance of engine. They also found that PM was substantially reduced for BE–diesel in comparison with neat diesel. Similar to conventional biodiesel, Cardone et al. (2002) found that NOx emissions tend to increase compared to fossil fuel, coming to agreement with Pang et al. (2006), whose experiments showed a slight increase of NOx emissions. This is due to the heat release that occurs in advance when an engine is fuelled with biodiesel, which generates higher temperatures inside the cylinder during the combustion process. As already mentioned, the higher temperature in combustion chamber would be in favour of NOx formation.

3.6 Conclusions on the ethanol use

3.6.1 PM emissions

In general, most studies show reductions concerning PM emissions for ethanol-petrol, ethanol-diesel and ethanol-biodiesel blends. The effect on spark-ignition engines is highly variable but their contribution on PM is also much smaller than diesels. The reduction of particulate emissions due to the introduction of oxygenated compounds depends on the molecular structure, oxygen content of the fuel (Kitamura et al. 2001; Miyamoto et al. 1998) and local oxygen concentration in the fuel plume (Donahue and Foster 2000).

Concerning ethanol-gasoline blends, a few studies have examined the potential of high ethanol blends to achieve future emissions standards (Euro 5), after appropriate vehicle modifications. These studies were generally successful, which suggests that attainment of future standards should be expected for high ethanol blends, provided that engine modifications are being made and a significant reduction of PM formation should be expected when using ethanol in spark ignition direct injection (SIDI) engines. According to an AEA Technology study (Reading et al. 2002) which compared emissions from an E10 splash blended ethanol-gasoline mixture with gasoline in a Euro 3 passenger car tested on the NEDC cylcle, there is much variability associated with emissions from bioethanol, although there does appear to be a consistent decrease in PM emissions. The decrease of PM emissions in passenger cars concerning ethanol-petrol blends with 10% ethanol, is in the order of -46%, ranging from -33% to -59%.

Concerning E10 ethanol-diesel blends, regardless of the engine category, driving conditions, cetane number etc. the average decrease of PM emissions concerning passenger cars is in the order of -5%, ranging from -67% to +65%. However, the use of E10 ethanol-diesel blends in heavy-duty vehicles is expected to result in more significant reductions with an average value in the order of -23%, ranging from -44% to +6%.

In addition, in the cases where cetane number is a variable, by increasing the cetane number to match the one of the diesel fuel, PM emissions are decreased with an average value in the order of -25%, ranging from -20% to -29%, as shown from experiments conducted on passenger cars fuelled with E10 blends (Corkwell et al. 2003). There are no similar tests available for HDVs.

3.6.2 NOx emissions

Effects NOx emissions with the use of ethanol blends in either diesel or gasoline are less consistent (Mulawa et al. 1997; Reuter et al. 1992; Rice et al. 1991).

The main conclusion from using ethanol-gasoline blends up to E10, is that based on all data no significant change can be seen concerning NOx emissions. Some studies indicate that E10 blends generally cause higher emissions of NOx compare to neat gasoline (CARB 1998; Koshland et al. 1998; NRC 1999; Reuter et al. 1992) and (Hsieh et al. 2002) and some studies indicate mixed results (He et al. 2003b; Knapp et al. 1998). Concerning E20 ethanol-gasoline blends there is an average increase of NOx emissions in the order of 25%, ranging from -17% to +79%, (Augin and Graham 2004; Karlsson 2006; Orbital 2004). Finally, DeServes (2005) tested three Euro 4 flexifuel cars over different driving cycles with up to E85 blends and found significant reductions (up to -70%) from all vehicles when using an E85 blend. As this concerns new technology vehicles and a blend which is widely used in Sweden, such a finding needs to be repeated with additional tests to explore whether this has a universal character.

The ethanol-diesel blends are reported to lead to increased NOx emissions in most of the studies (Cole et al. 2001; Corkwell et al. 2003; Fanick and Williamson 2002). However, results with E10 vary from a significant reduction in the order of -49% to a significant increase in the order of 51%, with an average value in the order of +3%. In theory, bioethanol vehicles should emit fewer nitrogen oxides (as alcohol fuels burn at a lower temperature than petrol). In practice the compression ratio is often increased to improve engine efficiency, which raises the combustion temperature and offsets any NOx emission benefit. According to EECA (Energy Efficiency and Conservation Authority) exhaust emissions from modern vehicles do not differ significantly when using ethanol blends. In older vehicles, without catalysts and fully functional emission control systems, ethanol may result in slight increases in NOx.

4 Second generation biofuels

Second generation biofuels derive from biomass-to-liquid technologies. Typical examples are Bio-DME, biomethanol, mixed alcohols and Fischer-Tropsch diesel.

- Bio-DME (Bio-Dimethyl-Ether):. Bio-DME can be produced from Biomethanol using catalytic dehydration or it can be produced from syngas using DME synthesis. DME can be used in the compression ignition engine
- Biomethanol: Biomethanol is the same as methanol but it is produced from biomass. Biomethanol can be blended with petrol up to 10-20%
- Mixed Alcohols: (mixture of mostly ethanol, propanol and butanol, with some pentanol, hexanol, heptanol and octanol). Mixed alcohols are produced from syngas with catalysts similar to those used for methanol. Mixed alcohols are superior to pure methanol or ethanol because they have higher energy content. Also, when blending, the higher alcohols increase compatibility of gasoline and ethanol, which increases water tolerance and decreases evaporative emissions. In addition, higher alcohols have also lower heat of vaporization than ethanol, which is important for cold starts
- Fischer-Tropsch diesel or BTL (Biomass to liquids): BTL diesel is produced using the Fischer-Tropsch gas-to-liquid technology. BTL diesel can be mixed with fossil diesel at any percentage without need for infrastructure change. It is likely that BTL diesel (which is chemically different than the methyl-ester biodiesel produced, for example, from rapeseed or soybeans) will receive the most attention over the next years, especially in Europe. BTL Fuel is as clear and virtually free of sulfur and aromatic substances. Its ignition qualities (as measured by a very high cetane number) are excellent, thereby reducing noise and resulting in cleaner combustion than with conventional diesel.

