



Effect of Fuel Ethanol Content on Exhaust Emissions of a Flexible Fuel Vehicle

G. Martini, C. Astorga, T. Adam, A. Farfaletti, U. Manfredi, L. Montero, A. Krasenbrink, B. Larsen and G. De Santi



EUR 24011 EN - 2009

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Joint Research Centre
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JRC 54345

EUR 24011 EN
ISBN 978-92-79-13627-6
ISSN 1018-5593
DOI 10.2788/39589

Luxembourg: Office for Official Publications of the European Communities

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Printed in Italy

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Acknowledgements: R. Colombo, M. Duane, G. Lanappe, P. Le Lijour, M. Sculati.

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1 Summary and conclusions

Bioethanol is the most widely used biofuel in the world. This fuel is particularly popular in Brazil, in USA and in Sweden. The use of ethanol as transport fuel is considered also the most important option to achieve the ambitious target of reaching the 10% market share of fuels from renewable sources by 2020. In fact, compared to biodiesel, ethanol has a higher production potential due to a larger range of possible biomass sources from which this product can be obtained. Unless second generation biofuels are developed in the next future, it seems difficult to achieve the above mentioned target without large recourse to ethanol.

In general ethanol can be a very good fuel for thermal engines; in particular it is a very good component for fuels for positive ignition engines as ethanol it is completely mixable with gasoline and has a very high octane number. However ethanol has also some disadvantages which limit its maximum content in ethanol/gasoline blends when these are used in conventional spark ignition engines. The high latent heat of vaporization of ethanol making cold start in cooler climates more difficult, compatibility with some elastomers, driveability, are some of the main problems related to the use of ethanol as fuel component.

In order to overcome the problems associated with the use of blends containing high levels of ethanol, the car manufacturers have developed flexible fuel vehicles able to run with ethanol levels ranging from 0% to 85%. These vehicles are currently very popular in Brazil and in Sweden.

In other countries the future popularity of these vehicles will mainly depend on the strategy adopted to promote the market share of biofuels. As far as ethanol is concerned, there are in fact mainly two possible approaches to achieve the same global target in terms of bioethanol market share. One option is to introduce a minimum mandatory content of ethanol in standard gasoline (up to a maximum of 10% to avoid problems for the proper functioning of engines). The other option is to promote the use of high ethanol content blends like E85 (85% ethanol, 15% gasoline) and promoting, at the same time, the purchase of flexible fuel vehicles.

An experimental activity has been planned and carried out at the JRC to investigate the emissions of a flexible fuel vehicle using different ethanol/gasoline blends. The results of this experimental programme are briefly summarized below. The details of the work and the complete results are described in the first part of this document.

Three different fuels have been tested during this program: a standard commercial summer gasoline marketed in Italy used as base fuel and two gasoline/ethanol blends, which have been obtained by splash blending ethanol in the standard gasoline. The two gasoline/ethanol blends contained respectively 10% ethanol (E10) and 85% ethanol (E85).

The test vehicle was one of the most popular models of passenger car belonging to the flexible fuel vehicle category which are currently marketed in Europe.

Emission tests were carried out both following the European certification procedure (NEDC cycle) and using a US driving cycle (US 06). Regulated and unregulated emissions were measured.

In general the repeatability of emission measurements was not very good; only with E85 the measured emission levels were very repeatable. The poor repeatability might be linked to the very sophisticated engine management system which modifies the engine settings depending on the ethanol content of the fuel. Moreover the pre-conditioning procedure adopted might have been not sufficient to let the engine

fully adapt to the fuel after each fuel change. Nevertheless sound conclusions can be drawn for the NEDC cycle while for the US 06 this is more difficult due to the limited number of tests performed.

The results have shown that over the European NEDC cycle the vehicle complies with the Euro 4 emission standards with all the fuel with the only exception of CO with fuel E10. In some cases the CO value measured with fuel E10 resulted to be slightly higher than the limit (1 g/km).

CO and HC emissions measured over the NEDC cycle with fuel E10 resulted to be higher than with the other two fuels. On the contrary, E85 was the least emitting fuel as far as these emissions are concerned.

The influence of fuel composition was instead almost negligible for NO_x emissions. A statically significant increase of NO_x emissions was noticed only in the case of E85 and only over the extra-urban part of the NEDC cycle.

CO₂ emissions were reduced by about 4-6% with fuel E85 both over the NEDC and over the US06 cycle.

Similar trends have been found in a recent, major Canadian study, with the only exception that CO emissions were slightly reduced with E10 – a finding that may be explained by the different test cycles (Graham et al., 2008)

While particulate emissions measured over the NEDC cycle were very low, the PM levels turned out to be quite high over the US 06 cycle. In this case the emissions were comparable to those of a Euro 3 diesel car. This might be due to the very aggressive driving pattern of the US 06 cycle which contains very hard accelerations. In these conditions the engine is likely to work in open loop and with a very rich mixture.

The most significant effect of ethanol in the fuel was observed for emissions of carbonylic compounds. This effect increased with increasing ethanol concentration. In particular for acetaldehyde E85 resulted in a more than twenty fold increase in emissions. This represents the main concern associated with the use of flexible fuel vehicles.

Comparably with HC emissions, from the speciation of VOCs emissions the fuel E10 resulted to be the most emitting fuel while E85 the least emitting one. E85 resulted in a reduction of 57% of the sum of the speciated VOCs compared to standard gasoline, but with an enrichment of C₂ compounds. Emissions of toxic compounds such as benzene and 1,3-butadiene also decreased when E85 was used instead of standard gasoline. Contributions from ethene and propene prevailed regarding the potential of ozone formation.

Keeping in mind that this data comes from one single vehicle, and a limited number of tests these results suggest that with the European test cycle a flexible fuel vehicle has regulated exhaust emissions in line with conventional gasoline engine whatever is the fuel used. Compared to other similar works (“Emissions from Flexible Fuel Vehicles with different Ethanol blends”, AVL MTC AB 2005/10), the flexible vehicle tested in this work showed better emission performance with the E85 which resulted the least emitting fuel as far as HC and CO are concerned.

The decision to promote low ethanol blends and/or high ethanol blends and consequently flexible fuel vehicles is not just a political choice but there are other aspects to be taken into consideration and advantages and disadvantages for both these two approaches. These issues are discussed in the second part of the document.

Low ethanol blends

Advantages

- The blends can be used in standard conventional gasoline. The ethanol content is limited to a maximum of 15-20%
- No need of separate infrastructures.
- Limited effects on exhaust emissions with the exception of aldehydes. On the latest passenger car generation the effects are expected to be lower due to the high efficiency of the catalyst.

Disadvantages

- The increase of fuel volatility when ethanol is splash blended into gasoline. The major concerns related to the use of splash blended gasoline/ethanol blends is the possible increase of evaporative emissions due to a combination of factors:
 - Increased evaporative emissions due to the higher vapour pressure, both from the vehicle's fuel system and during the refilling operation.
 - Increased fuel permeation through plastic and rubber components of fuel system
 - Commingling effect
- Increase of fuel consumption on a volume base

In order to reduce the impact of ethanol on evaporative emission, future European gasoline vehicles will have to be adapted for these fuels as already happened in the USA where gasoline vehicles are equipped with larger carbon canisters and with tank made of low permeation materials. This issue has been already taken into consideration in the future Euro 5 emission standards since from 2009 the reference fuel for vehicle certification will have to contain 5% of ethanol.

High ethanol blends

Advantages

- Vapour pressure is very low, therefore there is no effect on evaporative emissions
- Vehicles can be optimized to take advantage from the higher octane number

Disadvantages

- Need of separate infrastructures for E85 distribution.
- Need of dedicated vehicles.
- Significant increase of exhaust emissions for most compounds

2 Introduction

According to the literature, the success of bioethanol as alternative fuel is linked to some clear advantages if compared with fossil fuels. But there are also disadvantages which have been described in latest studies.

Advantages:

- Very high octane number
- As a renewable fuel produces lower CO₂ emissions compare to conventional fuels
- It reduces some pollutant emissions
- Its ozone forming potential is lower than that of gasoline and diesel
- It contains no sulphur and is biodegradable

Disadvantages:

- It increases evaporative emissions (when blended with gasoline at low percentages)
- Because of the lower vapour pressure and high latent heat of vaporization of neat ethanol, it makes cold start in cooler climates more difficult
- It increase acetaldehyde emissions (even if it reduces formaldehyde emissions)
- E85 vehicles give higher unregulated emissions (ethane and acetaldehyde) than gasoline fuelled vehicles

Due to its characteristics, neat ethanol cannot be used as transport fuel mainly because its high heat of vaporization and low volatility make cold start very difficult especially in cold climates. The most common way to overcome this problem is to blend ethanol with a small fraction of a much more volatile fuel such as gasoline; the most popular blend is E85 which consists of 85% ethanol and 15% gasoline by volume.

Although E85 has been extensively used worldwide, engine manufacturers guarantee problem-free operation without any modification only to catalyst equipped cars fuelled with gasoline containing no more than 5% ethanol. However modern catalyst-equipped cars are probably able to run without any problem with up to 20% ethanol which seems to be the upper limit for cold climates.

Mixture preparation is also important to achieve low exhaust emissions with engines fuelled with ethanol/gasoline blends, especially at cold start. The use of flexible-fuelled vehicles (FFV) is the preferred approach in USA; these vehicles have just one tank and the engine can adapt automatically the ignition timing and mixture strength on the basis of a signal from a sensor measuring the ethanol/gasoline ratio.

There is currently an on-going debate about the best approach to increase the penetration of ethanol in the transport sector in Europe. One approach is to use blends with a low content of ethanol (max 10%). In this case the future vehicles will need to be modified in order to reduce the impact of such blends on evaporative emissions. In fact, ethanol added to gasoline increases the vapour pressure of the mixture as well as the permeation through the plastic materials used to build tanks and fuels systems. Another possible approach is to introduce the E85 fuel instead of low percentage blends and to promote the use and the diffusion of dedicated vehicles (flexible fuel vehicles).

3 Experimental work

3.1 Test vehicle

The test vehicle was a Ford Focus flexible fuel car which is able to run on gasoline/ethanol blends with an ethanol content ranging from 0 to 85% v/v. The vehicle was certified to comply with the Euro 4 emission limits. The main data of the vehicle are listed here below (Table 1):

Table 1

Vehicle Type	Passenger car
	Ford Focus 1.8 Duratec Flexi-fuel
Emission level	EURO 4
Category	M1
Displacement (cm ³)	1798
Max. Power (kW @ rpm)	92 @ 6000
Inertia Class (kg)	1265
Cylinder	4
Max. Torque (Nm @ rpm)	165 @ 4000
Aspiration	Aspirated
Combustion Type	Homogeneous Stoichiometric
Injection System	MPI
After-treatment device	Three Way Catalyst
Year	2007
Odometer reading	1325

3.2 Test fuels

The main objective of this study was to compare the emissions of a flexible fuel vehicle when running on three different fuels:

1. Standard EN 228 gasoline (hereinafter **Gasoline**)
2. E10, consisting of standard gasoline fuel containing 10% of ethanol (hereinafter **E10**)
3. A blend of standard EN 228 gasoline and 85% of ethanol in mass (hereinafter **E85**)

The three test fuels were produced by using the same base fuel which was a standard commercial unleaded gasoline that can be found on the market.

The main properties of the three test fuels are described in Table 2 – Test fuels.

Table 2 – Test fuels

Property	Unit	Gasoline	E10	E85
Density @ 15 C	kg/l	0.7423	0.7413	0.7857
Sulphur Content	mg/kg	22	14	3
Octane Number RON		95.1	98.6	107.8
Octane Number MON		85.0	86.9	89.00
DVPE	kPa	58.1	79.3	35.16
Distillation				
Evaporated @ 70 ° C	% vol	21.9	46.6	4.9
Evaporated @ 100 ° C	% vol	54.8	59.9	-
Evaporated @ 150 ° C	% vol	90	90.2	-
F.B.P.	° C	192	188	79.5
Aromatics				
Aromatics	% v/v	30.8	32.3	1.5
Olefins	% v/v	10.5	-	-
Benzene	% v/v	0.82	0.54	0.1
MTBE	% v/v	4.3	-	-
Oxygen content	% m/m	0.8	3.2	29.1
Ethanol content	% v/v	0	9.5	85.7

3.3 Emission tests

The emission tests were carried out on a chassis dynamometer using the New European Driving Cycle (NEDC, see Figure 1). Regulated emissions (HC, CO, NOx) were measured following the legislative measuring procedures. At least three back-to-back tests were carried out with each test fuel on each vehicle.

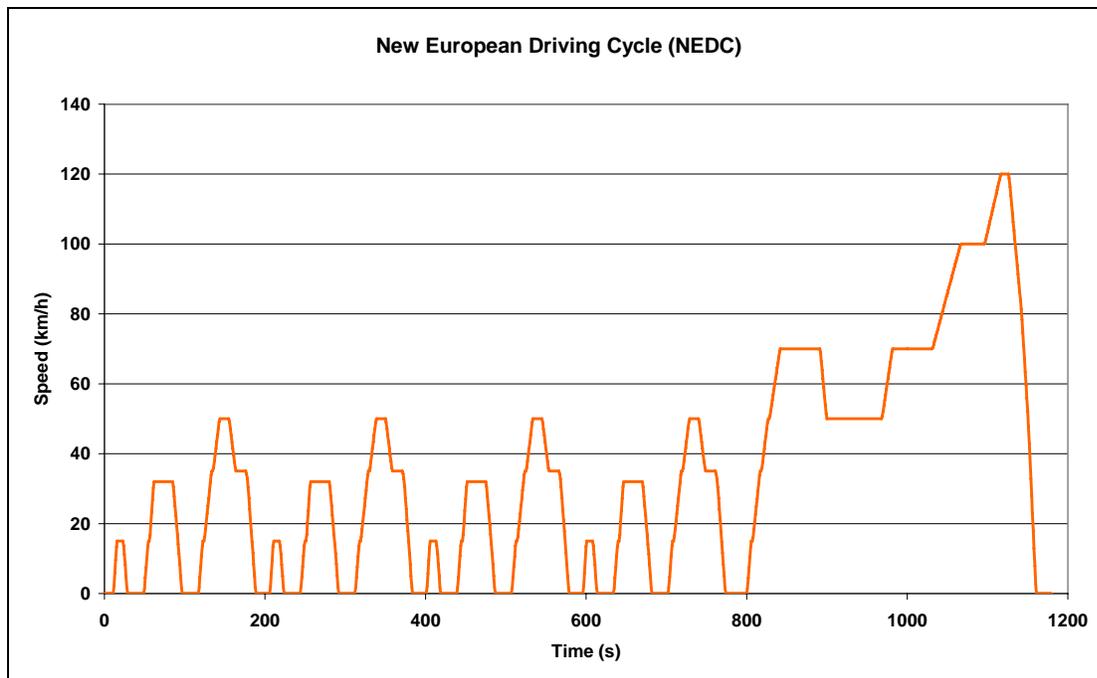


Figure 1 – NEDC cycle

In addition, some unregulated emissions were measured as well:

- Particulate matter (total mass)
- VOC speciation
- Aldehydes

After fuel change, the vehicle was conditioned in order to let the engine adapt to the new fuel. In fact the electronic management system is able to recognize the amount of oxygen contained in the fuel and to modify the engine settings in order to optimise the combustion process. For this purpose the vehicle was run at a constant speed of 70 km/h for another half hour after to the standard conditioning procedure (1 NEDC + 1 UDC).

In addition to European standard driving cycle (NEDC), the vehicle was tested over the US 06 driving cycle. The US 06 is a supplemental cycle complementing the US standard driving cycle (FTP 75) and represents aggressive highway driving conditions (high speed high load cycle, see Figure 2). This is a hot start cycle and it must be preceded by an appropriate conditioning of the vehicle; in this case the conditioning phase consisted of a cold start US 06 cycle, run just before starting the hot start cycle.

