

Iso-Stoichiometric Ternary Blends of Gasoline, Ethanol and Methanol: Investigations into Exhaust Emissions, Blend Properties and Octane Numbers

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ABSTRACT

Iso-stoichiometric ternary blends - in which three-component blends of gasoline, ethanol and methanol are configured to the same stoichiometric air-fuel ratio as an equivalent binary ethanol-gasoline blend - can function as invisible 'drop-in' fuels suitable for the existing E85/gasoline flex-fuel vehicle fleet. This has been demonstrated for the two principal means of detecting alcohol content in such vehicles, which are considered to be a virtual, or software-based, sensor, and a physical sensor in the fuel line. Furthermore when using such fuels the tailpipe CO₂ emissions are essentially identical to those found when the vehicle is operated on E85. Because of the fact that methanol can be made from a wider range of feed stocks than ethanol and at a cheaper price, these blends then provide opportunities to improve energy security, to reduce greenhouse gas emissions and to produce a fuel blend which could potentially be cheaper on a cost-per-unit-energy basis than gasoline or diesel.

The present work extends the validation process for these blends by presenting exhaust emissions measured from a vehicle fitted with a physical alcohol sensor and operated on several ternary blends equivalent to E85. These results show that existing emissions control technology can easily manage exhaust gas after treatment when a vehicle is operated on such blends. This is an important finding with regard to their manufacturer and regulatory acceptance.

Also, the impact of the methanol-containing nature of ternary blends was investigated. In order to do this, target ternary blends of gasoline, ethanol and methanol were prepared with the low oxygen content Coordinated European Council (CEC) emissions reference fuel CEC RF-02-03 and results of physicochemical analyses are presented. These include water tolerance, blend stability, thermal and oxidative stability, volatility and density. Nitrile rubber, Viton and silicone rubber seal swell properties are presented and discussed. In order to investigate octane effects, iso-stoichiometric blends equivalent to E15 were prepared and analyzed, and utilizing molar octane blending modelling the expected E85-equivalent blend octane indices can be predicted.

As a result of this work observations are made on air-quality and materials compatibility impacts, and the attractiveness of the approach from a governmental and customer view point.

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INTRODUCTION

Around the world, concerns with climate change and energy security have prompted the investigation and introduction of renewable fuels in order to reduce usage of

fossil oil. In the US, the Energy Independence and Security Act of 2007 has mandated that a total of 36 billion US gallons of ethanol be used in the fuel pool by 2022 [1], and in the European Union (EU) the Renewable Energy Directive

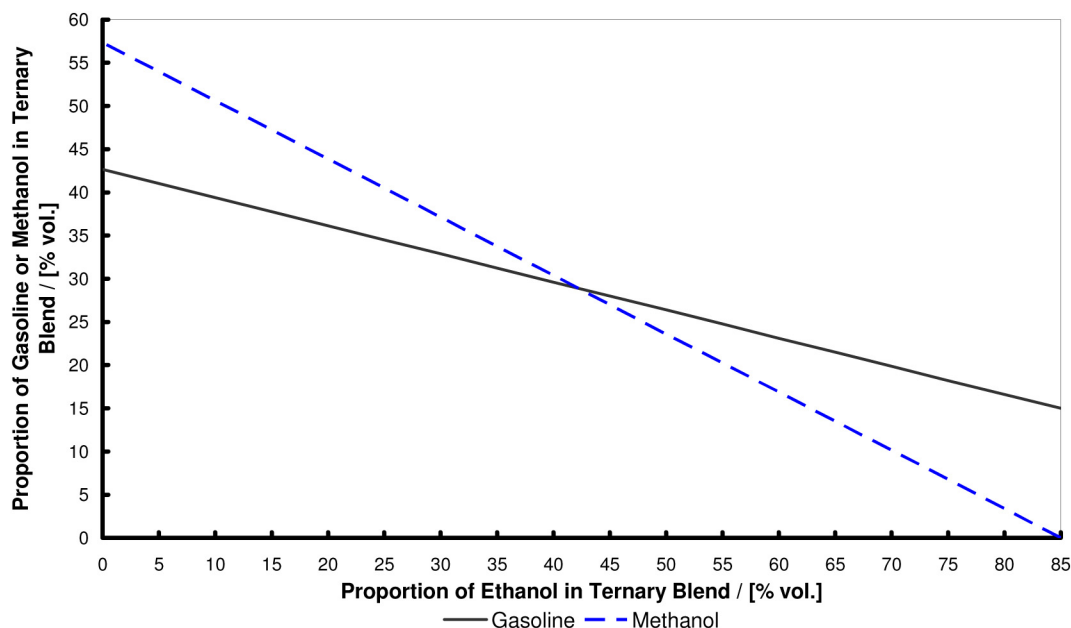


Fig. 1. Relationship between blend proportions of gasoline, ethanol and methanol in iso-stoichiometric ternary blends configured with a stoichiometric AFR of 9.7. Blend ratios determined using the Lotus Fuel Mixture Database [7]

(RED) seeks to establish a minimum proportion of renewable energy in the fuel pool of 10% by 2020 [2].