All these fuels can be derived from syngas which is produced by the gasification of biomass. However, it can be produced much easier from coal or natural gas, which is done on very large scales in power plants and in gas-to-liquid processes. Hence, similar fuels can be produced from both bio- and non-bio feedstocks.

There is not much that can be said with regard on the emissions with the use of second generation biofuels. Fischer-Tropsch biodiesel is expected to be of very high quality, with very low aromatics content and trace sulphur. Hence. it may lead to reduced emissions (especially of PM), much the same way as the Environmental Class 1 diesel in Sweden. In addition, second generation biofuels contain less oxygen compared to first generation biofuels and therefore tailpipe emissions from the second generation biofuels are closer to the emissions from neat diesel. Also, second generation biofuels derived from bioethanol are not expected to present deviations concerning tailpipe emissions compared to first generation bioethanol due to the fact that they do not differ in chemical composition. Of course, the exact impact will depend on the specifications of these fuels that have to be regulated in the future.

5 Conclusions – Recommendations

1. Use of pure biodiesel increases NOx emissions from both passenger cars and heavy duty vehicles, compared to pure fossil diesel (neat diesel). The increase is due to the high cetane number which advances combustion and the unsaturated character of the biodiesel components, which increase the flame temperature. NOx increases may be several percentage units (i.e. up to 30-40%) with the exact value depending on vehicle technology and operation conditions. Due to the significant increase, use of pure biodiesel should be avoided in vehicles operating in areas with air-quality problems, unless the engine has been properly tuned (e.g. in the case of captive fleets) to maintain low NOx performance with biodiesel use.

2. The effect of biodiesel blends on NOx emissions is highly dependant on engine technology. Available measurements have shown that B5-B10 blends show a marginal difference, i.e. in the order of 1%, which is within experimental uncertainty. B20-B30 blends may bring positive or negative effects of a few percentage units (5-6%). Given the current knowledge, use of biodiesel in blends up to B30 is not expected to lead to substantially differentiated air-quality conditions. Of course, such a conclusion needs to be considered each time in combination with the available level of technology. Emissions of upcoming vehicle and aftertreatment technologies may be more (or even less) affected by biodiesel blends. New experimental campaigns will be required to understand the effects. Also, durability (see recommendation no 5) is also an issue to consider.

3. Pure biodiesel and biodiesel blends have all been shown to consistently reduce PM mass, in the majority of tests. The reduction is monotonic and ranges from -10% for a B10 blend to almost -50% (one study reports a reduction of -77%) for pure biodiesel. The reductions originate from the same reasons that lead to higher NOx, i.e. combustion at higher temperature than neat diesel and the presence of oxygen in the fuel molecule. The PM reduction mainly originates from a significant reduction of the solid (soot) part of PM. The semi-volatile part is not reduced while, in some cases, it may also increase due to incomplete combustion of some of the heavy biodiesel components. These cases need to be better identified. Overall though, for a complete current vehicle fleet, use of biodiesel is expected to lead to reductions of PM.

4. With respect to the upcoming Euro 5 regulations on the control of the solid particle number, the effect of biofuel is expected either minimal or slightly positive, as the oxygen in the fuel molecule inhibits soot formation. Similar to particle number, the mean diameter of particles may also be lower than with neat biodiesel. However, the combination of lower particle number and diameter may result in more significant reduction of active surface. This, together with the higher semi-volatile content of biodiesel derived PM, may lead to the formation of volatile nanoparticles in the sub-50 nm range. These nanoparticles are equally (or, as several studies demonstrate, more toxic) than solid nanoparticles and are not controlled by the upcoming Euro 5 regulations. As a result, this may be a loophole in the control of PM emissions that needs to be examined by conducting more dedicated measurements of total particle number emitted from vehicles/engines of various technologies.

5. Most conclusions related to the effect of biodiesel on emissions originate from back to back tests of biodiesel over neat diesel. Some tests have shown that biodiesel may have faster ageing effects on engine components than pure diesel, due to its chemical character. Several manufacturers are against the use of blends of over 5% biodiesel because they expect that this will increase the maintenance and warranty costs for them and their customers. Therefore, the long-term effect of biodiesel use on emissions needs to be more thoroughly assessed. A couple of studies using biodiesel originating from waste cooking oils showed that even PM emissions, usually reduced when using biodiesel, actually increased over the neat diesel level after 80,000 km of biodiesel use, probably due to coking of the injectors. Therefore, the real-world performance of biofuels requires more attention.

6. There are contradicting statements concerning the effect of biodiesel on non-regulated pollutants and in particular PAHs. Earlier studies have generally shown that biodiesel has a positive effect in reducing these species. More recent studies on current technology passenger cars conducted by JRC, showed the opposite trend, with an over 150% increase in PAHs during the cold-start urban cycle. Clearly, this is an area which requires further attention. Possibly, the biodiesel feedstock as well as the ageing of the aftertreatment devices may be significant co-factors in the impact of biodiesel on non-regulated pollutants.

7. The effects of bioethanol on current spark-ignition vehicles are difficult to quantify. The only clear effect is the several times increase of acetaldehyde and formadelhyde emissions, mostly on cold-start conditions. After catalyst light-off the aldehyde levels are still higher than neat gasoline but only a few percentage units (e.g. 20-30%). NOx emissions are controlled by the stoichiometry and the catalyst condition rather than the fuel used. The tests in literature have been reporting a range of values, including both significant increases and reductions, when comparing neat gasoline with E85 blends. Current flexi-fuel vehicles use sensors to adjust ignition and injection, depending on the fuel used. However, slight deviations from optimal setting may shift the mixture to marginally rich or lean conditions, which greatly affect the performance of the catalyst. This is why no consistent effects can be observed for vehicles powered by ethanol blends. This causes questions on how these vehicles will perform in real-world driving, using fuels produced with different additive packages and how much ageing effects may affect their performance. On the other hand, some investigators have proposed that ethanol may lead to decreased PM emissions from Gasoline Direct Injection vehicles, in order to fulfil the upcoming solid particle number regulations at Euro 5 level.