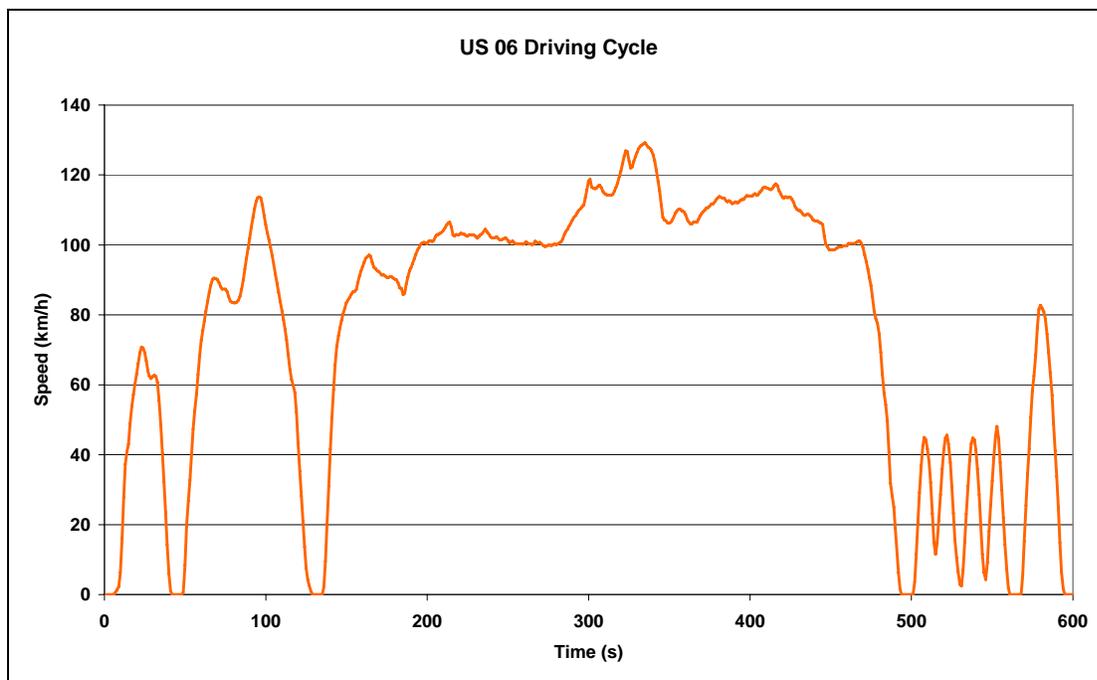


Figure 2 – US 06 Cycle

3.4 Instrumentation details

Regulated pollutant emissions were measured using a chassis dynamometer and a conventional CVS system with a critical flow Venturi.

To follow the legislative cycle, the driver was assisted by a driver aid system. Emission measurements were performed using the following analysers:

- **CO**: IR analyser.
- **NO_x**: chemiluminescence analyser.
- **HC**: FID analyser.

- **Particulate mass:** particulate samples were collected according to the legislative procedure for diesel vehicles using Pallflex T60A20 filters and the mass was determined by weighing.

A schematic layout of the emission test facility is illustrated in Figure 3.

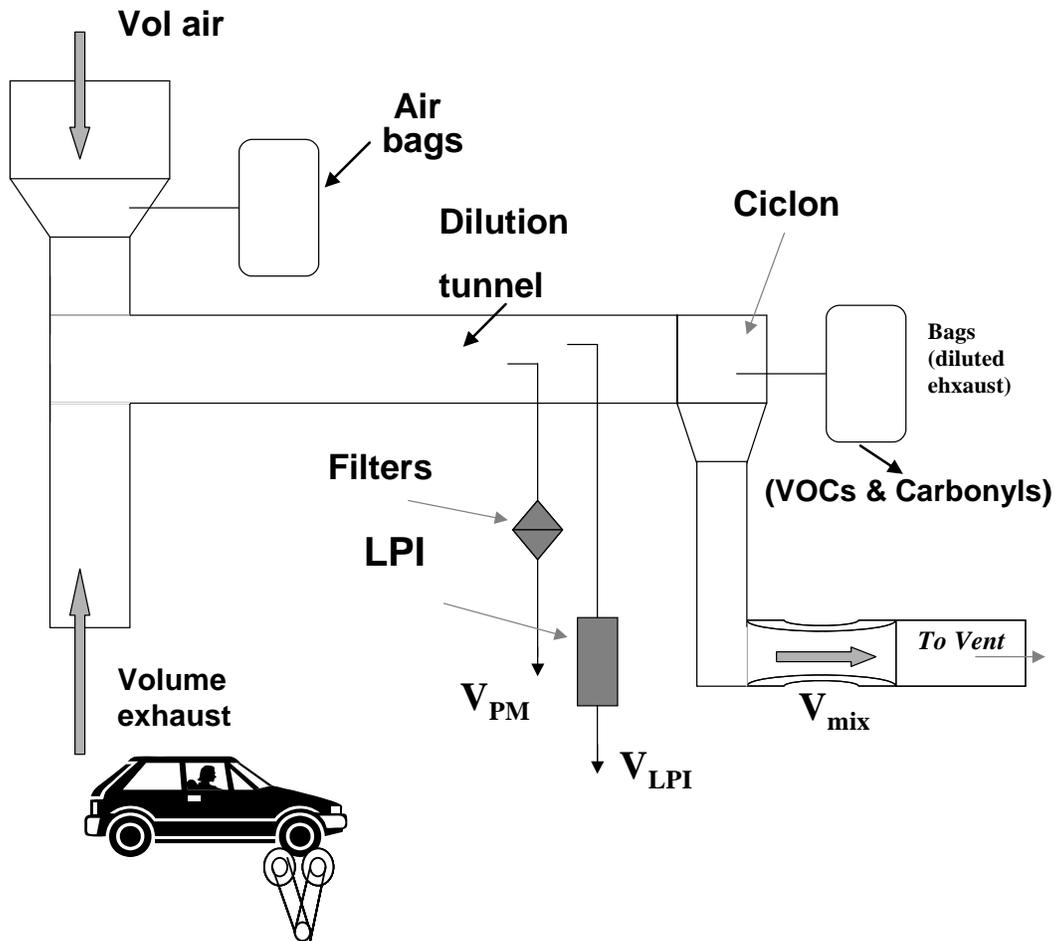


Figure 3.- Emission test facility Layout

4 Results

4.1 Regulated emissions

In this chapter the results regarding regulated emissions of the vehicle are presented and discussed. As already described in chapter 3.3, two different driving cycles were used: the European cycle for vehicle certification (NEDC) and the US06 supplemental cycle. The emission measurement results are given for both the cycles. For the statistical analysis all effects were tested by **Analysis Of Variance** (ANOVA) and the significance levels (p-value) are reported in the following chapters.

4.1.1 NEDC - Regulated emissions

In each plot three emission values are given: the first value/bar is referred to the whole cycle (Combined), while the second and the third bars are referred respectively to the urban part (UDC) and to the extra-urban part (EUDC) of the cycle. The error bars correspond to a 95% confidence interval.

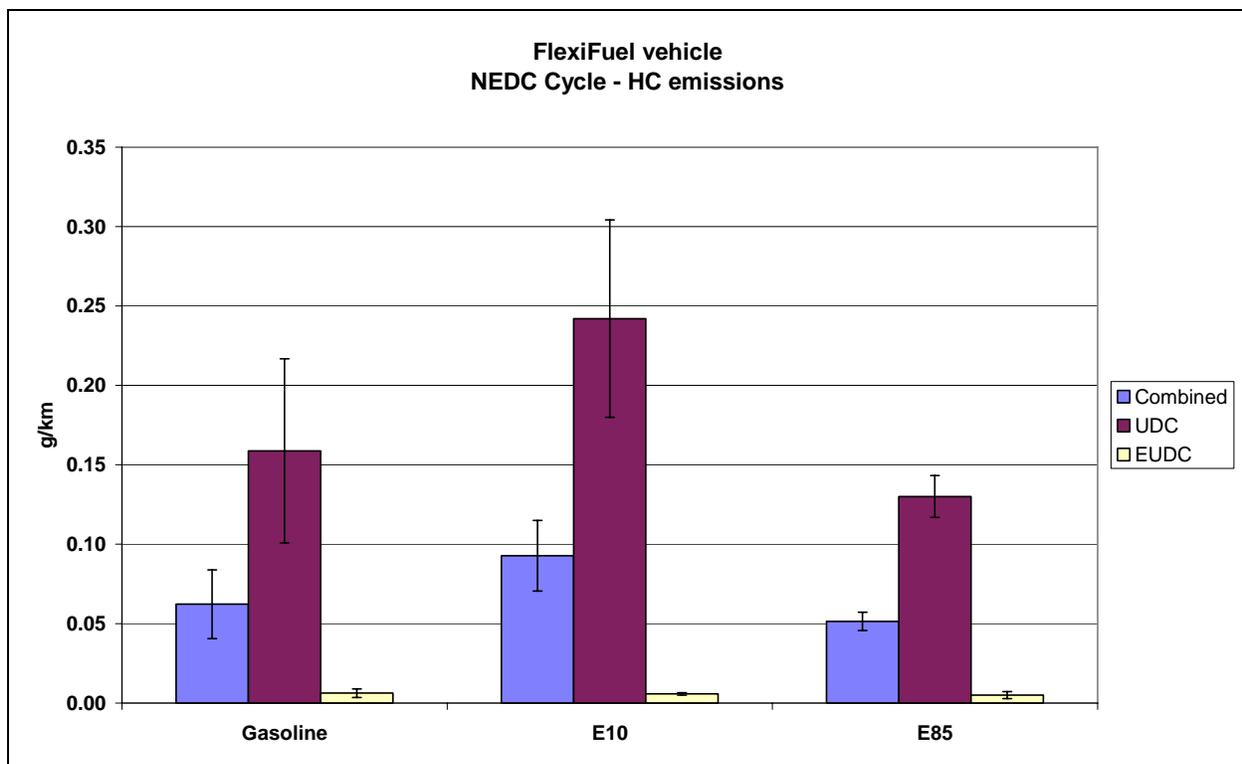


Figure 4 – HC emissions over the NEDC cycle

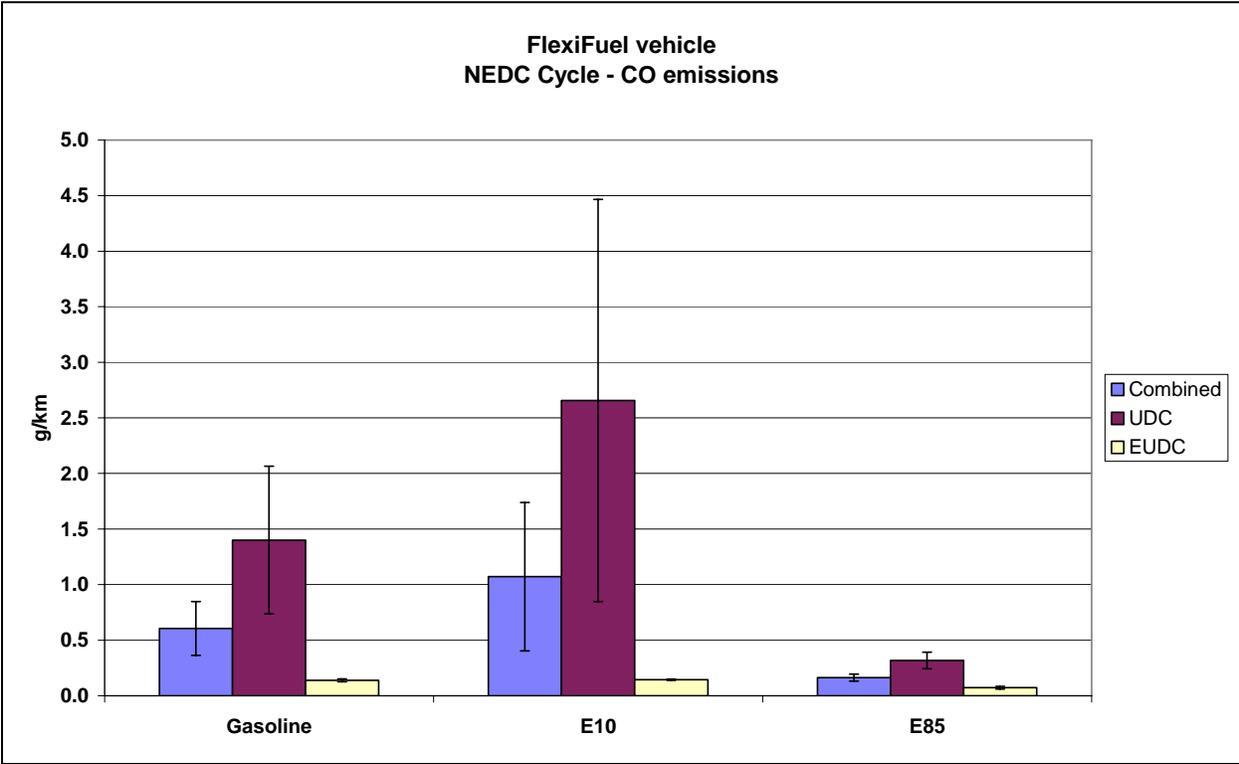


Figure 5 – CO emissions over the NEDC cycle

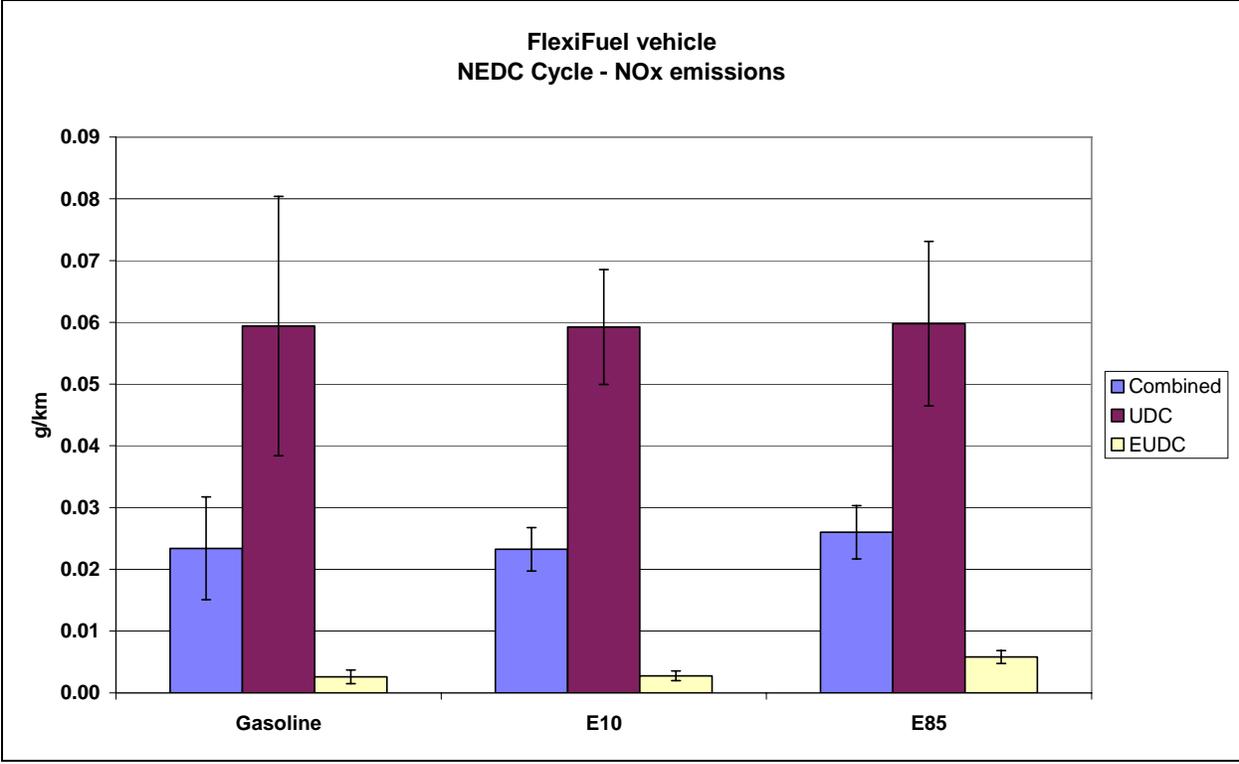


Figure 6 – NOx emissions over the NEDC cycle

Hydrocarbon emissions

Unburned hydrocarbon emissions are shown in Figure 4. For all the test fuels the combined emission levels are well below the Euro 4 emission standard (0.1 g/km). However the lowest emission value was obtained with the E85 fuel while E10 produced the highest hydrocarbon emissions ($p=0.002$).