It is usually imagined that a large proportion of the requirement will be met by blending ethanol into gasoline at a low rate, where it has one visible and one invisible benefit: renewability and energy security, and its octane enhancement, respectively [3]. The fact that it can provide a significant uplift in octane number, which a fuel supplier can then use to his benefit to reduce the volume of any other octane enhancers in the bulk gasoline [4], unfortunately means that its price is kept high and is closely tied to the price of gasoline. Consequently the high price of ethanol means that when it is used at high blend rates to make E85, the price of that fuel is high, too¹.

TERNARY BLENDS OF GASOLINE, ETHANOL AND METHANOL

Gasoline, ethanol and methanol are all miscible together. Previous work by the authors has shown that blending methanol into ethanol/gasoline blends to target stoichiometric air-fuel ratios (AFRs) can create ternary, or three-component, drop-in fuels as alternatives to binary gasoline/ethanol blends. Here we term these fuels 'GEM', after the individual components, and when referred to individually we identify the volume percentage after each identifying letter; hence what is widely known as E85 would be termed G15 E85 M0 in this work. At current prices it is possible to create such

GEM blends usable in E85/gasoline flex-fuel vehicles which are cheaper than gasoline in terms of cost per unit energy and which, when allied to the reported improvement in energetic efficiency when the vehicles are operated on such high-alcohol fuels, can provide an envelope for a pricing structure in which consumers, fuel suppliers and governments could all benefit [5,6].

It has been found that when configured in an 'iso-stoichiometric' manner, such blends have near-identical volumetric lower heating value (LHV), practically the same octane numbers when configured to constant stoichiometric AFRs, and extremely close enthalpies of vaporization (to $\pm 2\%$). [3,5,6]. For a fixed stoichiometric AFR the relationship between the blend components is defined by linear volumetric relationships. In the present paper we mainly concentrate on such 'GEM' ternary blends with a target stoichiometric AFR of 9.7, i.e. that of E85², and Figure 1 shows the volume relationship between the components for this case, as determined using the Lotus Fuel Mixture Database [7]. In this figure one can see that as the ethanol proportion is reduced, so that of the methanol must increase at a rate faster than that of the gasoline proportion. This is because as ethanol is removed, a similar volume unit of the binary gasoline-methanol mixture of equivalent stoichiometric AFR as ethanol (i.e. 9:1) has to be used to replace it; using the volumetric percentage terminology laid down above, this is G32.7 E0 M67.3, as was discussed in detail in [5].

¹Note that commercial E85 is often not configured with 85% ethanol. In summer months the ethanol component may only comprise 77%, and in winter months the gasoline concentration is often increased to 30% to aid cold starting. The composition of the gasoline component is also frequently altered to help in this respect.

²Equally ternary blends targeted at E10, E22, etc. could be arranged.

In [Figure 1](#) note that E85 contains no methanol (as is obvious from the name); that the binary equivalent of E85 for a gasoline and methanol mixture occurs at what might commercially be called 'M56', which is the left hand limit (where no ethanol is present); and the point at which the volumes of gasoline and methanol are equal occurs at approximately 42.5% ethanol. In our work historically we have called the first described Blend A (G15 E85 M0), the second Blend D (G44 E0 M56) and the third Blend B (G29.5 E42.5 M28)³.

Initial experimental results using four such GEM blends in a production vehicle showed that, provided a certain minimum level of ethanol was present, the blends were invisible to the vehicle's on-board diagnostics (OBD) system [5]. This is because ethanol functions well as a cosolvent for gasoline-methanol mixtures. The minimum level of ethanol concentration in a GEM blend was investigated further in a car certified to a higher emissions standard and using a physical sensor as opposed to the virtual sensor the first vehicle used. With the physical sensor car, no minimum requirement for ethanol was identified, despite repeated cold soaks to -20°C and cold start tests [6]. The mode of operation of the two sensing technologies, and how the different characteristics of the blend components ensures they operate satisfactorily, was discussed in detail in [6]. From these two test programmes of work it is presumed that a minimum ethanol concentration is required to ensure satisfactory operation of all of the vehicles in the fleet, since they do not all use the same alcohol sensing technology, and low-temperature phase separation of methanol may affect the virtual sensor vehicles more than the physical sensor ones. Further work to investigate some of the physicochemical characteristics of GEM ternary blends in detail, including phase separation, is planned and will be reported later [8]⁴.