8. Although pure ethanol is less volatile than gasoline, the splash blending of ethanol with gasoline up to E30 leads to a fuel of increased vapour pressure. This can reach 75 kPa compared to summer gasoline which is ~60 kPa. Increased vapour pressure may also lead to increased evaporation losses during refuelling and vehicle operation. There are two more reasons why evaporation losses of ethanol maybe higher. First, ethanol increases fuel permeation through elastomeric materials. Second, ethanol is a polar molecule and is difficult to desorb from the tank canister. This reduces the effective capacity of the canister which leads to increased vapour breakthrough. With

regard to species evaporating, these are light hydrocarbons rather than ethanol. Ethanol is successfully adsorbed by the active charcoal. Permeation and canister breakthrough can only become worse with vehicle ageing and significantly increase evaporation losses through the vehicle lifetime. This needs to be considered in areas where photochemical smog is an issue.

9. The addition of ethanol on diesel has been examined in E10 blends, by using additives to improve the miscibility of the two liquids and improve the cetane number, since ethanol has a very low natural cetane number. The nature of the additives used also determines, to a large extent, the effect of ethanol on diesel emissions. Due to the lower cetane number, ethanol should lead to a reduction of NOx emissions. Indeed, several studies have observed reductions for NOx when using E10 in diesel by as much as -9% for a complete operation cycle. However, when using an additive to increase the cetane number, NOx emissions may increase up to ~10%, due to the oxygen in the fuel. E10, similar to biodiesel, leads to consistent reductions to PM which regularly reach -30% or even -40% compared to neat diesel, especially if a cetane improver is used. An interesting option is to mix ethanol with biodiesel and fossil diesel (BE-Diesel). Recent studies have shown that biodiesel may act as a miscibility improver for ethanol in fossil diesel. The effects of this combination on emissions are similar to biodiesel blends. Therefore, use of ethanol in diesel may be used as a PM reduction agent.

10. A second generation of biofuels is being considered, which will be produced from a gas-to-liquid process. There are not many data available on the effect of these fuels on emissions. However, one should expect that due to the low aromatics content and the pure nature of these biofuels, emissions should improve compared to the current neat-diesel levels, similar to some environmental friendly diesels (such as the MK-1 diesel in Sweden).

6 References

Ali Y., Hanna M. and Borg J. 1995. Optimization of diesel, methyl tailowate and ethanol blend for reducing emissions from diesel engine Bioresource Technology 52, 237-243.

Altin R., Çetinkaya S. and Yücesu H. 2001. The potential of using vegetable oil fuels as fuel for diesel engines. Energy Conversion Management 42, 529-538.

Apace 1998, *Intensive Field Trial of Ethanol/Petrol Blend in Vehicles*. ERDC Project No. 2511, Apace Reasearch LTD, Energy Research and Development Corporation, Canberra, Australia, http://journeytoforever.org/biofuel_library/EthanolApace.PDF.

Augin K. and Graham L. 2004, *The evaluation of ethanol-gasoline blends on vehicle exhausts emissions and evaporative emissions*. Environmental Technology Centre, Emissions Research and Measurement Division, Ottawa, Canada,

Balat M., Balat H. and Oz C. 2008. Progress in bioethanol processing. Progress in Energy & Combustion Science doi: 10.1016/j.pecs.2007.11.001.

Bauer H., Dietsche K. and Jager T. 2004. *Diesel Engine Management*. Published by Robert Bosch GmbH Automotive Aftermarket Division.

CARB 1998, *Comparison of the effects of a fully-complying gasoline blend and a high RVP ethanol gasoline blend on exhaust and evaporative emissions*. California Air Resources Board, Sacramento, CA, http://www.arb.ca.gov/fuels/gasoline/ethanol/res9878.pdf.

CARB 1999, *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline. Final Report to the California Environmental Policy Council.* California Air Resources Board, Sacramento, CA, USA,

Cardone M., Prati M., Rocco V., Seggiani M., Senatore A. and Vitolo S. 2002. Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: engine performance and regulated and unregulated exhaust emissions,. Environmental Science and Technology 36, 4656-4662.

Cetinkaya M., Ulusoy Y., Tekin Y. and Karaosmanoglu F. 2005. Engine and winter road test performances of used cooking oil originated biodiesel. Energy Conversion and Management 46, 1279-1291.

Choi C., Bower G. and Reitz R. 1997. Effects of biodiesel blended fuels and multiple injection on DI diesel engine emissions. SAE Technical Paper 970218.

Cole R., Poola R., Sekar R., Schaus J. and McPartlin P. 2001. Effects of ethanol additives on diesel particulate and NOx emissions. SAE Technical Paper 2001-01-1937.

Colvile R., Hutchinson E., Mindell J. and Warren R. 2001. The transport sector as a source of air pollution. Atmospheric Environment 35, 1537-1565.

Corkwell K., Jackson M. and Daly D. 2003. Review of exhaust emissions of compression ignition engines operating on E-Diesel fuel blends. SAE Technical Paper 2003-01-3283.

Correa S. and Arbilla G. 2006. Aromatic hydrocarbons emissions in diesel and biodiesel exhaust. Atmospheric Environment 40, 6821-6826.

CRC 2004, *Fuel permeation from automotive systems. Prepared for: California Environmental Protection Agency.* . CRC Project N° E-65, Coordinating Research Council, Alpharetta, GA, USA,

Delgado R. and Izquierdo J. 2003, *Comparison of vehicle emissions at European Union annual average temperatures from E0 and E5 petrol*. Report LM030411, IDIADA, Tarragona, Spain, p.22.