It has to be said that compared to the other regulated compounds the repeatability of the HC emissions, as well as of CO emissions, turned out to be quite poor. This was especially true for the emissions measured over the urban part of the cycle which, as expected, accounts for almost the totality of the emissions. As known, for gasoline vehicles the biggest part of the emissions is emitted during the first seconds of the cycle when the engine and the catalyst are still cold. Despite this poor repeatability, statistical significance was obtained also for the urban part of the cycle ($p=0.002$).

In particular, a significant difference in the emission levels was noticed between the tests performed in the morning after 12 hours soaking and the tests performed in the afternoon after only 6 hours soaking (the minimum soak period time prescribed by the legislation is 6 hours).

The poor repeatability is probably linked to the sophisticated engine management system that controls the engine settings which are modified according to a number of inputs (i.e. the fuel composition, the lambda sensor signal, etc.).

CO emissions

As already mentioned, also for CO emissions the repeatability resulted to be quite poor, compared to the other regulated compounds. However, as for hydrocarbons the effects of increasing ethanol concentration in the fuel resulted statistically significant ($p<0.001$).

CO emissions present a pattern very similar to the HC emissions (see Figure 5). The lowest emissions were obtained with the E85 fuel while, again, E10 was the highest emitting fuel. E85 reduced by 73% the CO emissions compared to the levels measured with the standard gasoline.

Looking at the results of CO and HC emissions, it seems like if the engine was very well optimized for the extreme fuels (standard gasoline and E85) while this was not the case for E10. However it is very difficult to draw sound conclusions about the reason why E10 was the most emitting fuel without knowing the actual engine management strategy implemented in the ECU.

NOx emissions

Compared to CO and HC, NOx emissions appeared to be less sensitive to fuel quality. No statistically significant difference was observed among the three fuels regarding the emissions measured over the whole cycle and over the UDC ($P>0.6$). The E85 led instead to higher emissions ($p<0.001$) than the other two test fuels over the extra-urban part of the cycle (EUDC). However, this increase is almost negligible in absolute terms as the actual values measured over the EUDC are very low.

The percentage variation of the emissions with fuels E10 and E85 compared to the standard gasoline considered as base line are summarized in Table 3.

Table 3 – Percentage variation of emissions compared to the standard gasoline considered as baseline.

NEDC- Combined	E10	E85
HC	49% *	-17% *
CO	77% *	-73% *
CO2	0%	-4% *
NOx	-1%	11%
PM	-26% *	169% *
Formaldehyde	-5%	244% *
Acetaldehyde	149% *	2217% *
UDC		
HC	52% *	-18% *
CO	90% *	-77% *
CO2	-3% *	-5% *
NOx	0%	1%
EUDC		
HC	-7%	-19%
CO	3%	-48% *
CO2	1%	-4% *
NOx	6%	123% *

* Statistically significant at a level higher than 95%

4.1.2 US 06 - Regulated emissions

As already explained in chapter 3.2, the vehicle was tested over the US 06 driving cycle representing aggressive highway driving conditions. Only a limited number of tests were performed over this cycle and therefore it was not possible to perform any statistical analysis. The bars represent the average of two test fuels in the case of E85 and the standard gasoline and the result of only one test for E10.

Since the vehicle had been certified according to the European legislative cycle, it is not fully correct to compare the absolute values measured over this cycle with the relevant US emission standards. Nevertheless, the results show that the emissions are below or very close to the correspondent limits.

Due to the limited number of tests (only 1 valid test for the fuel E10) and the poor repeatability it is difficult to draw reliable conclusions. Anyway the differences among the fuels are smaller than over the NEDC, probably because the US 06 is a hot cycle and therefore the efficiency of the TWC is very high.

Only in the case of CO the fuel E10 gives much higher emission than the other test fuels ($p=0.005$) confirming that it is the most critical fuel for this car.

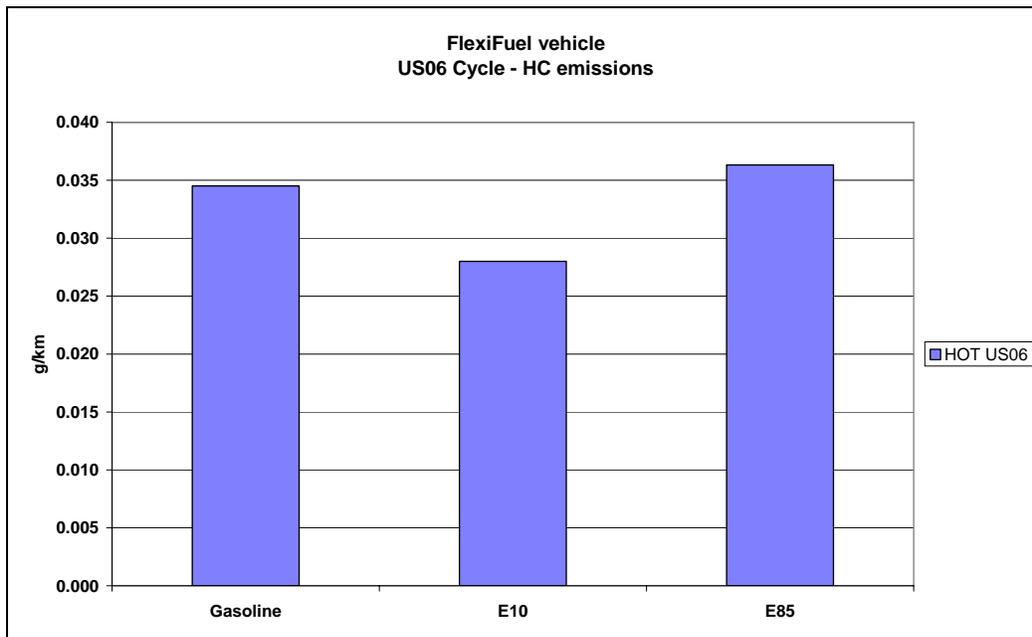


Figure 7 – HC emissions over the US 06 cycle

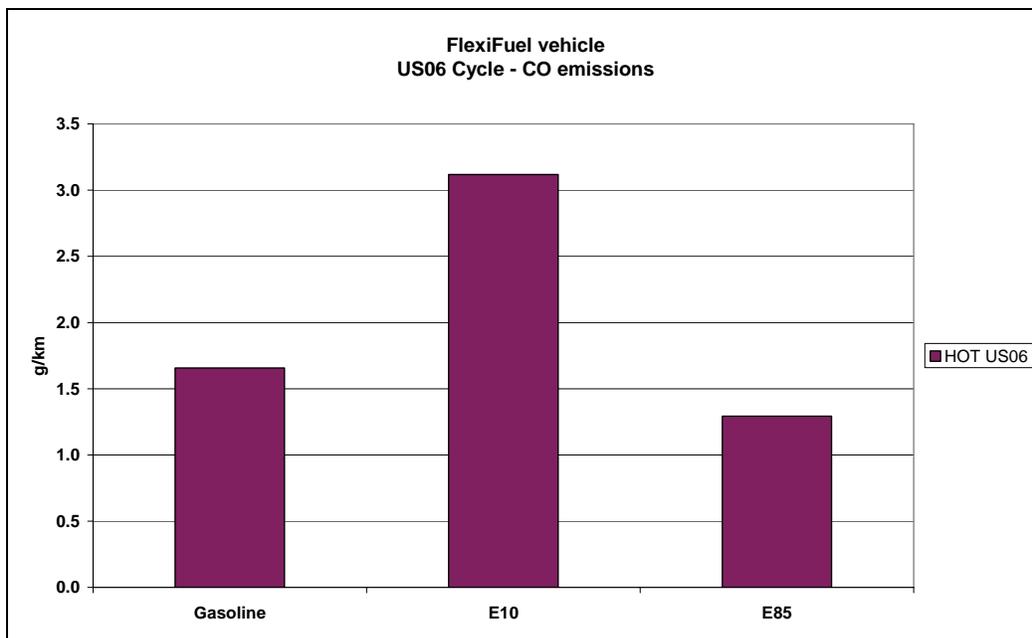


Figure 8 – CO emissions over the US 06 cycle

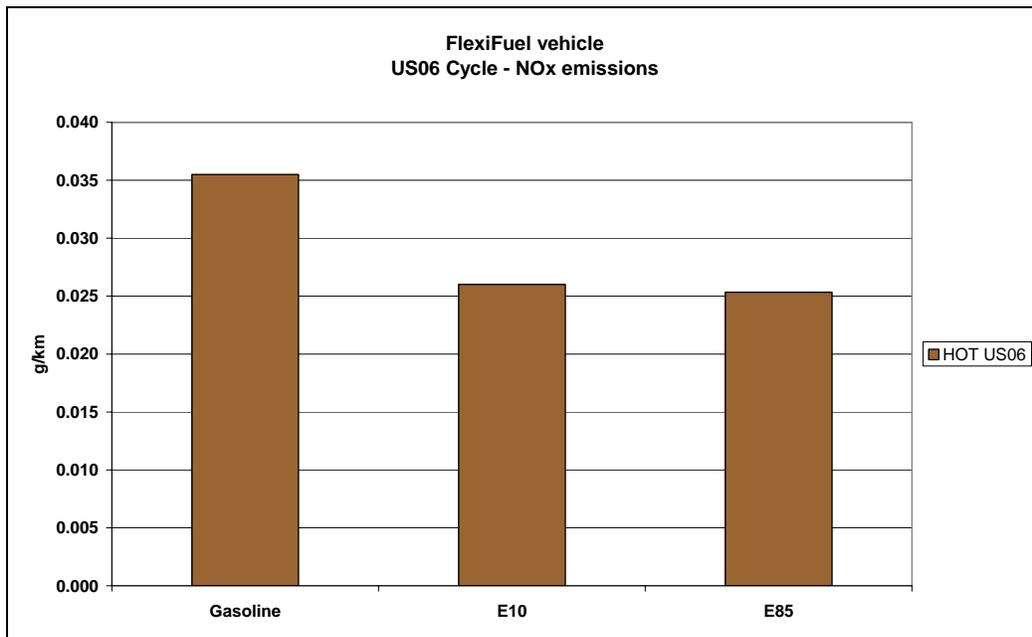


Figure 9 – NOx emissions over the US06 cycle

4.2 Unregulated emissions: particulate matter

Particulates emissions are not regulated for gasoline vehicles. However, in this program it was decided to measure particulate emissions as well to have a complete picture of the influence of the test fuel on emissions.

The total mass of particulates was measured following the methodology prescribed for diesel vehicles and the results are presented in Figure 10 and Figure 11.

As expected, PM emissions resulted to be very low when measured over the NEDC cycle. With E85 a slight increase of PM emissions was noticed ($p < 0.001$). However it should be noted that the standard filters used to measure the particulate mass were still white at the end of the tests; this suggests that the mass collected on the filters was organic material rather than soot.

PM emission levels turned out to be quite high over the US 06 cycle. The measured levels were comparable to those of a Euro 3 diesel car. This might be due to the very aggressive driving pattern of the US 06 cycle which contains very hard accelerations. In these conditions the engine is likely to in open loop and with a very rich mixture.

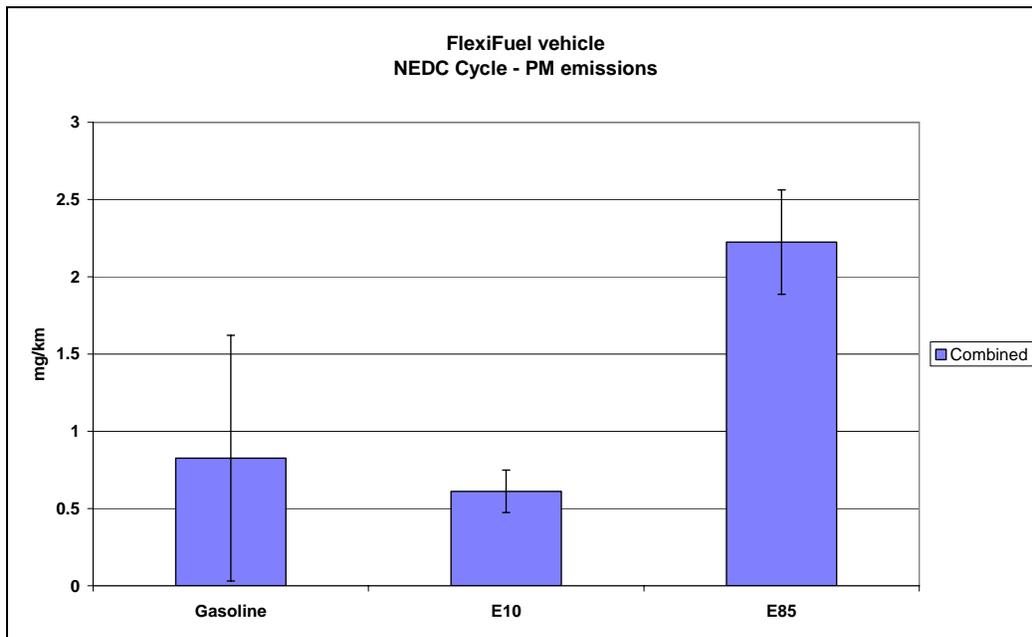


Figure 10 – PM emissions over the NEDC cycle

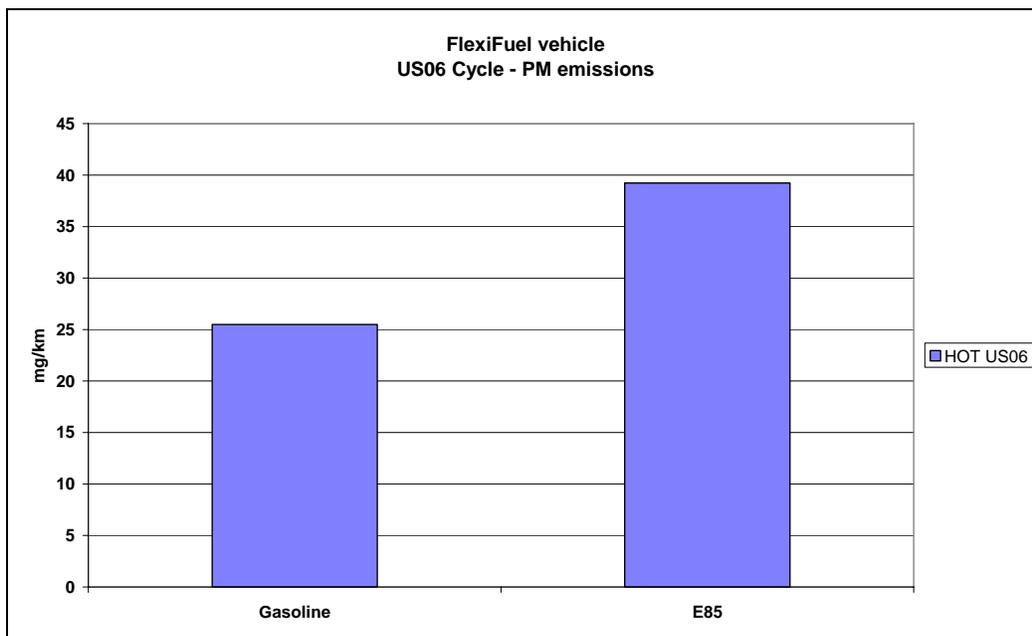


Figure 11 – PM emissions over the US 06 cycle

4.3 Unregulated emissions: CO₂

The CO₂ emissions measured over the two test cycles used in this programme are presented in Figure 12 and in Figure 13. Both the plots show that the fuel E85 reduced the CO₂ emissions by about 4-6% compared to the standard gasoline (NEDC: P<0.001, US06: P=0.005).