For all their advantages in terms of combustion, alcohol fuels are known to be more aggressive towards certain materials commonly used in the construction of vehicle fuel systems, and a degree of upgrade to some of them has to be carried out. The industry plainly has the knowledge of how to make a flex-fuel vehicle for gasoline-ethanol mixtures because so many have been manufactured (indeed, in the US, at no increase in price to the customer, in reaction to the CAFÉ regulations). Furthermore, since 15,000 vehicles which could be fuelled with M85 or gasoline were in daily use in California [9] the industry understands what needs to be done to facilitate the widespread use of methanol. However, there is no detailed knowledge or understanding of what might happen when the ternary blending approach described above is used. Knowledge of this is important since it has already been shown that when configured to a stoichiometric AFR of 9.7 the fuels are effective drop-in

alternatives to E85 as far as the combustion and control systems are concerned, but the likely level of their aggressivity towards flex-fuel fuel system materials needs to be better understood. A later section of this paper will discuss this in detail. However, in order to gain acceptance with legislators, it is also necessary to show that a correctly-functioning exhaust after treatment (EAT) system can control the emissions of a flex-fuel car such that there is no degradation in exhaust emissions. The next section discusses this.

EXHAUST EMISSIONS FROM TERNARY BLENDS

The properties of the blend fuels used in the vehicle emissions tests discussed in this section are given in [Table 1](#). These blends were all made from a control gasoline which was separately quarantined and analyzed prior to specifying the blends. This gasoline was also used as the control fuel for emissions testing. In [Table 1](#), the mixture densities and volumetric energy content were calculated from

$$\rho = \sum_{i=1}^k \left[\rho_i \left(\frac{V_i}{V} \right) \right]. \quad (1)$$

This leads to the expression for the volumetric energy density of the mixture in the form

$$\rho Q_{\text{LHV}} = \sum_{i=1}^k \left[\rho_i \left(\frac{V_i}{V} \right) Q_{\text{LHV}i} \right]. \quad (2)$$

If density, ρ , is expressed in units of [kg/l] and the energy content, Q_{LHV} , is expressed in units of [MJ/kg], the units of volumetric energy density are [MJ/l]. There are theoretical limitations to the use of this simple approach which are caused by the non-linear molecular packing characteristics of the different molecules contained in the blends, which ultimately can be characterized by measuring the partial molar volumes of some of the mixtures considered. However, mixture density measurements made by Sasol showed that there was no appreciable effect of this phenomenon for the E15-equivalent blends (see later). The results shown in the present work are testament to the fact that the simplistic approach defined above is easily sufficient to enable a modern FFV to operate on the E85-equivalent blends without activating any vehicle malfunction indicator lights. Future work is intended to quantify the effect of molecular packing in the E85-equivalent blends.

More details on the fuel blends used for this work, and the rationale behind their choice, can be found in [Appendix 1](#) and [\[5,6\]](#). The E15-equivalent blends were only assessed for

³When referred to as blend names and ratios in this manner, the figures refer to the volume percentages of each component.

⁴Note that it is possible to produce ternary blends of other alcohols with gasoline, should their use be beneficial with regard to the utilization of all available feed stocks, or even quaternary (or higher number) blends; examples of these may be mixtures of gasoline, methanol and butanol with or without ethanol respectively.

Table 1. GEM ternary blend components (top) and fuels (bottom) used in the vehicle tests described. Properties calculated using Lotus Fuel Mixture Database [7] or measured to the relevant ASTM standards where applicable

Fuel Component	Gasoline	Ethanol	Methanol
Formula	Various	C ₂ H ₅ OH	CH ₃ OH
Stoichiometric AFR	14.18	8.96	6.44
Density (kg/l)	0.731	0.789	0.791
Gravimetric LHV (MJ/kg)	43.12	26.80	19.90
Volumetric LHV (MJ/l)	31.52	21.15	15.75
Carbon Intensity (gCO ₂ /l)	2297.3	1509.7	1088.0
Carbon Intensity (gCO ₂ /MJ)	72.88	71.38	69.10
RON (to ASTM D2699)	95.3	108.6	108.7
MON (to ASTM D2700)	85.0	89.7	88.6
Sensitivity	10.3	18.9	20.1