DeServes C. 2005, *Emissions from Flexible Fuel Vehicles with different ethanol blends*. 5509, AVL MTC, Haninge, Sweden, p.46.http://www.vv.se/fud-resultat/Publikationer_000001_000100/Publikation_000077/8050509_Report%20051018_Vv.pdf.

Dockery D. and Pope C. 1994. Acute respiratory effects of particulate air pollution. Annual Review of Public Health 15, 107-132.

Donahue R. and Foster D. 2000. Effects of oxygen enhancement on the emissions from a DI diesel via manipulation of fuels and combustion chamber gas composition. SAE Technical Paper Series 2000-01-0512.

Durbin D., Cocker R., Sawant A.A., Johnson K., Miller J.W., Holden B.B., Helgeson N.L. and Jack J.A. 2007. Regulated emissions from biodiesel fuels from on/off-road applications. Atmospheric Environment 41, 5647-5658.

EC 2004, *Promoting Biofuels in Europe*. European Commission, Directorate-General for Energy and Transport, Brussels, Belgium,

Ecklund E., Bechtold R., Timbario T. and McCallum P. 1984. State-of the-art report on the use of alcohols in diesel engines. SAE Transactions 840118, 684-702.

Egeback K., Henke M. and Rehnlund B. 2005, *Blending of ethanol in gasoline for spark ignition engines*.

EPA 2002, *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions, Draft Technical Report*. EPA, Ann Arbor, MI, USA,

EurObserv'ER 2005, *Barometre des Biocarburants*. European Commission Brussels, Belgium, p.12.http://www.energies-renouvelables.org/observ-er/stat_baro/observ/baro167b.pdf.

EurObserv'ER 2007, *Biofuels Barometer*. European Commission, Brussels, Belgium, http://www.energies-renouvelables.org/observ-er/stat_baro/observ/baro179_b.pdf.

Fanick E. and Williamson I. 2002. Comparison of emission and fuel economy characteristics of ethanol and diesel blends in a heavy-duty diesel engine, in *International Symposium on Alcohol Fuels XIV*, Phuket, Thailand.

Fernando S. and Hanna M. 2004. Development of a novel biofuel blend using ethnaol–biodiesel–diesel miscroemulsions: EB–diesel. Energy and Fuels 18, 1695-1703.

Fontaras G., Samaras Z. and Miltsios G. 2007. Experimental evaluation of cottonseed oil-diesel blends as automotive fuels via vehicle and engine measurements, in *8th International Conference on Engines for Automobile*, Naples.

Fontaras G., Tzamkiozis T., Pistikopoulos P. and Samaras Z. 2008, *Study on the application of vegetable oils and their methylesters as fuels for diesel engines. Final report in the framework of PAVET research project*. LAT Report No. 08.RE.0002.V1 Thessaloniki,

Gautam M. and Martin D. 2000. Emission characteristics of higher-alcohol/gasoline blends. Power Energy 214, 165-182.

Gerdes K. and Suppes G. 2001. Miscibility of ethanol in diesel fuels. Industrial and Engineering Chemistry Research 40, 949-956.

Giannelos P., Shizas S., Lois E., Zannikos F. and Anastopoulos G. 2005. Physical, chemical and fuel related properties of tomato seed oil for evaluating its direct use in diesel engines. Industrial Crops and Products.

Graboski M. and McCormick R. 1998. Combustion of fat and vegetable oil derived fuels in diesel engines. Progress in Energy & Combustion Science 24, 125-164.

Grisanti A.A., Aulich T.R. and Knudson C.L. 1995. Gasoline Evaporative Emissions: Ethanol Effects on Vapor Control Canister Sorbent Performance. SAE Technical Paper 952748.

He B., Shuai S., Wang J. and He H. 2003a. The effect of ethanol blended diesel fuels on emissions from a diesel engine. Atmospheric Environment 37, 4965-4971.

He B., Wang H., Hao J., Yan X. and Xiao H. 2003b. A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels. Atmospheric Environment 37, 949-957.

Herwick G. 2006. Ethanol blended gasoline and mitigation strategies, T. F. s. Consulting, ed.

Hsieh W., Chen R., Wu T. and Lin T. 2002. Engine performance and pollutant emission of an SI engine using ethanol-gasoline blended fuels. Atmospheric Environment 36, 403-410.

Jankowski A. and Sandel A. 2003. Exhaust emissions reduction problems of internal combustion engines fueled with biofuels. Journal of KONES Internal Combustion Engines 10, 3-4.

Karlsson H. 2006, *Emissions from conventional gasoline vehicles driven with ethanol blend fuels*. Swedish Road Administrator,

Kass M., Thomas J., Storey J., Domingo N., Wade J. and Kenreck G. 2001. Emissions from a 5.9 l diesel engine fueled with ethanol diesel blends. SAE Technical Paper Series 2001-01-2018.

Kegl B. 2008. Effects of biodiesel on emissions of a bus diesel engine. Bioresource Technology 99, 863-873.

Kitamura T., Ito T., Senda J. and Fujimoto H. 2001. Extraction of the suppression effects of oxygenated fuels on soot formation using a detailed chemical kinetic model. JSAE Review 22, 139-145.

Knapp K., Stump F. and Tejada S. 1998. The effect of ethanol fuel on the emissions of vehicles over a wide range of temperatures. Air Waste Management Association 7, 646-653.

Knothe G. 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Processing Technology 86, 1059-1070.

Knothe G. and Sharp C. 2006. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters and alkanes in new technology engine. Energy and Fuels 20, 403-408.

Knothe G. and Steidley K. 2005. Kinematic viscosity of biodiesel fuel components and related compounds, influence of compound structure and comparison to petrodiesel fuel components. Fuel Processing Technology 84, 1059-1065.