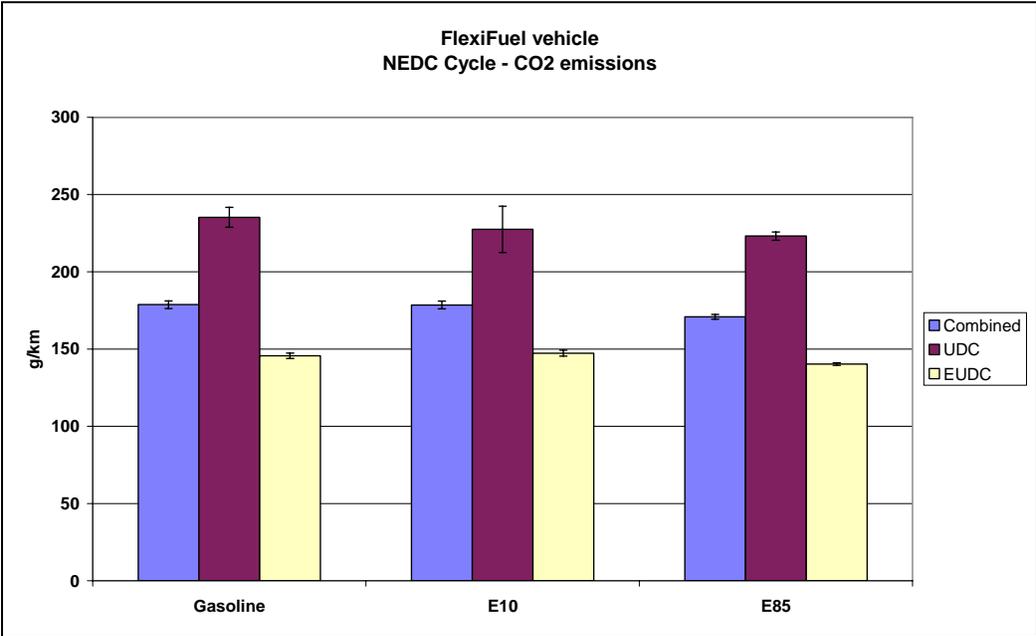


Figure 12 – CO2 emissions over the NEDC cycle

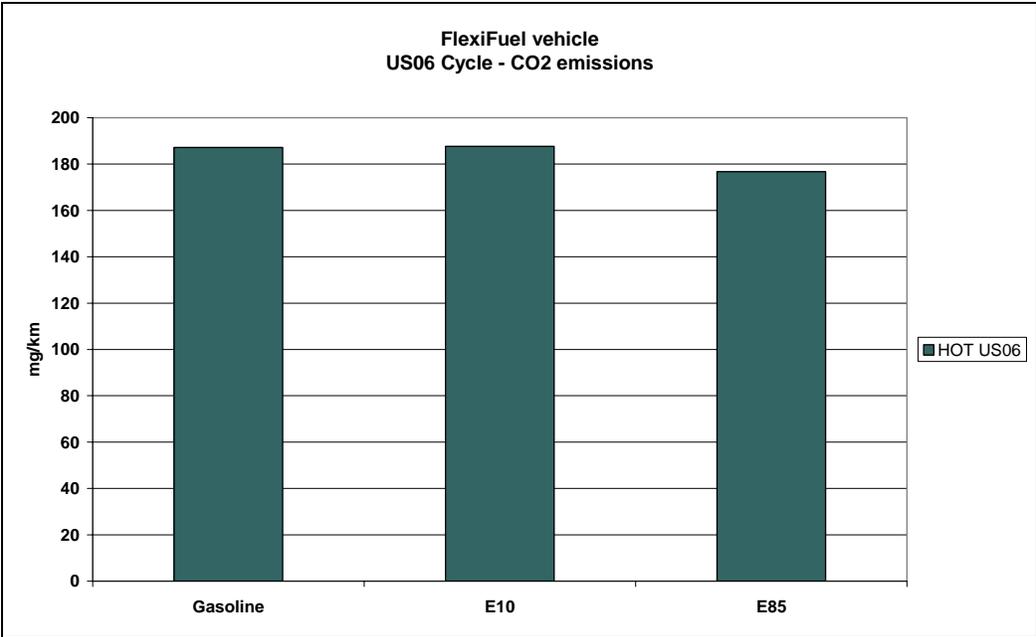


Figure 13 – CO2 emissions over the US 06 cycle

4.4 Unregulated emissions: Volatile Organic Compounds (VOCs)

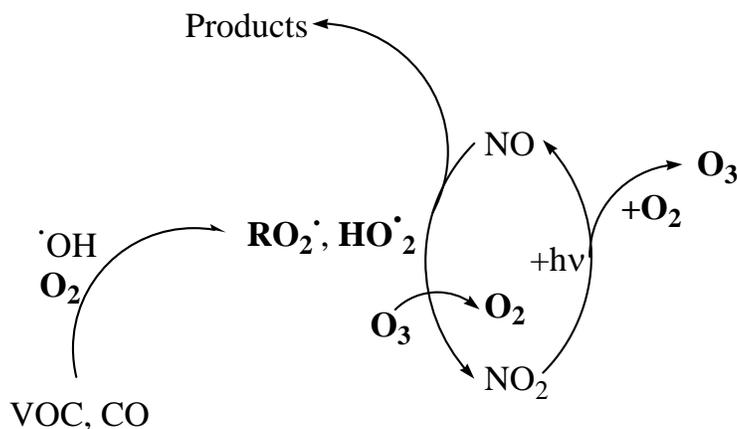
Photochemical smog is one of the most serious air pollution problem in Europe today. Episodes with high concentration of ozone and NO_x may cause damage to human health and vegetation. The abatement of such pollutant is one of the biggest challenges to environmental authorities at national and European level as it was recognized by producing the third Air Quality daughter Directive exclusively devoted to O₃ [2002/3/EC].

Being a secondary air pollutant, the formation of ozone depends on the concentrations of the ozone precursors (volatile organic compounds, VOCs) and nitrous oxides. The photooxidation of hydrocarbons, *i.e.* incomplete combustion from internal combustion engines is a strong cause of carbonyls [8]. Together with the emissions of NO_x from anthropogenic sources -which acts as a kind of “catalyst”- the production of ozone in the atmosphere is a function of the VOCs present at the ground base level.

Mechanisms of reaction for VOCs

The formaldehyde is one of the key species in the chain reactions that causes formation of ozone in the troposphere and one of the major sources of 'OOH radicals. The figure below shows a summarize vision for the main reactions of the cyclic mechanism involved in the oxidation of hydrocarbons.

The most important part of this cyclic mechanism is the formation of 'OOH with its subsequent involvement as an oxidant in O₃ formation and in 'OH production [9].



Cyclic Reaction Mechanism for Ozone formation from VOCs in the presence of NO_x

Secondary Organic Aerosol (SOA) particles are produced in the atmosphere as a result of oxidation of volatile organic compounds by O₃, OH and NO₂. One especially interesting group of organic compounds that has been shown to efficiently form SOA particles are carbonyls and in particular the acid-catalyzed heterogeneous reactions of organic compounds (*e.g.*, carbonyls, alcohols, and alkenes). Secondary organic aerosols have been linked to health effects, blamed for reduced visibility in scenic areas, and are believed to generate a net cooling effect in the troposphere. The U.S. EPA regulates aerosols under the national ambient air quality standards and is under pressure to toughen those standards to include finer particles.

Leaded by the interest on the Smog development phenomena and the Secondary Organic Aerosol (SOA) formation, we have been measuring different VOC same incorporated in the Ozone directive as well as some C1-C3 carbonyl compounds

4.4.1 Unregulated emissions: VOCs speciation

Volatile Organic Compounds (VOCs) are not regulated for gasoline vehicles. However, in the performed tests, it was decided to measure the C₂-C₉ hydrocarbons, as they present an issue for air quality as ozone precursors. The Ozone Directive 2002/3/EC, in force since 2003, obliges member states to monitor not only ozone itself, but also its photochemically reactive precursors in the air, including the NMHC (non-methane hydrocarbons) or VOCs (Table 4).

Table 4 – The 30 hydrocarbon species (VOCs) listed as being ozone precursors requiring monitoring (2002/3/EC).

Ethane	1,3-butadiene	i-octane (2,2,4-trimethyl pentane)
ethene (ethylene)	n-pentane	benzene
ethyne (acetylene)	i-pentane (2-methylbutane)	toluene
Propane	1-pentene	ethylbenzene
Propene	<i>trans</i> -2-pentene	<i>m+p</i> -xylene
n-butane	isoprene (2-methyl-1,3-butadiene)	<i>o</i> -xylene
i-butane (2-methyl propane)	n-hexane	1,2,4-trimethylbenzene
1-butene	i-hexane (2-methylpentane)	1,2,3-trimethylbenzene
<i>trans</i> -2-butene	n-heptane	1,3,5-trimethylbenzene
<i>cis</i> -2-butene	n-octane	

Once emitted in the air, each VOC reacts at a different rate and with different reactions mechanisms, and therefore, it can influence differently the ozone formation at ground level. In urban areas, the major contributor to ozone precursors is road traffic, which is why determining the contribution of hydrocarbons from vehicle emissions is of high importance.

For the present study, the light-duty vehicle was driven on a chassis dynamometer (Zoellner GmbH) with a constant volume sampler (flow 7.5 m³/min). Exhaust samples of the vehicle were collected in Tedlar™ bags during the driving cycle test and analysed straight ahead after the sample collection. A sample volume of 80 ml out of the 10 liters collected in the bags was needed for the analysis, allowing replicate analysis when necessary. A thermal desorption unit (UNITY™) and an auxiliary sampling device (Air Server™, Markes International, Pontyclun, UK) were used to collect the samples from the bags. Chromatographic separation and detection were performed with a GC 6890 (Agilent, Wilmington, USA) equipped with a dual flame ionization detector (FID). More details can be found elsewhere [1].

4.4.1.1 Results obtained with the NEDC cycle

The results discussed in this section are based on a complete dataset for VOCs based on replicate experiments. The sum of the speciated hydrocarbons emitted by each fuel was calculated as propane equivalents and plotted together with the THC measured online (Fig. 1). As expected, the VOCs emissions resulted to be lower than the THC. First of all because the 30 hydrocarbon species determined by the VOC method represent only a subset of all VOCs known to be emitted by vehicle exhaust (>300 species) and secondly, because the THC method is based on the assumption that propane can be used as a representative calibrant for all VOCs. The main reason for the discrepancy between the VOC data and the THC is likely to be the presence of non-combusted residues of ethanol in the exhaust together with carbonyls. Indeed, this discrepancy gradually increases with an increasing ethanol concentration in the test fuel.

Before discussing the effect of the increasing fuel content of ethanol on the emissions of VOC or THC, it must be kept in mind that, in general, these emissions were low for all tests and that the measurement precision of THC and in particular VOCs is not as good as the precision of the regulated gases (NO_x, CO). Thus, minor effects of adding ethanol to the fuel may pass unobserved for THC and VOC.

The statistical analysis of the data (ANOVA) demonstrated significant differences of the emissions of VOCs ($p < 0.001$) and THC ($p = 0.011$) when varying the ethanol content of the fuel. However, the trend is difficult to explain. As seen in Figure 14, there is a significant maximum for E10 for both parameters. There is also a minimum for E85, which resulted significant for VOCs but not for THC. Similar findings have already been published by others for light duty gasoline vehicles operating on low-blend ethanol, gasoline and E85 [2].

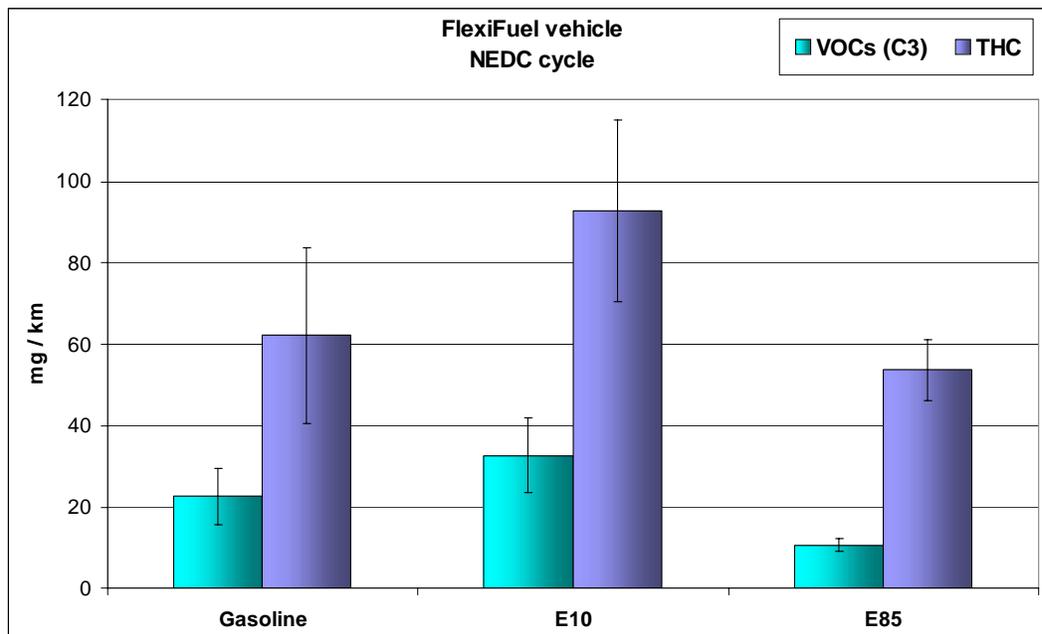


Figure 14 – VOCs and THC emissions over the NEDC cycle (95% confidence).

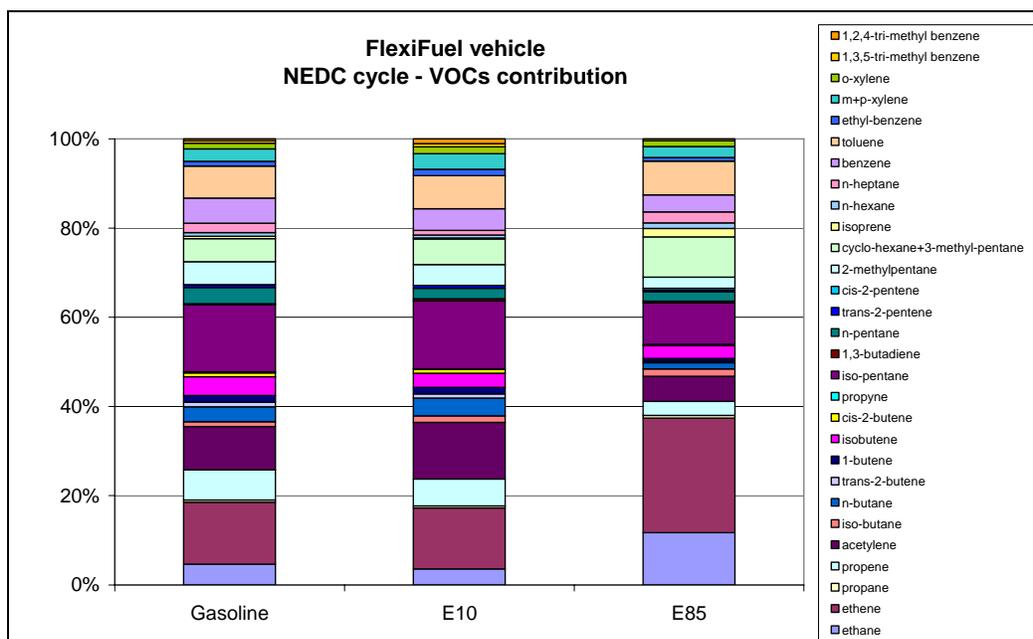


Figure 15 – VOCs relative contribution over the NEDC cycle.

In Figure 15, the relative contribution of the individual hydrocarbons to the sum of VOCs is shown. The composition of the exhaust from the test vehicle is very similar for gasoline and E10, which does not help explaining the increased emissions for E10.

The use of E85 resulted in a general reduction in the VOCs emission of 57% compared to the use of gasoline (Figure 14). Also, the composition of the exhaust was affected (Figure 15) and tended to be more enriched with the C₂ compounds, which is understandable for a fuel consisting of 85% C₂H₅OH.

The perhaps most interesting finding for VOCs is the significant emission reduction for the toxic and carcinogenic compounds 1,3-butadiene and benzene [3,4] as shown in Figure 16 (results for 1,3-butadiene were multiplied by a factor of 5 for better visualization). This must be kept in mind when evaluating the possible impact on the environment of an increased emission for acetaldehyde and formaldehyde as discussed elsewhere in this report. These results (86% and 71% reduction for 1,3-butadiene and benzene when using E85) are in agreement with results found previously in our group for LD EURO 3 vehicles [5] with blended gasoline and in agreement with literature data [2].