Koshland C., Sawyer R., Lucas D. and Franklin P. 1998, *Evaluation of automotive MTBE combustion byproducts in California reformulated gasoline, Health and environmental assessment of MTBE, Report to the Governor and Legislature of the State of California as Sponsored by SB 521, vol.III: Air quality and ecological effects*.

Kumar M., Ramesh A. and Nagalingam B. 2003. An experimental comparison of methods and Jatropha oil in a compression ignition engine. Biomass Bioenergy 25, 309-318.

Lapuerta M., Rodriguez-Fernandez J. and Agudelo J. 2008. Diesel particulate emissions from used cooking oil biodiesel. Bioresource Technology 99, 731-740.

Li N., Hao M., Phalen R., Hinds W. and Nel A. 2003. Particulate air pollutants and asthma: A paradigm for the role of oxidative stress in PM-induced adverse health effects. Clinical Immunology 109, 250-265.

Lockhart M., Nulman M. and Rossi G. 2001. Estimating Real Time Diurnal Permeation from Constant Temperature Measurements. SAE Technical Paper 2001-01-0730.

Lofvenberg U. 2002. E-Diesel in Europe, a new available fuel technology, in *International Symposium on Alcohol Fuels XIV*, Phuket, Thailand.

Marshall W., Schumacher L. and Howell S. 1995. Engine Exhaust Emissions Evaluation of a Cummins L10E When Fueled with a Biodiesel Blend, Society of Automotive Engineers. SAE Technical Paper 952363.

Martini G., Astorga C. and Farfaletti A. 2007a. Effect of biodiesel fuels on pollutant emissions from Euro 3 LD diesel vehicles, J. Joint Reasearch Centre, ed.

Martini G., Manfredi U., Mellios G., Krasenbrink A., De Santi G., McArragher S., Thompson N., Baro J., Zemroch P., Boggio F., Celasco A., Cucchi C. and Cahill G.F. 2007b. Effects of Gasoline Vapour Pressure and Ethanol Content on Evaporative Emissions from Modern European Cars. SAE Technical Paper 2007-01-1928.

McCormick R., Graboski M., Alleman T. and Herring A. 2001. Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. Environ. Sci. Technol 35, 1742-1747.

McCormick R. and Parish R. 2001, *Technical barriers to the use of ethanol in diesel fuel*. NREL/MP-540-32674, NREL,

McCormick R., Williams A., Ireland J., Brimhall M. and Hayes R. 2006, *Effects of biodiesel blends on vehicle emissions, Annual Operating Plan Milestone 10.4*. NREL/MP-540-40554, National Renewable Energy Laboratory,

Merrit P. 2005. Regulated and Unregulated Exhaust Emissions Comparison for Three Tier II Non-Road Diesel Engines Operating on Ethanol-Diesel Blends. SAE Technical Paper 2005-01-2193.

Miyamoto N., Ogawa H., Nurun N., Obata K. and Arima T. 1998. Smokeless, low NOx high thermal efficiency and low noise diesel combustion with oxygenated agents as main fuel. SAE Technical Paper Series 980506.

Mulawa P., Cadle S., Knapp K., Zweidinger R., Snow R., Lucas R. and Goldbach J. 1997. Effect of ambient temperature and E-10 fuel on primary exhaust particulate matter emissions from light-duty vehicles. Environmental Science and Technology 31, 1302-1307.

Munack A., Kauffman A., O. S., Krahl J. and Bunger J. 2005, *Comparison of Shell Middle Distilate, Premium Diesel Fuel and Fossil Diesel Fuel with Rapeseed Oil Methylester* Institute of Technology and Biosystems Engineering, Braunschweig,

Murayama T., Miyamoto N., Yamada T., Kawashima J. and Itow K. 1982. A method to improve the solubility and combustion characteristics of alcohol–diesel fuel blends. SAE Technical Paper Series 821113.

NRC 1999, *Ozone-forming potential of reformulated gasoline*. Commission on Geosciences, Environment and Resources, National Research Council, Washington DC

NREL 2006, *Biodiesel handling and use guidelines*. DUE/GO-102006-2358, U.S Department of Energy,

Orbital 2004, *Market Barriers to the uptake of biofuels study. Testing gasoline containing 20% ethanol.* Phase 2B - Final Report, Australian Department of Environment and Heritage

p.193.http://www.environment.gov.au/atmosphere/fuelquality/publications/biofuels-2004/pubs/biofuels-2004.pdf.

Owen K. and Coley T. 1995. *Automotive Fuels Hanbook, Second Edition*. Published by SAE Inc. .

Pang X., Shi X., Mu Y., He H., Shuai S., Chen H. and Li R. 2006. Characteristics of carbonyl compounds emission from a diesel-engine using biodiesel-ethanol-diesel as fuel. Atmospheric Environment 40, 7057-7065.

Peckham J. 2001. Ethanol-diesel raises safety, performance, health concerns:autos, in *Diesel Fuel News*, 9-11.

Pugazhvadivu M. and Jeyachandran K. 2005a. Investigations on the performance and exhaust emissions of a diesel engine using preheated waste frying oil as fuel

Renewable Energy

30, 2189-2202.

Pugazhvadivu M. and Jeyachandran K. 2005b. Investigations on the performance and exhaust emissions of a diesel engine using preheated waste frying oil as fuel. Renewable Energy 30, 2189-2202.

Pundir B., Singal S. and Gondal A. 1994. Diesel Fuel Quality: Engine Performance and Emissions. SAE Technical Paper Series, Paper No 942020

Radich 2006, *Biodiesel performance, costs, and use*. US Energy Information Administration, http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/index.html.

Reading A., Norris J., Feest E. and Payne E. 2002. Bioethanol emissions testing. AEA Technology E&E/DDSE/02/021

Reuter R., Benson J., Burns V., Gorse J., Hochhauser A., Koehl W., Painter L., Rippon B. and Rutherford J. 1992. Effects of oxygenated fuels and RVP on automotive emissions. SAE Technique Paper-920326.

Rice R., Sanyal A., Elrod A. and Bata R. 1991. Exhaust gas emissions of butanol, ethanol, and methanol gasoline blends. Journal of Engineering for Gas Tourbines and Power 113, 377-381.

Schuetzle D., Han W., Srithammavong P., Akarapanjavitz N., Norbeck J. and Corkwell K. 2002. The evaluation of diesel/ethanol fuel blends for diesel vehicles in Thailand: Performance and Emissions studies, in *International Symposium on Alcohol Fuels XIV*, Phuket, Thailand.

Schumacher L., Marshall W. and Wetherell W. 1995. Biodiesel emissions data from Series 60 DDC engines, in *American Public Transit Association Bus Operations and Technology Conference*, Reno, NV.

Sharp C., Howell S. and Jobe J. 2000. The effect of biodiesel fuels on transient emissions from modern diesel engines, Part I. SAE Paper No. 2000-01-1967.

Shi X., Yu Y., He H., Shuai S., Wang J. and Li R. 2005. Emission characteristics using methyl soyate–ethanol–diesel fuel blends on a diesel engine. Fuel 84, 1543-1549.

Spreen K. 1999, *Evaluation of oxygenated diesel fuels, Final Report for Pure Energy Corporation*. Southwest Research Institute, San Antonio, TX.,

Starr M. 1997. Influence on transient emissions at various injection timings, using cetane improvers, biodiesel, and low aromatic fuels. SAE Technical Paper-972904.

Sze C. 2007. Impact of test cycle and biodiesel concentration on emissions. SAE 2007-01-4040

Szybist J., Song J., Alam M. and Boehman A. 2007. Biodiesel combustion, emissions and emission control. Fuel Processing Technology 88, 679-691.

Tat M.I. 2003. nvestigation of oxides of nitrogen emissions from biodiesel-fueled engines, in *Mechanical Engineering Department*, Iowa State University, Iowa.

TNO 2004, *Compatibility of pure and blended biofuels with respect to engine performance, durability and emissions, Report 2GAVE 04.01*.

Tsolakis A., Megaritis A., Wyszynski M. and Theinnoi K. 2007. Engine performance and emissions of a diesel engine operating on diesel-RME (rapeseed methyl ester) blends with EGR (exhaust gas recirculation). Energy and Fuels 32, 2072-2080.

Tzamkiozis T., Fontaras G., Ntziachristos L. and Samaras Z. 2008. Effect of biofuels on PM emissions from a Euro 3 common rail diesel passenger car, in *European Aerosol Conference*, Thessaloniki, Greece.

Yamane K., Ueta A. and Shimamoto Y. 2001. Influence of physical and chemical properties of biodiesel fuels on injection, combustion and exhaust emission characteristics in a direct injection compression ignition engine. International Journal of Engine Research 2, 249-261.

Yang H.-H., Chien S.-M., Lo M.-Y., Lan J.C.-W., Lu W.-C. and Ku Y.-Y. 2007. Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing. Atmospheric Environment 41, 7232-7240.

Yen-Cho C. and Chung W. 2002. Emissions of submicron particles from a direct injection diesel engine by using biodiesel. Journal of Environmental Science and Health 37, 829-843.

Zervas E., Montagne X. and Lahaye J. 2003. Emissions of regulated pollutants from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio. Environmental Science and Technology 37, 3232-3238.

Annex: Literature data on the effect of biofuels on NOx and PM emissions

Table A. 1: Effect of biodiesel blends on NOx emissions, compared to neat diesel

Study	B5	B10	B20	B25	B30	B35	B50	B70	B75	B100	Fuel	Vehicle	Technology	Driving Cycle	Remarks concerning Load, cetane number, EGR etc
[1]		1%		3%		1%	6%		10%	10%	Biodiesel	HDV			
[2]	0%		2%							10%	Biodiesel	HDV			
[3]			1.20%							5.8%	Biodiesel	HDV			
[4]			3%							13%	Biodiesel	HDV			
[5], [22]			0%				1%	-1%		-2%	Biodiesel	HDV		FTP	
[5]			24%				2%	2%		0%	Biodiesel	HDV			
[6]		3.50%	5%		6.9%		16%			28%	Biodiesel	HDV			
[8]		-12%									Biodiesel	PC	Euro 3	NEDC	
		10%									Biodiesel	PC	Euro 3	NEDC	
		0%									Biodiesel	PC	Euro 3	NEDC	
		-11%									Biodiesel	PC	Euro 3	ARTEMIS	
		18%									Biodiesel	PC	Euro 3	ARTEMIS	
		-4%									Biodiesel	PC	Euro 3	ARTEMIS	
		-10%									Biodiesel	PC	Euro 3	ARTEMIS	
		16%									Biodiesel	PC	Euro 3	ARTEMIS	
[9]										12%	Methylester Soyate	HDV	EuroIII		
[11], [24]			3%								Biodiesel	HD-DDC	1991	FTP	27 different blends of biodiesel
[15]			10%								Biodiesel (cooking oil)	D.E		FTP transient cycle	
[16]	8-13%										Rapeseed biodiesel	PC	Euro 1	on-road cycles	Ford Mondeo
[17]			8%							15%	Soy-based bd	HD engine		on-road cycles	
[18]			5%								Soy-based bd	HD-DDC	1991	on-road cycles	Series 60
			14%								Soy-based bd	HD-DDC	1992	on-road cycles	Series 60
			15%								Soy-based bd	HD-DDC	1993	on-road cycles	Series 60
[19], [20]										12%	Soy-based bd	HD-Engine	1997	FTP transient cycle	Cummins N14
										12%	Soy-based bd	DDC	1997	FTP transient cycle	Series 50
										0%	Soy-based bd	HD-Engine	1995	FTP transient cycle	Cummins B5.9
[21]			29%								Biodiesel	pickup truck			6 different blends of biodiesel
[25], [33]			3%								Biodiesel	HD-DDC	2003	FTP transient cycle	Series 60
[26]						7%					Biodiesel	HD-DDC		WVU truck dr. cycle	Series 60