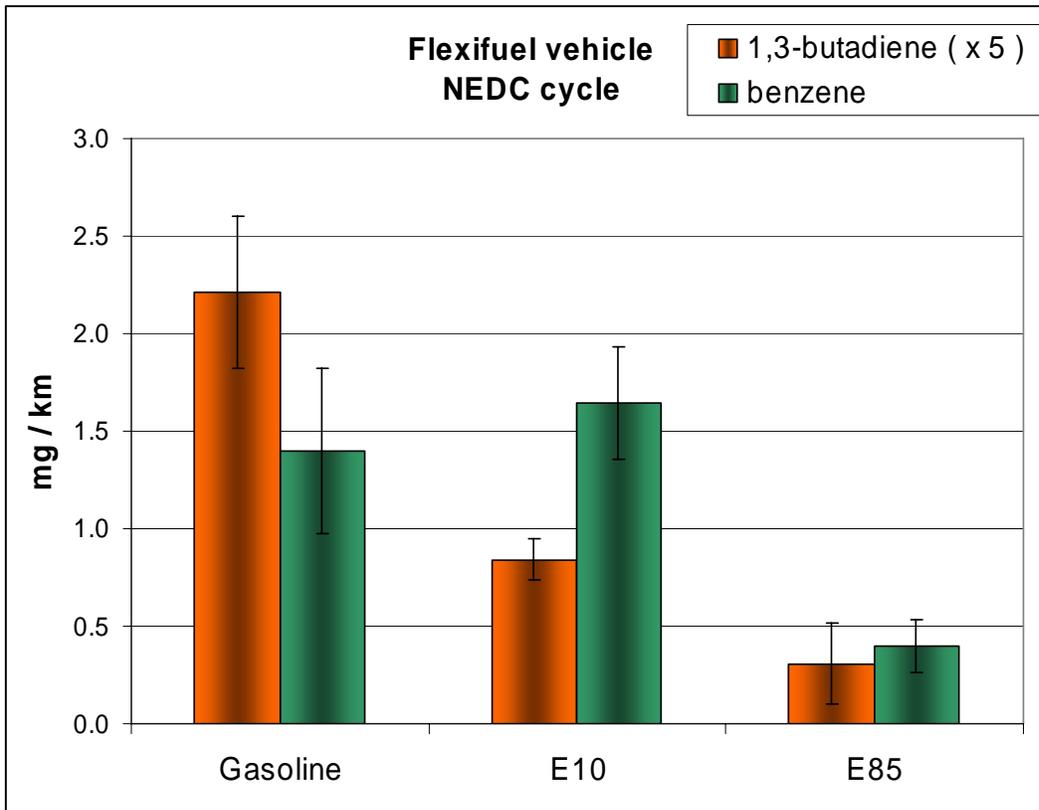


Figure 16 - Emissions of 1,3-butadiene and benzene over the NEDC cycle (95 % confidence). Results for 1,3-butadiene were multiplied by 5 for better visualization.

The relative contribution of each individual VOC to the potential ozone formation can be estimated by the Maximum Incremental Reactivity (MIR) approach [6]. The technical background for this approach is as follows: Carter used a chemically detailed box model to quantify the ozone formed from 180 different VOC in 39 cities across the United States. Eighteen different reactivity scales were developed from those model calculations. The scales differ in the assumptions about the levels of NOx and the measure of ozone impact (such as impact on the peak ozone versus integrated impact over time). One scale, the Maximum Incremental Reactivity (MIR) scale, was chosen for regulatory application in California. MIR values for individual VOCs were calculated in 10-hour box model simulations and were defined as the maximum sensitivity of the peak ozone concentration ($[O_3]_p$) to a small increase in the initial conditions and emissions of the VOC (E_i). MIR is determined for the input ratio of VOC to NOx that leads to the maximum sensitivity to VOC:

$$MIR_i = \max \left\{ \frac{\partial [O_3]_p}{\partial E_i} \right\} \quad (\text{eq.1})$$

over all VOC/NOx.

Using the calculated MIR values, it is possible to calculate the potential of ozone formation for each of the VOCs (PO_3), according to the equation:

$$PO_3 \left[\frac{g}{km} \right] = \sum_i \left\{ MIR_i \left[\frac{gO_3}{gVOC} \right] \times E_i \left[\frac{g}{km} \right] \right\} \quad (\text{eq. 2})$$

The potential of ozone formation for each individual hydrocarbon present in the vehicle exhaust was estimated by the MIR approach. It ranged from 0.1 to 44.0 mg of O₃ / km, and it was decreased by 58% from gasoline to E85. The average relative contribution of the individual VOCs to the PO₃ for the different fuels is depicted in Figure 17, showing the typical prevalence of ethene and propene for vehicle exhaust. A similar relative contribution was found for both cycles for ethene and propene (about 25 and 16% respectively) when using gasoline and E10. In the case of the E85 fuel, their contribution to ozone potential formation was 50% and 7%. This fact highlights the importance of the performance of VOC analyzers in the C₂-C₃ range.

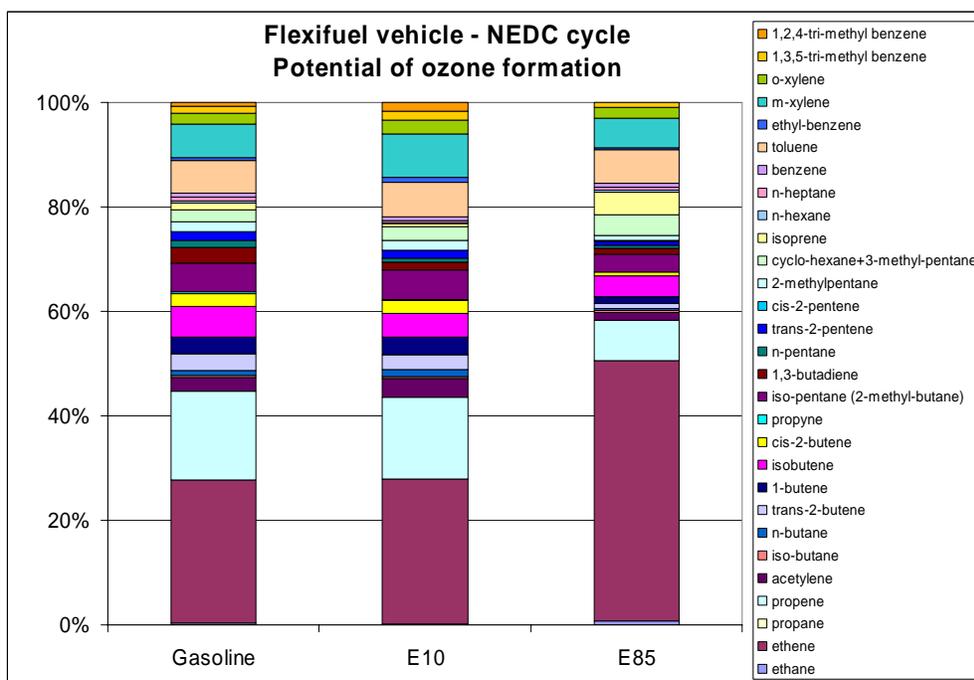


Figure 17 – VOCs relative contribution to ozone formation, NEDC cycle.

4.4.1.2 Results obtained with the US 06 cycle

A complete series of experiments was not conducted with the US 06 test cycle and replicates were not carried out for gasoline and E10. Furthermore, measurements were only taken at the hot phase of test cycle US 06, whereas the complete cycle (hot and cold phase) was considered for the NEDC. Therefore, the results cannot be directly compared with those obtained by the complete dataset for the NEDC cycle and it is not possible to derive statistically valid conclusions. However, some general tendencies may be discussed.

The repeatability of the experiments was inferior to that for NEDC as it appears in Figure 18 for the THC and VOCs determinations, which makes it impossible to determine any effect of ethanol in the fuel. The VOCs values for gasoline and E85 obtained with the US 06 cycle were higher than the values found for the NEDC cycle and the contributions of VOCs to the emitted THC were also higher, namely 73%, 52%, 83 % for gasoline, E10 and E85 respectively, which resulted in a higher ozone formation potential of the exhaust (0.1-112 mg O₃/km). Although the total VOCs correlated with the THC, the results are not easy to explain, further investigation with a higher number of replicates are needed.

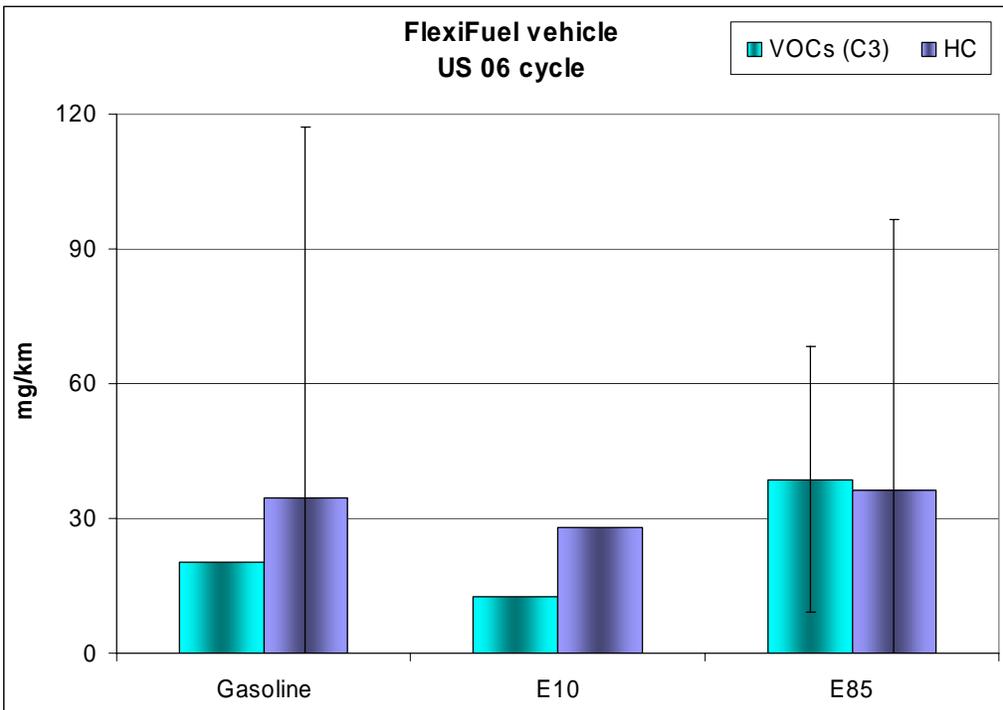


Figure 18 – VOCs and HC emissions over the US 06 cycle (hot phase).

The data less influenced by the low repeatability of the experiments - those obtained on the relative composition of the emitted VOCs - are compared for the NEDC and the US 06 test cycles, considering the ozone formation potential of fuel E85 (Figure 19). A higher relative contribution from ethene (70%) was found for the US 06 cycle (against 50% for NEDC). On the other hand, the aromatics relative contribution to ozone formation was found to be lower for the US 06 than for the NEDC cycle (6% against 16% respectively).

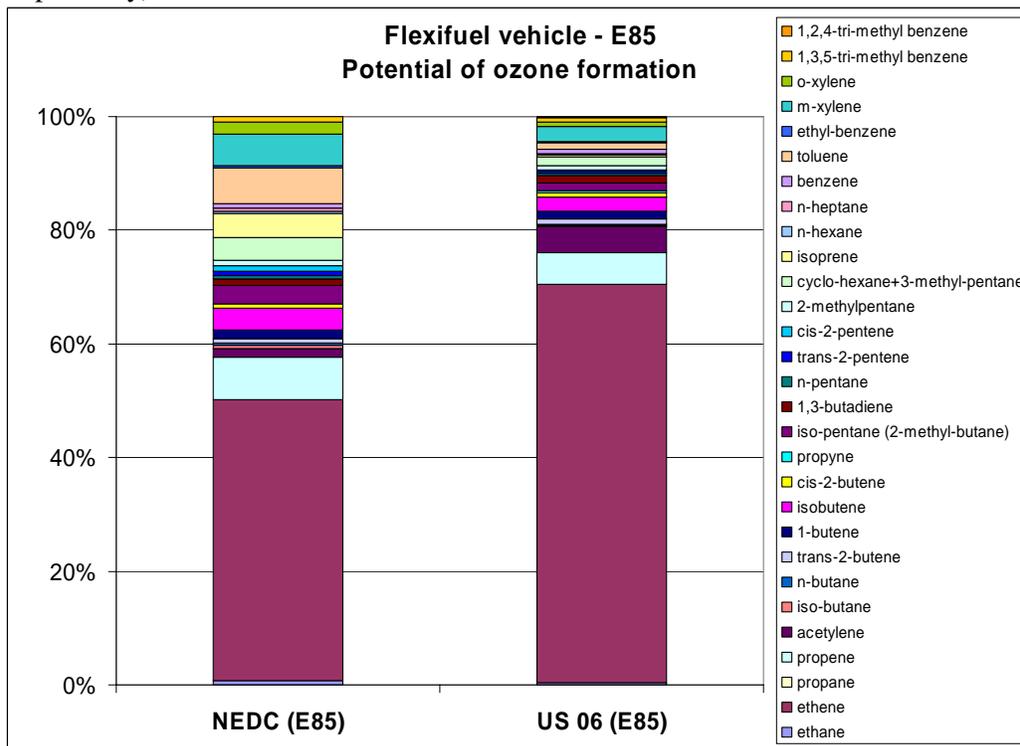


Figure 19 –Relative contribution of VOCs to the ozone formation for fuel E85 (NEDC and US 06 cycles).

4.4.2 CARBONYLS: sampling & analysis methodology

In Europe, carbonyls are not included in any monitoring protocol in the vehicle exhaust stage and their concentration is not measured in regular basis but we have chosen to do it in this report. Indeed, one of the main drives for the work presented below was to know the raise of acetaldehyde emitted when increasing the percentage of EtOH in the fuel.

All tests were performed in same Euro 4 flexible fuel vehicle fuelled with three different fuels already mentioned: a standard commercial gasoline complying with the EN228 specifications and two ethanol/gasoline blends contained respectively 10% (E10) and 85% (E85) ethanol in volume.

The emission tests were carried out following the European legislative procedure for vehicle certification (NEDC cycle). A US driving cycle was used as well (US 06) but not the entire set of experiments was conducted for this cycle.

Three replicates were taken for each test except of the reference fuel at the beginning of the program. Only two of these samples were suitable for F1 so result was not statistically significant and we had to repeat test for that fuel at the end of the program. For the final statistical evaluation (ANOVA) all test results from F1 were pooled together.

In the absence of any regulation and emissions control of these pollutants we found a lack of references regarding the limits which could be acceptable for this group of compounds. We have taken into account to the Brazilian restrictions for emissions of total amount of carbonyls (20 mg/km) [12] and the US Federal test Procedure for Emissions Standards (0.015 g HCHO/mi). We have to be aware when referring to these values that the cycles in which those results were obtained are not the same as the European one, EDC. We have to make conclusions with much precaution since the emissions are very much depending on the driving mode and so on the cycle.

The analytical method used here has been developed on the basis of the “compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (2nd Edition)” [EPA/625/R-96/-1-b]; Compendium Method TP-11A: Determination of Formaldehyde in Ambient Air Using Absorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC).

Sampling was done according to the standard of the European Monitoring network, EMEP [13]. The air sample (flow 0.9-1 l/min) was drawn through the 2,4-dinitrophenylhydrazine (DNPH) coated C18 cartridges (Waters Sep-Pak DNPH-cartridges). Carbonyls are hereby collected as their non-volatile 2,4-dinitrophenylhydrazone derivatives. These cartridges were eluted in the laboratory with 2.5 ml of acetonitrile, diluted with 2.5 ml of H₂O and stored at 5°C until analysis. Further dilution (1/10) was required for samples coming from vehicle fuelled with E85 due to the high concentration of acetaldehyde in these samples. The samples were analysed by HPLC-UV (high performance liquid chromatography) with a thermostated (20°C) 30 cm x 3.9 mm C18-coated silica gel (4µm) column (NOVO-PAK) run in the gradient mode (0.9 ml/min). Detection and quantification were carried out at 360 nm. The eluents were H₂O (A-eluent) and acetonitrile (B-eluent). The gradient was programmed from 50% B to 90% B in 42 min. The detection limit for this method was in the range of 5-20 ng for formaldehyde hydrazone (S/N = 3). Samples volume of 20 liters was taken in DNPH cartridges.

Values of acetaldehyde, acrolein and acetone as well as propionaldehyde have been also quantified. It has not been possible to separate chromatographically the two picks corresponding to acrolein and acetone. By means of the chromatographic method used these two last compounds, acrolein and acetone, are coming together as already reported by other authors [14].

As we can see in Figure 20, there is a patent effect of the increasing fuel content of ethanol on the emissions of carbonyls. A 149% increase in emissions was observed for formaldehyde with E85 ($p=0.02$) together with a 244% increase for acetaldehyde with E10 ($p=0.01$) and a 2200 % increase for E85 ($p<0.001$).

Same statistical significance was not found in the tests performed for the reference fuel F1. Only two sampling tests for carbonyl compounds were valid .The lack of repetitions leads to the unreliability of results (see Figure 20). Tests with the same reference fuel were repeated at the end of the program with better results. This time, the results for formaldehyde and acetaldehyde came out much better and we got suitable results to be compared to the values obtained with E10 and E85. We have treated these results separately (and we shown them in Figure 20 as “Gasoline Rep”) since we needed to be certain that no memory effect for acetaldehyde is found after running so many test with E85 previously. We could confirm that no memory effect was observed taking into consideration of the high amount of EtOH in the fuel.

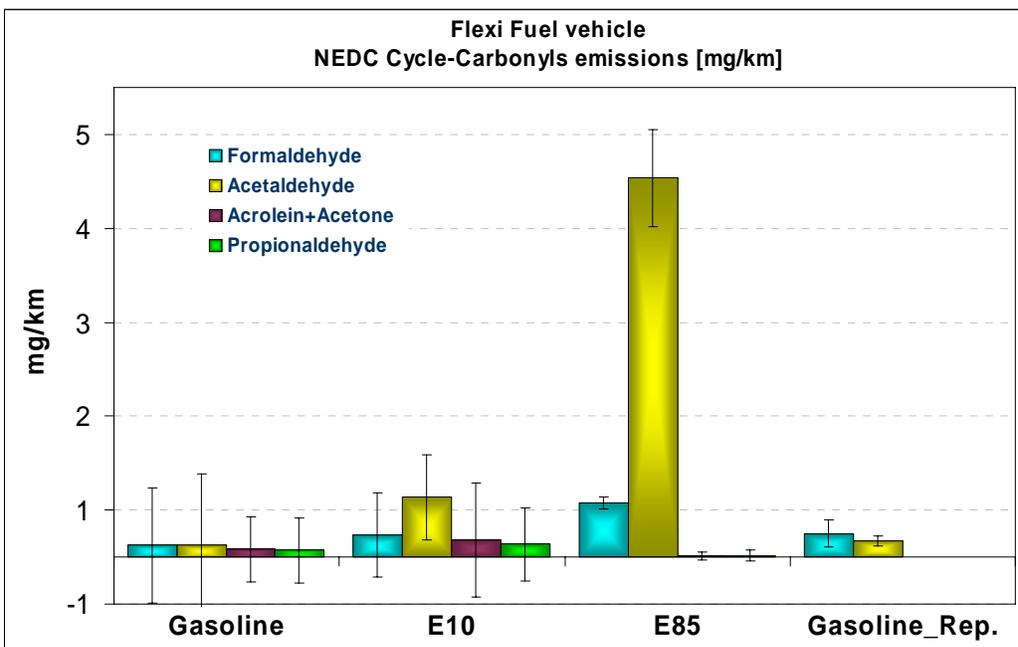


Figure 20 – Carbonyl emissions for gasoline, E10 and E85 (NEDC cycle).

There was no significant effect for the emissions of acetone and acrolein and propionaldehyde in any test.

The sum of the carbonyls found in the exhaust for the test performed with reference fuel is equal to 0.42 mg/km. (below 0.02 g/km ceiling valued for the sum of carbonyls suggested by Brazilian law, beware of the difference in the cycle). These levels are also comparable to the carbonyl emissions that we found in previous test performed in our laboratory for same technology Euro 4 vehicles fuelled with gasoline

The results obtained for acetaldehyde were, as expected, very high for E85. We have already mentioned that an important driver to include the analysis of carbonyls in this work is the belief that adding EtOH up to 85 % in the gasoline the amount of acetaldehyde is in some cases exceptionally high (see Figure 20).

It grasps our attention the high values for acetaldehyde obtained for E85 tests. The HCHO / CH₃CHO (which usually > 1) is upturned when increasing the amount of EtOH in the blend. Formaldehyde was

slightly more abundant only in the exhaust from the reference fuel (1.43) while in both blends E10 and E85 the ratio $\text{HCHO} / \text{CH}_3\text{CHO}$ is <1 . This ration comes down to 0.37 for E10 and to 0.14 for the E85.

This situation may have consequences as it has been found in studies of air quality in Brazilian cities, where the formaldehyde/acetaldehyde ratios vary if we compare with other cities (i.e Europe) [10]. Same results are found in tunnels where only light-duty vehicles fueled mainly with gasohol (a mixture containing 78-80% (v/v) gasoline and 20-25% ethanol) are circulating Formaldehyde/acetaldehyde ratios were <1 .

The high amount of CH_3CHO found for the emissions during the EDC were even higher for the American cycle. Very possibly, the more realistic character of this cycle leads to a much higher content of CH_3CHO in the exhaust. The ratio $\text{HCHO} / \text{CH}_3\text{CHO}$ is 0.03 for this cycle; almost 6 times lower that the ratio we found for the EDC cycle. The absolute value has duplicated the amount of CH_3CHO emitted when the vehicle is running the EDC cycle. We present results corresponding this American cycle below (Figure 21). Only values for E85 fuel have been included for this cycle. The measurements were only taken at the hot phase of test cycle US 06.

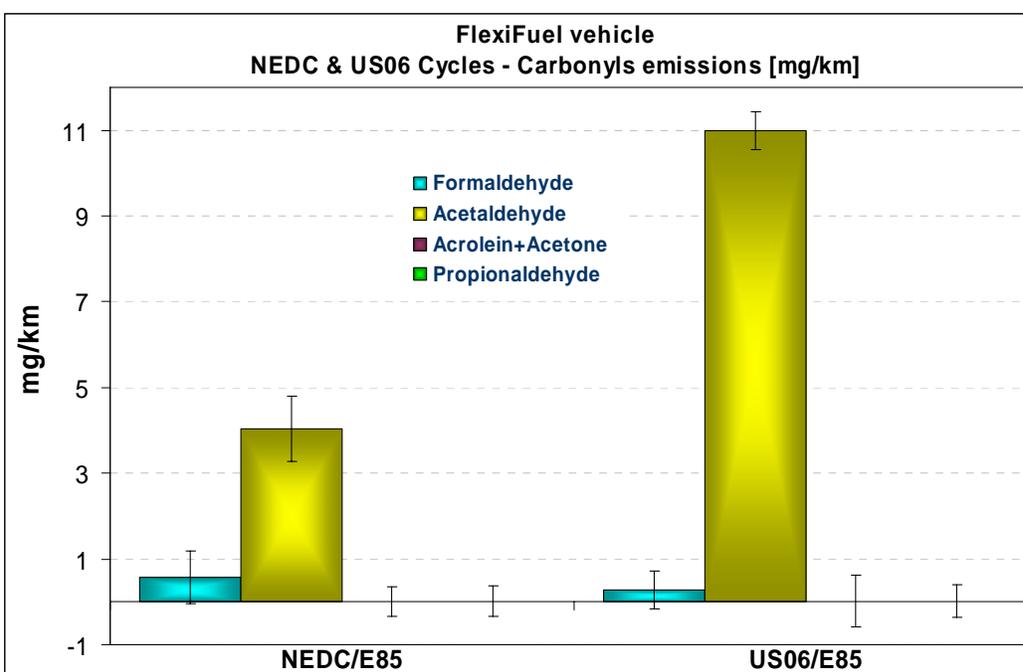


Figure 21 – Carbonyl emissions for E85 (NEDC US06 cycle).

We have to make notice also that in some of this analysis we have found an unidentified peak close to the acetaldehyde. That means that we could be facing a stereo-spatial isomer for the hydrazone derivative of acetaldehyde which has not been taken into account for the quantification due to the lack of confirmation that this peak corresponds to acetaldehyde. This situation has been not observed in any analysis for this compound in previous programs but it must be said that we never faced such a high values of CH_3CHO in the emissions of any vehicle tested in our laboratories before. Most probably further MS analysis would be performed for the confirmation of this hypothesis. If that is confirmed we would be facing even a higher amount of acetaldehyde.

5 Conclusions

A flexible fuel vehicle was tested for exhaust emissions using three different fuels: a standard commercial gasoline complying with the EN228 specifications currently in force and two ethanol gasoline blends obtained by splash blending ethanol in the standard gasoline.

The two ethanol/gasoline blends contained respectively 10% (E10) and 85% (E85) ethanol in volume.

The emission tests were carried out following the European legislative procedure for vehicle certification (NEDC cycle). A US driving cycle was used as well (US 06).

Regulated emissions (CO, HC, NO_x) were measured along with some unregulated emissions (Aldehydes, VOC speciation, PM).

From the results the following conclusions can be drawn:

- The emissions measured over the European driving cycle with the standard gasoline and the E85 fuel were well below the Euro 4 emission limits, the standards the vehicle was certified for. Only with E10 in some tests CO emissions resulted to be slightly higher than the limit (1 g/km).
- The repeatability of the emission measurements was not as good as for conventional gasoline vehicles especially with the fuel E10 and, to a lesser extent, with the standard gasoline. The repeatability was instead much better with the fuel E85. The reason of the not very good repeatability might be linked to the sophisticated engine management system of the vehicle, which has to adapt the engine settings to the variable ethanol content in the fuel. In addition, the special pre-conditioning procedure adopted in order to let the engine adapt to the new fuel after the fuel change, might have not been sufficient to ensure a consistent engine behaviour during the tests performed with the same fuel.
- The poor repeatability obviously affected the confidence interval of the measured emission levels; nevertheless sound conclusions can be drawn:

Regulated emissions – NEDC cycle

- o As far as CO and HC emissions are concerned, E10 resulted to be the most emitting fuel while E85 the least emitting one. However, while for E10 the increase of emission was mainly noticed over the urban part of the cycle (UDC), with E85 HC e CO emission were reduced over the extra-urban part as well.
- o E85 caused a slight increase of combined NO_x emissions compared to the other two fuels, but only the increase of NO_x measured over the extra-urban part of the cycle was statistically significant although the difference is small in absolute terms.

Regulated emissions – US06 cycle

- o Due to the limited number of tests (only 1 valid test for the fuel E10) and the poor repeatability it is difficult to draw reliable conclusions. Anyway the differences among the fuels resulted to be smaller than over the NEDC, probably because the US 06 is a hot cycle and therefore the TWC operates with very high efficiency.
- o Only in the case of CO the fuel E10 gives much higher emission than the other test fuels confirming that it is the most critical fuel for this car.

Unregulated emissions - NEDC Cycle

- o CO₂ emissions were reduced when the E85 fuel was used. Compared to the standard gasoline CO₂ emissions were reduced by about 4% when the E85 was tested.

- The fuel E85 caused a slight increase of particulate emissions (total mass) which in any case resulted to be well below 2.5 mg/km (50% of the Euro 5 emission limit for diesel vehicles).
- Comparably with HC emissions, for the VOCs emissions the fuel E10 resulted to be the most emitting fuel while E85 the least emitting one. E85 resulted in a reduction of 57% of the sum of the speciated VOCs compared to standard gasoline, but with an enrichment of C₂ compounds. Emissions of toxic compounds such as benzene and 1,3-butadiene also decreased when E85 was used instead of standard gasoline. Contributions from ethene and propene prevailed regarding the potential of ozone formation.

Unregulated emissions - US 06 Cycle

- The level of CO₂ measured over the US 06 cycle confirmed that the E85 reduces these emission by about 4-6%.
- PM emission levels turned out to be quite high over the US 06 cycle. The measured levels were comparable to those of a Euro 3 diesel car. This might be due to the very aggressive driving pattern of the US 06 cycle which contains very hard accelerations. In these conditions the engine is likely to work in open loop and with a very rich mixture.
- Contributions of VOCs to the emitted THC over the US 06 cycle were higher in comparison with NEDC cycle, which resulted in a higher ozone formation potential of the exhaust. Ethene was found to contribute over the US 06 cycle to 70% of the total ozone (against 50% over the NEDC cycle), and aromatics relative contribution to ozone formation was lower (6% against 16% for the NEDC cycle). Finally, literature data about flexifuel vehicles is rather scarce and results show discrepancies, thus making a comparison difficult.

Unregulated emissions - carbonyls

- Results for reference gasoline is comparable to emissions on any equivalent Euro 4 vehicle tested previously in our laboratory.
- There is a patent effect of the increasing fuel content of ethanol on the emissions of acetaldehyde, which is statistically significant and considerably high when E85 is used.
- Contributions over the US 06 cycle were higher in comparison with NEDC cycle
- By having a better knowledge of the potential emitters for ozone precursors we are trying to prevent and/or avoid the formation on smog episodes and to extend the availability of data to be used in the chemical models in order to strength their capability to thereby to anticipate the smog episodes in this region of particular risk.

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7 Issues related to the use of bioethanol as transport fuel

There are some potential problems associated with the use of bioethanol as gasoline component. In particular, the main concern is that a massive use of bioethanol can have a negative impact on the air quality due to an increase of some VOC emissions and of the ozone formation potential. Some of the aspects related to the impact of ethanol used as transport fuel on the environment have been extensively investigated but there are still open questions that need further research.

7.1 *Bioethanol as transport fuel (extract from Auto-Oil II report) [3]*

Bioethanol has been used in various mixture proportions with gasoline or diesel fuel; the most popular blends by volume are:

- E5-E26G (5-26% ethanol + 95-74% gasoline)
- E85G (85% ethanol + 15% gasoline)
- E15D (15% ethanol + 75% diesel)
- E95D (95% ethanol +5% water with ignition improver)

There is a number of advantages and disadvantages of bioethanol used as transport fuel:

Advantages:

- Very high octane number
- As a renewable fuel produces lower CO₂ emissions compare to conventional fuels
- It reduces some pollutant emissions
- Its ozone forming potential is lower than that of gasoline and diesel
- It contains no sulphur and is biodegradable

Disadvantages:

- It increases evaporative emissions (when blended with gasoline at low percentages)
- Because of the lower vapour pressure and high latent heat of vaporization of neat ethanol, it makes cold start in cooler climates more difficult.
- It increase acetaldehyde emissions but reduces those of formaldehyde.
- E85G vehicles give higher unregulated emissions (ethane and acetaldehyde) than gasoline fuelled vehicles.

Due to its characteristics neat ethanol cannot be used as transport fuel mainly because its high heat of vaporization and low volatility make cold start very difficult especially in cold climates. The most common way to overcome this problem is to blend ethanol with a small fraction of a much more volatile fuel such as gasoline; the most popular blend is E85 which consists of 85% ethanol and 15% gasoline by volume.

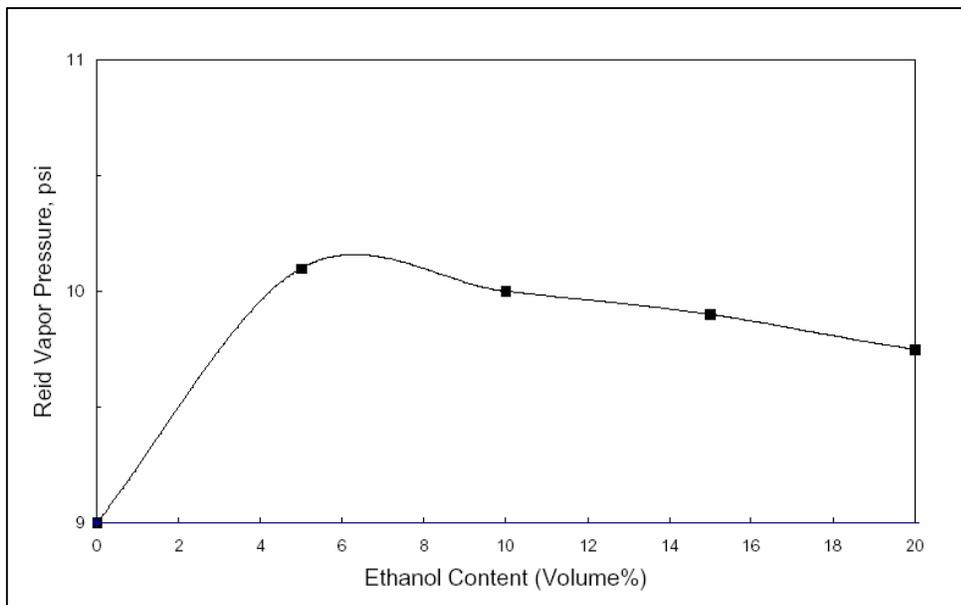
Although E85 has been extensively used worldwide, engine manufacturers guarantee problem-free operation without any modification only to catalyst equipped cars fuelled with gasoline containing no more than 5% ethanol. However modern catalyst-equipped cars are probably able to run without any material problem with up to 20% ethanol which seems to be the upper limit for cold climates.