Table A. 1: Effect of biodiesel blends on NOx emissions, compared to neat diesel

Study	B5	B10	B20	B25	B30	B35	B50	B70	B75	B100	Fuel	Vehicle	Technology	Driving Cycle	Remarks concerning Load, cetane number, EGR etc
[27]			-4%								Soy-biodiesel	Transit bus		CSHVC	
			0%								Soy-biodiesel	HDV	2005	CILCC	
			2%								Soy-biodiesel	HDV	2005	Freeway	
[28]			2%							-25%	biodiesel-pinus	HD engine		ESC test	MAN D
[29]			-1%								waste frying oil methylester	LD engine			Land Rover
[30]			1.3%				5%			32%	rapeseed biodiesel	1- cyl D.E		FTP	20% EGR
			4.1%				25%			35%	rapeseed biodiesel	1-cyl D.E		FTP	10% EGR
			8.6%				31%			38%	rapeseed biodiesel	1cylinder D.E		FTP	NO EGR
[31]			4%							13%	soybean biodiesel	DI-D.E	1997		Cummins N-14
[32]			-3.7%							11%	biodiesel	marine D.E		C-3	50% load
			0%							24%	biodiesel	marine D.E		C-3	100% load
[34]				1%						4%	Diesel +RME	PC	Euro 3	NEDC	Common Rail
				-3%						16%	Diesel +50% Soybean+50% Sunflower				
				-2%							Diesel + Palm Oil				
				6%						16%	Diesel +RME				Unit Injector
				2%						19%	Diesel +50% Soybean+50% Sunflower				
				0%							Diesel + Palm Oil				
[7]		0.40%									biodiesel	PC	Euro 3	NEDC	

Table A. 2: Effect of biodiesel blends on PM emissions, compared to neat diesel

Source	B5	B10	B20	B25	B30	B35	B50	B70	B75	B100	Fuel	Vehicle	Technology	Driving Cycle	Remarks
[1]		-7%		-15%		-26%	-28%		-37%	-47%	Biodiesel	HDV			
[2]	-5%		-10%							-48%	Biodiesel	HDV			
[4]			-10%							-47%	Biodiesel	HDV			
[5], [22]			-15%				-28%	-33%		-38%	Soy-based biodiesel	LDV	1993	FTP cycle	
[5]			-13%				-63%	-68%		-70%	Biodiesel	PC		US06 cycle N1 type (B20 for PC)	
[6]		-34%	-24%		-38%		-27%			-34%	Biodiesel	PC			
[8]		1%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-25%									Biodiesel	PC	Euro 3	NEDC	Common rail
		0%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-5%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-14%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-24%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-23%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-17%									Biodiesel	PC	Euro 3	NEDC	Common rail
		-9%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-12%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-8%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-2%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-18%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-5%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-11%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
		-22%									Biodiesel	PC	Euro 3	ARTEMIS	Common rail
[9]										-77%	Methylester Soyate	HDV	EuroIII		EGR
										-73%	Methylester Oleate	HDV	EuroIII		EGR
[10]			-15%								Yellow-greased biodiesel	F350 7.3L	EuroII	FTP	
			-9%								Soy-based biodiesel	HDV	Euro III	FTP	
			-1%								Soy-based biodiesel	F700	1993	AVL8-mode	

Table A. 2: Effect of biodiesel blends on PM emissions, compared to neat diesel

Source	B5	B10	B20	B25	B30	B35	B50	B70	B75	B100	Fuel	Vehicle	Technology	Driving Cycle	Remarks
[11], [24]			-3%								biodiesel	HD-DDC	1991		average from 27 biodiesel blends
[12]					-21%			-32%			waste cooking oil biodiesel	4-stroke engine		typical road conditions	
[13]		-20%									rapeseed oil biodiesel	tractor			type 306 LSA
[14]										-42%	soyate methylester	D.E			Yanmar
[15]			-10%								Methylester of waste cooking oil	Modern D.E		FTP transient cycle	
[18]			-10%								Soy-based biodiesel	HD-DDC	1991		series 60 engine
			-15%								Soy-based biodiesel	HD-DDC	1991		series 60 engine
			-36%								Soy-based biodiesel	HD-DDC	1991		series 60 engine
[19], [20]										-35%	Soy-based biodiesel	HD-Engine	1997	FTP transient cycle	Cummins N14
										-35%	Soy-based biodiesel	DDC	1997	FTP transient cycle	Series 50
										-35%	Soy-based biodiesel	DDC	1995	FTP transient cycle	Cummins B5.9
[25]			-25%								Biodiesel	HD-DDC	2003	FTP transient cycle	series 60 engine
[26]						-25%					Biodiesel	HD-DDC		WVU truck driving cycle	series 60 engine and Cummins 855
[27]			-30%								Soy-biodiesel	HDV	2005	CILCC	
			-30%								Soy-biodiesel	HDV	2005	Freeway-cycle	International class truck
[34]						-27%				-68%	Biodiesel	PC	Euro 3	NEDC	Fiat Croma, common rail
						-6%				-3%		PC	Euro 4	NEDC	VW Passat, unit injector
[7]		-36%													

Table A. 3: Effect of ethanol blends in NOx emissions, in comparison to neat gasoline/diesel