Mixture preparation is also important to achieve low exhaust emissions with engines fuelled with ethanol/gasoline blends, especially at cold start. The use of flexible-fuelled vehicles (FFV) is the preferred approach in the USA; these vehicles have just one tank and the engine can adapt automatically the ignition timing and mixture strength on the basis of a signal from a sensor measuring the ethanol/gasoline ratio.

7.2 Effect of ethanol on gasoline volatility [4] [7]

One major concern associated with the use of ethanol as a gasoline component is the alcohol's effect on gasoline front-end volatility as determined using the Reid vapour pressure (RVP) metric (DVPE in Europe legislation). It is well-known that the addition of ethanol to gasoline at low ethanol concentrations results in an increase in RVP of approximately 1 psi (Figure 22. Higher RVP values mean that the fuel is more volatile or, in other words, the higher the RVP value, the more fuel will evaporate at a given temperature. Figure 1 shows a typical curve of RVP change in response to the addition of ethanol to gasoline. As shown, due to the non-ideal behaviour of the ethanol gasoline blend, RVP increases dramatically with the addition of any ethanol and then levels off at about 1 psi above the RVP of the base gasoline at higher concentrations. The RVP is measured at 37.8 °C.

Figure 22 – Effect of ethanol content on vapour pressure of gasoline/ethanol blends



As a consequence of the effect above described, if a certain amount of ethanol is splash blended in a commercial gasoline the RVP will increase above 60 kPa that is the maximum value during the summer period allowed by the European legislation; on the other hand, in a refinery the volatility of a gasoline/ethanol blend could be corrected to match the specification but it would require modifications to the lay-out of the refinery itself.

It is clear that an increase of the volatility of the fuel results in increased evaporative emissions during the refilling operation. This effect will be larger where the service stations are not equipped with vapour recovery systems.

7.3 Effects of ethanol on evaporative emissions [5] [4] [21]

One of the major concerns related to the use of splash blended gasoline/ethanol blends is the possible increase of evaporative emissions due to a combination of factors:

- Increased evaporative emissions due to the higher RVP
- Increased fuel permeation through plastic and rubber components of fuel system
- Commingling effect

Evaporative emissions from motor vehicles can be defined as all the VOCs emissions from a vehicle that do not come from the engine's exhaust. These non-tailpipe hydrocarbons come from a variety of sources, including non-fuel "background" sources such as tires, paint, vinyl components, and adhesives. The major source of evaporative emissions has been from the vehicle's fuel storage, delivery and handling systems.

On a vehicle in good conditions three main sources of evaporative emissions depending on the fuel quality can be identified:

-Running losses

"Running losses" emissions are those evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and loss from the carbon canister. These emissions are not currently regulated in Europe.

-Breathing losses through the vent of the tank (mainly dependent on the gasoline volatility and on the effectiveness of the evaporative emission control system)

The fuel tank, by design, is vented to the atmosphere through an activated carbon trap (canister). During the engine operation, in certain operating conditions and under the control of the ECU (Electronic Control Unit), part of the combustion air is drawn by the engine through the canister; in such way the activated carbon is purged and the fuel vapours burned in the engine. The amount of air drawn through the canister is controlled by means of a valve (purge valve) located on the line connecting the canister with the air intake manifold.

-Fuel permeation through plastic and rubber components of fuel system (dependent on the chemical species contained in the gasoline).

Gasoline also escapes the vehicle's fuel system by permeation through the plastic and rubber components; e.g., hoses, seals, and in some cases, such as with a non-metallic tank, the fuel tank itself. Advances in materials and design have reduced the permeation emissions component to very low levels.

An unintended source of HC emissions may occur from leaks in the system. Leaks may occur in the vapour and/or the liquid system as a result of deterioration and/or faulty service techniques. Examples of deterioration are corrosion of metallic components (e.g., fuel lines, tanks), cracking of rubber hoses from heat and ozone exposure, hardening of seals, and mechanical failures.

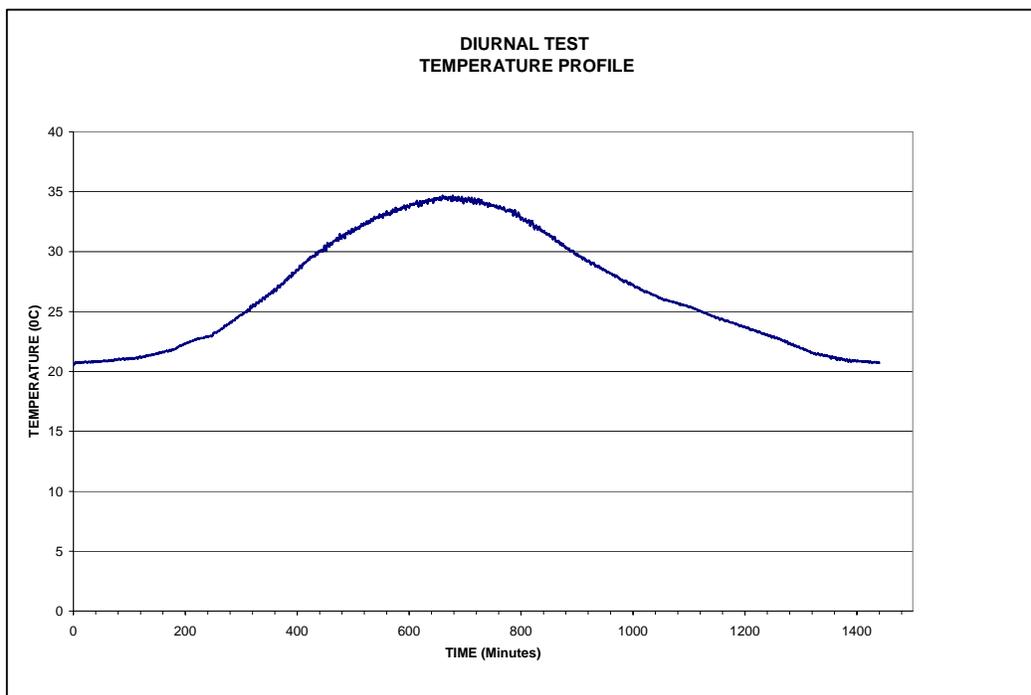
In Europe a new standard for evaporative emissions and the procedure to measure them was set by the Directive 98/69/EC. The evaporative emission standard is closely connected to the legislative certification test that is divided into two different tests: the "Hot Soak" test and the "Diurnal" test.

Hot soak emissions are usually attributed to the evaporation of the gasoline in the fuel system after the vehicle is shut off; diurnal emissions are instead the evaporative emissions occurring from a vehicle while it is not being operated.

In the Hot Soak test the car is driven over a NEDC+ECE15 cycle and then, within 7 minutes, pushed into the SHED that is a sealed cell by means of which it is possible to measure the amount of hydrocarbons released by the vehicle. The Hot Soak test lasts 1 hour and the vehicle is kept at a constant temperature of 27 °C. After the end of the Hot Soak test, the vehicle is kept at about 20 °C for minimum 6 hours and then the Diurnal test can be started.

The Diurnal test lasts 24 hours and the temperature inside the SHED is varied between 20 °C and 35 °C (see Figure 23). The sum of the mass of the HC released by the vehicle during the Hot Soak and the Diurnal test has to be below the limit that currently is 2 g/test.

Figure 23 – Temperature profile of the diurnal test



7.3.1 Breathing losses

Breathing losses are influenced significantly by a number of factors. [22] [29] [23]. Regarding the fuel, the most important parameter is gasoline volatility; in general, the higher the volatility the higher the evaporative emissions. However this relationship between the volatility and evaporative emissions is not linear, as canister breakthrough can occur when it becomes saturated. In this condition the canister is not able to trap gasoline vapours any more and therefore they are released in air in an uncontrolled way.

If the evaporative emissions are measured using the standard procedure, the DVPE can have a large influence on the final result; a gasoline with a higher DVPE than the fuel specifications can easily lead to higher evaporative emissions, also because the legislative procedure requires the use of a gasoline

having a RVP of 60 kPa for certification purposes. As a consequence, the evaporative emission control systems are designed to meet the legislative standard with such a gasoline.

The residual HC concentration in the canister after purging plays an important role as well; in fact, canister breakthrough tends to occur more easily when the residual HC adsorption concentration increases. In other words, this means a reduction of the working capacity of the canister. Polar molecules like ethanol (or water) or heavier hydrocarbons are usually harder to purge from the carbon. It has been shown that activated carbon affinity for ethanol vapours is greater than for olefins and aliphatics [30]. Therefore it is possible that ethanol's propensity to be tightly held by activated carbon [42], in conjunction with its hygroscopic nature may decrease the working capacity of the canisters used to control evaporative emissions and result in increased diurnal emissions.

For the above mentioned reasons, in the USA a revised certification procedure including also ethanol-containing gasolines has been adopted. Starting from the entry into force of the Euro 5 emission standards, a reference fuel containing 5% of ethanol will have to be used for vehicle certification in Europe as well.

Breathing losses depend also on the temperature in the fuel tank. The following plot shows the HC concentration in the vented vapour space above liquid gasoline as a function of the temperature. For example, if temperature is increased from 70 °F to 95 °F (approximately from 20 to 35 °C), the HC concentration will increase from 20 to 50% due to evaporation. This leads to an increase of pressure and therefore some vapour must be expelled.

Temperature in the tank obviously depends on the ambient temperature but can be affected significantly by driving the vehicle. In fact, if the engine has a fuel return, part of the fuel supplied by the fuel pump to the engine is returned to the tank and as a consequence, the temperature of the fuel in the tank can reach temperatures well above the ambient one.

In contrast, if the vehicle is left parked for long time the temperature of the fuel can be lower than the ambient. In fact, it has to be taken into account that the temperature profile in the tank is usually different from the ambient temperature profile. First of all, there is a time lag of the tank temperature with respect to the ambient temperature; both the maximum temperature and the minimum one will be reached later compared to ambient. Furthermore, the range from minimum to maximum temperature in the tank is narrower (about 87% of the range of ambient temperature variation); in particular, the maximum temperature in the tank is somewhat lower than the ambient maximum temperature.

Some factors are related to the correct functioning of the evaporative emission control system: the capacity and the condition of the carbon trap, the condition of the lines and the connectors and of the activated carbon, the correct functioning of the purge valve, the presence of a leak, etc.

A large experimental programme has been carried out at the JRC jointly with EUCAR and CONCAWE to investigate the effect of different gasoline/ethanol blends on evaporative emissions from the current European passenger car generation. The main findings of this work are summarized here below [46]:

While disentangling fuel, canister weight and other time related effects was difficult, several clear conclusions could still be drawn from the results.

1. The vehicles tested differed in their level of evaporative emissions and in the extent of their response to fuel changes. All cars met the 2 g/test emission limit on the first test on fuel A, the

reference fuel with DVPE of 60 kPa. Some vehicles slightly exceeded the limit on subsequent tests on fuel A, probably related to increased canister loading in later tests.

2. A key fuel variable that affects evaporative emissions is vapour pressure (DVPE). In general, increasing fuel DVPE above that of the reference fuel used for system development increased evaporative emissions. The effect appeared to be non-linear (as expected for a canister breakthrough effect). The ethanol blends with final DVPE around 75 kPa gave considerably higher evaporative emissions than the other fuels in several tests over most of the vehicles.
3. Differences between the other fuels with DVPE in the range 60-70 kPa were small. Furthermore, due to the combination of DVPE variations, the presence or absence of ethanol, and to significant changes of canister weight, it is difficult to draw any reliable conclusions on the influence of each single parameter. The engineering margin built into the system may also explain the reduced fuel effect in this volatility range.
4. A limited number of tests carried out using modified test procedures suggest that the increase of fuel vapour pressure alone may not satisfactorily explain the influence of ethanol on total evaporative emissions. An increase of fuel permeation rate or a reduction in canister working capacity due to ethanol could explain the different emissions measured with fuel A and A5E in repeated tests carried out on one of the test vehicles after the main programme.
5. This programme has shown that the test protocol used for this fuel evaluation was not able to return the vehicle to a consistent condition at the start of each test. For most of the vehicles, the canister weight increased with successive tests. This meant that emissions on base fuel A increased with test number after testing on other fuels. The main weight increase was noticed over the first two to three tests; after this the canister weight either flattened out or increased less steeply. This is most likely due to increased vapour loading on the canister, which is not sufficiently purged during the vehicle conditioning prescribed by the regulatory test procedure. Extra purging carried out on some vehicles between tests reduced this effect. Starting the test at such high canister weights may be not representative of real-world operating conditions, but is a very severe test of the evaporative control system. For any further work, a more extensive canister conditioning procedure is needed to ensure that the canister system is properly conditioned to the new fuel at the start of each test.
6. The increase in canister loading could be due to two factors, increased hydrocarbon loading, a build up of ethanol in the canister, or both. It is not clear from this work what is the relative size of these effects. Heavy hydrocarbons are known to be harder to purge from the canister. Ethanol is a polar molecule and is also known to be harder to purge from the active carbon in the canister. Ethanol was found in the VT SHED vapour of tests on pure hydrocarbon fuels following use of ethanol-containing fuels.
7. Measurements of regulated exhaust emissions showed no clear effects of fuel properties or other parameters such as different canister loadings. However, the test programme was not designed to look at exhaust emissions. Specific conditioning between tests and multiple testing is essential for such studies.
8. Volumetric fuel consumption (litres/100 km) increased with increasing ethanol content. This increase was roughly proportional to the oxygen content of the fuel. However neither CO₂ emissions nor energy consumption (MJ/100km) showed any effect of ethanol content.
9. Speciated hydrocarbon emissions from the VT SHED Diurnal tests generally show relatively high levels of light hydrocarbons (C4-C6) and low levels of ethanol. The main sources of the

light hydrocarbons are probably canister bleed emissions and breathing losses. Heavier hydrocarbons like aromatics were also found in significant concentrations. In this case the main source of emissions is likely to be fuel permeation.

7.3.2 Fuel Permeation

Fuel permeation through plastic and rubber components of fuel system is one component in the total evaporative emissions from a vehicle. Permeation [24] does not occur through an identifiable opening; instead individual fuel molecules penetrate (i.e. they effectively mix with) the walls of the various assembly components and eventually find their way to the outside. Fuel permeation is significant only for plastic or elastomeric materials.

Ethanol is believed to lead to an increase of the permeation due to the tendency of ethanol to evaporate more readily than other fuel components and to the smaller size of the ethanol molecule. A study on fuel permeation [24] has been performed using tanks with an ethylene vinyl alcohol (EVOH) layer used to reduce permeation. It has been demonstrated that methanol contained in the fuel has a two-fold effect: it “opens” the way through the EVOH barrier layer for the hydrocarbon components (that in absence of methanol would permeate only in minimal amounts) and represents a large part of the evaporative emissions due to fuel permeation. The effect of ethanol is expected to be much less severe as diffusion of ethanol through the EVOH layer is orders of magnitude slower than methanol.

What is not very well known is the contribution of the fuel permeation to the total evaporative emissions. If permeation accounted for the majority of the evaporative emissions, the role of the gasoline RVP and its effect on breathing losses would be less important.

“Fuel Permeation from Automotive Systems” - Final Report, CRC Project No. E-65, September 2004 [5]

A study co-sponsored by the California Air Resources Board (CARB) and Georgia-based Coordinating Research Council has been recently carried out with the objective of investigating the effect of gasoline/ethanol blends on permeation.

The study, found that a 5.7%-by-volume ethanol blend, which is the standard in California, increases permeation emissions by 65% compared with MTBE-blended RFG and 45% over non-oxygenated fuels, on average. "Emissions increased on all 10 vehicle fuel systems studied when ethanol replaced the MTBE in the test gasoline," the study concludes. The average permeation emissions increase with ethanol gasoline was 1.4 grams/day (g/d) higher than emissions with the MTBE gasoline, and 1.1 g/d higher than emissions with a non-oxygenated gasoline.