Fuel	Source	E5	E10	E30	E70	E85	Speed	Load	Cetane number	Vehicle	Technology	Driving Cycle	Remarks concerning engine characteristics
Ethanol-petrol blend	Reading et al.		no consistent change							PC	Euro 3	NEDC	compared to petrol
Ethanol-petrol blend	GAVE Project				-70%	-70%				Flex-Fuel PC	Euro 4	NEDC and Artemis	
5% ethanol, 20% biodiesel and 75% diesel	Pang et al.	slightly higher								Gas eng. and D.E			EQ491i gasoline engine, Cummins 4B D.E
ethanol blend	Reuter et al.		4.80%							PC	Pre-ECE		
ethanol-diesel blend	Bratsky et al.		no consistent change							Diesel PC			
Ethanol-diesel blend	Corkwell et al.		1.00%							different vehicles		combination of cycles	all data
Ethanol-diesel blend			-2.00%						equal cetane number data	different vehicles		combination of cycles	all data
Ethanol-diesel blebd			20.00%						no cetane improver	PC	2001	FTP cycle	1.9 l. VW, turbo-charged, direct injection
Ethanol-diesel blebd			25.00%						with cetane improver	PC	2001	FTP cycle	1.9 l. VW, turbo-charged, direct injection
Ethanol-diesel blebd			19.00%						no cetane improver	PC	2001	US 06	1.9 l. VW, turbo-charged, direct injection
Ethanol-diesel blebd			12.00%						with cetane improver	PC	2001	US 06	1.9 l. VW, turbo-charged, direct injection
Bioethanol-diesel blend	He et al.		-2.00%	######						Diesel engine			4-stroke direct injection
Ethanol diesel blends	Cole et al.		-49.00%				3000rpm	15%	with additives, but no discussion about cetane improvers	Diesel engine			1.9 l., VW, turbo-charged, direct injection, 4 cylinder

			-49.00%				1500rpm	all loads					
			51.00%				low speed	low load					
			51.00%				high speed	high load					
Ethanol diesel blends	Fanick et al.		7.00%							HD Diesel engine		FTP transient cycle	12.7 l., Detroit Diesel, DDC 60
Ethanol-diesel blend, cetane number 52	Lofvenberg et al.		-5.00%							HD truck		5 mode test	11 l. direct injection diesel engine
Ethanol diesel blend, cetane number 51.7	Schuetzle et al.		-6.00%						no cetane improver	truck		ECE and EUDC	truck, equipped with indirect injection engine, turbo-charged, no cetane improver
Ethanol diesel blend, cetane number 56.3			-7.00%						with cetane improver	truck		ECE and EUDC	truck, equipped with indirect injection engine, turbo-charged, with cetane improver
Ethanol diesel blend	Merrit et al.		2.00%						with addtive packages	Diesel engines		FTP and ISO 8178 8-mode test	8.1 l.
			5-9% reductions										2 different engines, 6.8 l., 8.1l. and 12.5l.
Ethanol blends	Kass et al.		2.00%				100%	18%	no discussion about the cetane number	Diesel engine		AVL 8 mode test	5.9 l., Cummins, turbo-charged, direct injection, 6 cylinder
			6.00%				95%	40%					
			-4.00%				95%	69%					
			-6.00%				89%	95%					
			0.00%				32%	84%					
			2.00%				21%	63%					
			9.00%				11%	25%					

Table A. 4: Effect of ethanol blends in PM emissions, in comparison to neat gasoline/diesel

Fuel	Source	E5	E10	E30	Speed	Load	Cetane number	Vehicle	Technology	Driving Cycle	Remarks concerning engine characteristics
Ethanol-petrol blend	Reading et al		-46.00%					PC	Euro 3	NEDC	compared to petrol
5% ethanol, 20% biodiesel and 75% diesel	Pang et al.	22-40% reductions						Diesel engine			Cummins 4B D.E
Bioethanol-diesel blend	Corkwell		-13.00%								all data
Bioethanol-diesel blend			-25.00%				equal cetane number data				all data
Ethanol-diesel blend			-16.00%				with cetane improver	PC	2001	FTP cycle	1.9 l. VW, turbo-charged, direct injection
Ethanol-diesel blend			-29.00%				no cetane improver	PC	2001	FTP cycle	1.9 l. VW, turbo-charged, direct injection
Ethanol-diesel blend			-17.00%				no cetane improver	PC	2001	US 06	1.9 l. VW, turbo-charged, direct injection
Ethanol-diesel blend			-20.00%				with cetane improver	PC	2001	US 06	1.9 l. VW, turbo-charged, direct injection
Ethanol- diesel blend, cetane number 52	Lofvenberg et al.		-31.00%					HD truck truck		5 mode test	11 l. direct injection diesel engine
Ethanol diesel blend	Schuetzle et al.		34.00%				no cetane improver, cetane number 51.7			ECE and EUDC	2.5 l., Ford, indirect injection engine, turbo-charged

Ethanol diesel blend			18.00%				with cetane improver, cetane number 56.3	truck		ECE and EUDC	2.5 l., Ford, indirect injection engine, turbo-charged
Ethanol diesel blend	Merrit et al.		13-30% reductions				with additive packages	Diesel engines		FTP and ISO 8178 8-mode test	3 different engines, 6.8l., 8.1l. and 12.5l.
Ethanol -diesel blend	Fanick et al.		-28.00%					HD Diesel engine			12.7 l., Detroit Diesel, DDC 60
Ethanol-diesel blends	Cole et al.		-67.00%		1320 rpm	max	with additives, but no discussion about cetane improvers	Diesel engine			1.9 l., VW, turbo-charged, direct injection, 4 cylinder
			-37.00%		2000 rpm	max					
			-16.00%		2000 rpm	165.9 Nm					
			-1.00%		1500 rpm	105.5 Nm					
			50.00%		2500 rpm	60.4 Nm					
			65.00%		3000 rpm	60.4 Nm					
Ethanol blends	Kass et al.		-19.00%		100%	18%	no discussion about the cetane number	Diesel engine		AVL 8 mode test	5.9 l., Cummins, turbo-charged, direct injection, 6 cylinder
			-14.00%		95%	40%					
			-13.00%		95%	69%					
			-33.00%		89%	95%					
			-33.00%		32%	84%					
			-44.00%		21%	63%					
			6.00%		11%	25%					