Effects of Gasoline Ethanol Blends on Permeation Emissions Contribution to VOC Inventory From On-Road and Off-Road Sources - The American Petroleum Institute -2005 [43]

The American Petroleum Institute (API) evaluated the change in VOC inventory resulting from the impacts of ethanol on permeation emissions of fuel components. The estimates were made for ethanol blends in California and several areas outside of California using test data on gasoline blends containing 5.7% ethanol by volume. The study relied upon the CRC E-65 program data for on-road vehicles and drew upon data from the literature for estimating permeation inventories for off-road equipment and portable containers. The study focused on California and on three other areas in the United States – Atlanta, Houston, and the New York City/New Jersey/Connecticut ozone non-attainment areas.

Results of the summer inventory analysis showed that in California, ethanol in gasoline increases VOC permeation emissions by 25 tons per day in 2003, dropping to about 17 tons per day in 2015. The decrease in the ethanol impact is due to fleet turnover of vehicles, equipment, and portable containers with permeation controls. Corresponding summertime increases in the additional areas are as follows:

- Atlanta: 5.2 tons per day in 2003, 4.8 tons per day in 2015
- Houston: 6.9 tons per day in 2003, 6.2 tons per day in 2015
- New York/NJ/Connecticut area: 28 tons per day in 2003, 23.2 tons per day in 2015

7.3.3 Commingling Effect [4]

Although all gasoline, including ethanol-gasoline blends, should comply with the same RVP limits, the marketing of ethanol-blends in areas where non-ethanol blends are also being sold would lead to a general increase in the RVP of gasoline used in that area. This increase in RVP is the result of what is referred to as the “commingling effect” that results from the mixing of ethanol-containing and non-ethanol-containing gasolines in vehicle fuel tanks.

As an illustration of the commingling effect, consider a motorist who brings his car to a service station for refueling when the tank is half full. If one assumes that the original fuel in the tank contains a 10% ethanol-blend at a given RVP and that the fuel added to the tank at the station is a non-ethanol blend of the same RVP, the overall effect will be to turn the non-ethanol gasoline into a 5% ethanol blend by volume. Referring back to Figure 1, this will cause the RVP of the non-oxygenated gasoline to increase by about 1 psi; since that gasoline represents 50% of the fuel in the tank, the average RVP of all the fuel will increase by about half that amount, or about 0.5 psi..

The increase of the RVP of the gasoline could lead, as discussed above, to an increase of the evaporative emissions even if the RVP of all the gasolines meet the specifications.

Of course the impact of the commingling effect on evaporative emission depends on a number of factors:

- Spatial distribution of the gasoline/ethanol blends
- The market shares of ethanol- and non-ethanol-containing gasolines.
- The ethanol content of the gasoline/ethanol blend
- The amount of gasoline remaining in the tank at the moment of the refueling
- The RVP levels of the gasolines.

7.3.4 Other studies

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 - 1998 [8]

A study carried out by CARB in 1998 [8] investigated the effect of ethanol on evaporative and exhaust emissions. In particular, the study compared the effects of a standard gasoline (having a RVP of 7.0 psi) and a high RVP gasoline/ethanol blend (containing 10% of ethanol and having a RVP of 8.0 psi) on exhaust and evaporative emissions from 12 light-duty vehicles.

The data of this test programme indicated that a high RVP ethanol blend significantly increases overall emissions of NO_x, THC, NMOG, ozone forming potential, toxics and decreases emissions of CO.

More in details, the results of the tests showed a significant increase of the combined evaporative and exhaust HC emissions (+ 18-23 %; the value depends on the calculation method used).

Proposed Determination Pursuant to Health and Safety Code Section 48830(g) of the Ozone Forming Potential of Elevated RVP Gasoline Containing 10 Percent Ethanol – California Air Resources Board – 1998 [6]

This report [6] presents the CARB staff's assessment of the ozone forming potential of elevated RVP gasoline containing 10% ethanol.

A table summarizing a large body of existing emission test data shows that gasoline blended with ethanol with an increase in RVP has higher evaporative emissions than similar gasoline with a lower RVP. A one psi increase in RVP results in significant increases in evaporative emissions of up to 40%. Increases in oxygen content appear to generally result in a slight decrease in exhaust hydrocarbon emissions. Based on the ARB predictive model, staff estimates that adding 10% ethanol (3.5% wt oxygen) could reduce exhaust hydrocarbon emissions by about 3% compared to a complying Californian reformulated gasoline with 2.0% wt oxygen.

Furthermore, although data from test programmes have shown a reduction of specific reactivity in terms of ozone forming potential of both exhaust and evaporative emissions with ethanol blends, the increase in evaporative emissions from a 1 psi increase in RVP is so substantial that the resultant ozone forming potential significantly increases when exhaust and evaporative emissions are combined. Finally, the U.S. EPA complex model estimates that high RVP gasoline containing 10% ethanol will result in increases in total hydrocarbons of 3% for exhaust emissions by 40 percent for evaporative emissions.

As a consequence of the assessment results, the CARB staff recommend to not exempt 10% ethanol blends from the RVP standard.

Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline – California Environmental Protection Agency – 1999 [42]

This report addresses the impact of ethanol/gasoline blends on air quality. The main conclusions drawn from the analyses conducted by CARB can be summarized as follows:

- In comparison to the non-MTBE components of gasoline, the atmospheric formation of toxic compounds from ethanol and alkylates is relatively slow. The major products of concern for ethanol are acetaldehyde (a toxic air contaminant) and peroxyacetyl nitrate (PAN, an eye irritant and cause of plant damage). However, the elimination of MTBE thanks to the introduction of ethanol should lead to lower emissions of formaldehyde that can compensate the higher levels of the above mentioned pollutants.
- The inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tank results in a combined gasoline having a higher RVP than the ethanol-free gasoline and in an increase of the evaporative emissions.
- Ethanol-containing gasoline may lead to increases in evaporative emissions because rubber, plastic and other materials are permeable to ethanol and because ethanol may reduce the working capacity of the carbon canister used to control evaporative emissions on board of motor vehicles.
- Since relatively little ethanol is produced in California, it will probably all be shipped by rail or trucks. The estimated statewide impact on heavy duty trucks emissions is a 0.06% increase.

- As long as the CaRFG3 (California Reformulated Gasoline Phase 3) regulations address the potential for ethanol to increase evaporative emissions and cause more rail and truck traffic, the substitution of ethanol and alkylates for MTBE in California's fuel supply will not have any significant impact on air quality.

Comparison of fuel tank evaporative emissions from E0 and E5 petrol - IDIADA, Report LM030411 - 2003

The objective of the study was to determine the evaporative emissions of a fuel tank with respect to temperature changes when 5% ethanol is added to commercial European petrol.

The tests are designed to determine the differences in evaporative emissions between the European Union average temperatures (real world conditions) and the higher temperatures used as standard for fuel analysis.

The European Union annual average temperatures are:

- Maximum: 14,8°C.
- Minimum: 6,8°C.
- Average: 10,8°C.

and the European Union summer average temperatures are:

- Maximum: 22,3°C.
- Minimum: 12,6°C.
- Average: 17,5°C.

These temperatures are based on the average temperatures of the principal city of each Member State of the European Union (EU).

The main conclusions are:

- THC emissions

Regarding the tests with fuel tank without canister:

- The results demonstrate that regarding changes in the temperature without a canister the lines of evolution of the THC emissions follow a different pattern if E0 or E5 is used.
- At a Reid vapour pressure of 37-38 °C used as a standard for the fuel analysis, the gasolines with ethanol emitted more THC emissions than the gasolines without ethanol.
- However, at the average annual and summer temperatures of the European Union the differences between the emissions are not significant. That is to say, they are within the margin of error of the measurements.

Regarding the tests with fuel tank and canister:

- Since the beginning of the 1990's all new cars have been fitted with a canister that absorbs and later eliminates THC emissions. The THC emissions in gasolines with and without ethanol in fuel tanks and canister are much lower than emissions in fuel tanks without canister, (about 99% less for this test).
- With the canister the differences between the emissions of all the gasolines at all temperatures are insignificant.

Issues Associated with the Use of Higher Ethanol Blends (E17-E24) – NREL 2002 [7]

This report [7] published by the U.S. National Renewable Energy Laboratory (NREL) reviews the issues associated with utilizing higher ethanol blends (E17-E24); Subjects include technical vehicle issues, emissions, infrastructure, market issue and regulatory and policy considerations.

The key conclusions are the following:

- Technical issues:
 - Higher ethanol blend impact on conventional fuel systems could vary according to control system technology and vehicle age. Manufacturer involvement is needed to assess this issue.
 - Higher ethanol blends will operate effectively on conventional vehicle catalysts.
- Emissions
 - Preliminary emissions data indicate that the volatility of higher ethanol blends is less than in 10% blends.
 - CO emissions are typically lowered in ethanol blended fuels. This trend could also influence the rate of ozone formation in the atmosphere.
 - E85 data show different trends for “ozone-forming potential” and “specific reactivity”.
 - More research is needed to thoroughly assess the impact on emissions of higher ethanol blends.
- Infrastructure issues
 - Separate infrastructure is needed to distribute higher ethanol blends.

“Effects of Fuel Ethanol Use on Fuel-Cycle Energy and Greenhouse Gas Emissions”, Center for Transportation Research - Argonne National Laboratory – 1999 [44]

The report presents the results of the evaluation of effects on per-vehicle-mile fuel-cycle petroleum use, greenhouse gas (GHG) emissions, and energy use of using ethanol blended with gasoline in a mid-size passenger car, compared with the effects of using gasoline in the same car. The analysis includes petroleum use, energy use, and emissions associated with chemicals manufacturing, farming of corn and biomass, ethanol production, and ethanol combustion for ethanol, and petroleum use, energy use, and emissions associated with petroleum recovery, petroleum refining, and gasoline combustion for gasoline.

Use of E10 (10% ethanol and 90% gasoline by volume) achieves:

- 6% reduction in petroleum use,
- 1% reduction in GHG emissions, and
- 3% reduction in fossil energy use.

Use of E85 (85% ethanol and 15% gasoline by volume) achieves:

- 73–75% reduction in petroleum use,
- 14–19% reduction in GHG emissions, and
- 34–35% reduction in fossil energy use.

Use of E95 (95% ethanol and 5% gasoline by volume) achieves:

- 85–88% reduction in petroleum use,
- 19–25% reduction in GHG emissions, and
- 42–44% reduction in fossil energy use.

(Results: per Vehicle Mile Traveled with Ethanol Blends, Current Corn and Ethanol Production Case for Corn-Based Ethanol)

“Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85”, Emissions Research and Measurement Division, Environmental Science and Technology Centre, Environment Canada – 2008 (47)

The report presents the results of the evaluation of effects. The results of two recent vehicle emission studies are described in that paper, along with a statistical analysis of the changes in tailpipe emissions due to the use of ethanol that includes the results from these two studies in combination with results from other literature reports. The first study evaluates the effect of two low blend ethanol gasolines (E10, E20) on tailpipe and evaporative emissions from three multi-port fuel injection vehicles and one gasoline direct injection vehicle at two different test temperatures. The second study evaluates the differences in tailpipe emissions and fuel consumptions of paired flexible fuel and conventional gasoline vehicles operating on California RFG Phase 2 and/or E85 fuels at 20 °C. The vehicles were tested over the four-phase FTP or UDDS and US06 driving cycles. Tailpipe emissions were characterized for criteria pollutants (CO, NO_x, NMHC, NMOG), greenhouse gases (CO₂, CH₄, N₂O), and a suite of unregulated emissions including important air toxics (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein), and ozone reactivity. In the low blend ethanol study, evaporative emissions were quantified and characterized for NMHC. While contradicting, results can be seen among the various literature reports and with these two new studies, the statistical analyses of the aggregated data offers much clearer pictures of the changes in tailpipe emissions that may be expected using either low blend ethanol gasoline (E10) or E85. The results of the statistical analysis suggest that the use of E10 results in statistically significant decreases in CO emissions (-16%); statistically significant increases in emissions of NMHC (9%), NMOG (14%), acetaldehyde (108%), 1,3-butadiene (16%), and benzene (15%); and no statistically significant changes in NO_x, CO₂, CH₄, N₂O or formaldehyde emissions. The statistical analysis suggests that the use of E85 results in statistically significant decreases in emissions of NO_x (-45%), NMHC (-48%), 1,3-butadiene (-77%), and benzene (-76%); statistically significant increases in emissions of formaldehyde (73%) and acetaldehyde (2540%), and no statistically significant change in CO, CO₂, and NMOG emissions.

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EUR 24011 EN – Joint Research Centre – Institute for Environment and Sustainability

Title: Effect of Fuel Ethanol Content on Exhaust Emissions of a Flexible Fuel Vehicle

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Luxembourg: Office for Official Publications of the European Communities

2009 – 52. – 21 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1018-5593

ISBN 978-92-79-13627-6

DOI 10.2788/39589

Abstract

The European Union is aiming at increasing the market share of biofuels in order to improve the security of supply of transport fuel and to reduce CO₂ emissions. The target is to reach a 10% of fuels from renewable sources on energy basis in the transport sector by 2020 and biofuels represent one of the most important options. Bioethanol and biodiesel represent the only biofuels currently available on the market in big quantities and technologically mature. Bioethanol is probably the most broadly employed alternative fuel in the world (mainly in Brazil, USA and Sweden).

An experimental program was carried out at the JRC to investigate the emissions of a flexible fuel vehicle using different ethanol/gasoline blends. In this report we will focus on the effect of fuel ethanol content on exhaust emissions from a Flexible Fuel vehicle and on some issues related to the use of bioethanol as transport fuel.

The test vehicle was a passenger car currently marketed in Europe and one of the most popular models belonging to the flexible fuel vehicle category. Emission tests were carried out both following the European certification procedure (NEDC cycle) and using a US driving cycle (US 06). Regulated and unregulated emissions were measured.

Three different fuels have been tested: a standard commercial summer gasoline marketed in Italy used as base fuel and two gasoline/ethanol blends, which have been obtained by splash blending ethanol in the standard gasoline. The two gasoline/ethanol blends contained respectively 10% ethanol (E10) and 85% ethanol (E85).

In general the repeatability of emission measurements was not very good; only with E85 the measured emission levels were very repeatable. The poor repeatability might be linked to the very sophisticated engine management system which modifies the engine settings depending on the ethanol content of the fuel. Nevertheless sound conclusions can be drawn for the NEDC cycle while for the US 06 this is more difficult due to the limited number of tests performed.

The results have shown that over the European NEDC cycle the vehicle complies with the Euro 4 emission standards with all the fuel with the only exception of CO with fuel E10. In some cases the CO value measured with fuel E10 resulted to be slightly higher than the limit (1 g/km). CO and HC emissions measured over the NEDC cycle with fuel E10 resulted to be higher than with the other two fuels. On the contrary, E85 was the least emitting fuel as far as these emissions are concerned. The influence of fuel composition was instead almost negligible for NO_x emissions. A statically significant increase of NO_x emissions was noticed only in the case of E85 and only over the extra-urban part of the NEDC cycle. CO₂ emissions were reduced by about 4-6% with fuel E85 both over the NEDC and over the US06 cycle.

Similar trends have been found in a recent, major Canadian study, with the only exception that CO emissions were slightly reduced with E10 – a finding that may be explained by the different test cycles. While particulate emissions measured over the NEDC cycle were very low, the PM levels turned out to be quite high over the US 06 cycle. In this case the emissions were comparable to those of a Euro 3 diesel car. This might be due to the very aggressive driving pattern of the US 06 cycle which contains very hard accelerations. In these conditions the engine is likely to work in open loop and with a very rich mixture. The most significant effect of ethanol in the fuel was observed for emissions of carbonylic compounds. This effect increased with increasing ethanol concentration. In particular for acetaldehyde E85 resulted in a more than twenty fold increase in emissions. This represents the main concern associated with the use of flexible fuel vehicles. Comparably with HC emissions, from the speciation of VOCs emissions the fuel E10 resulted to be the most emitting fuel while E85 the least emitting one. E85 resulted in a reduction of 57% of the sum of the speciated VOCs compared to standard gasoline, but with an enrichment of C₂ compounds. Emissions of toxic compounds such as benzene and 1,3-butadiene also decreased when E85 was used instead of standard gasoline. Contributions from ethene and propene prevailed regarding the potential of ozone formation.

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LB-NA-24011-EN-C



ISBN 978-92-79-13627-6