Fuel Blend	Blend A	Blend C	Blend D4	Blend D
GEM Component Ratios (by volume percentage)	G15 E85 M0	G37 E21 M42	G40 E10 M50	G44 E0 M56
Equivalent GEM Component Ratios (by molar percentage)	G6.68 E93.32 M0	G15.51 E21.73 M62.76	G16.92 E10.25 M72.83	G18.19 E0 M81.81
Stoichiometric AFR	9.69	9.71	9.65	9.69
Density (kg/l)	0.781	0.769	0.767	0.765
Gravimetric LHV (MJ/kg)	29.09	29.56	29.46	29.66
Volumetric LHV (MJ/l)	22.71	22.71	22.60	22.69
Carbon Intensity (gCO ₂ /l)	1627.9	1623.9	1613.9	1620.2
Carbon Intensity (gCO ₂ /MJ)	71.69	71.49	71.42	71.41
RON (to ASTM D2699)	107.4	106.4	105.6	106.1
MON (to ASTM D2700)	89.7	89.3	89.0	89.0
Sensitivity	17.7	17.1	16.6	16.2

physicochemical properties and no vehicle tests were carried out on these. The primary objective was to obtain reliable octane data that could be used to accurately estimate octane

values of the E85-equivalent GEM blends as discussed below.

The emissions cycle chosen for this test was the New European Drive Cycle (NEDC). [Table 2](#) shows the legislated maxima at Euro 5⁵.

Table 2. Euro 5 emissions limits when tested on the New European Drive Cycle

CO	HC	NMHC	NOx
g/km	g/km	g/km	g/km
1	0.1	0.068	0.06

The vehicle used was a production Saab 9-3 BioPower, fitted with a turbocharged 2.0 litre port-fuel injection engine capable of operating on gasoline or E85 or any mixture of the two. Further details on this are included in [Appendix 2](#). It also had an automatic gearbox and was certified to Euro 5 emissions level. No modifications were made to the vehicle for any of the tests discussed here, and it operated with the production OBD system fully operational throughout, since one of the reasons for conducting the test was to test the hypothesis that it is possible to configure iso-stoichiometric ternary blends that are invisible to the engine management system of any vehicle already calibrated to operate on gasoline-ethanol blends.

The vehicle was prepared in the same manner for each fuel blend and the same test procedure was followed for all tests. Each fuel blend was tested over two days, with a cold ambient test and a hot test being conducted on each day; however, only the cold test results are reported here since those are the only ones relevant to emissions testing. The requisite adaptation of the vehicle engine management system (EMS) to each test alcohol blend was achieved during the vehicle pre-test conditioning cycle. The overall procedure employed was:

1. Drain tank and fuel system completely.
2. Fill with 25 litres of the new test fuel blend.
3. Present the car at the Emissions Laboratory where a pre-test conditioning procedure was conducted before the overnight soak. In [\[5\]](#), this was found to be sufficient to achieve adaptation of the engine management system.
4. The next morning, run a cold NEDC test followed by a hot test.
5. Leave the car in the Emissions Laboratory overnight.
6. The next morning, run a cold NEDC test followed by a hot test.
7. Remove the car and repeat the process for the next test fuel from step 1.

A photograph of the test vehicle on the rolling road dynamometer during testing is shown in [Figure 2](#). The order in which the fuel blends were tested was firstly gasoline, then Blend A (G15 E85 M0), C (G37 E21 M42), D (G44 E0 M56) and finally D4 (G40 E10 M50), followed by a repeat test of the gasoline to check test variability. CO₂ emissions and efficiency from the vehicle are reported in detail in [\[6\]](#). In summary it was found that the vehicle delivered lower tailpipe CO₂ and greater efficiency when operated on the alcohol fuel blends, with broadly comparable results for each. This was a similar result to that found with the earlier, Euro 4 emissions level car which used a virtual alcohol concentration sensing system [\[5\]](#).

During these tests no malfunction indicator lights (MILs) were illuminated and the vehicle functioned and drove perfectly regardless of fuel blend use. When operated on the alcohol blends, the 'BioPower' meter on the dashboard continually indicated that the vehicle believed it was fuelled with an E85 blend, regardless of which GEM ternary blend was actually being used. Further details of this, and related cold start tests at -20°C, can be found in [\[6\]](#).

Emissions from these tests are shown in [Figures 3, 4, 5, 6](#), in all of which the highest value on the y-axis represents the legal maximum for the Euro 5 emissions level; hence, from inspection of the figures, the proportion of the legal maximum can be gauged. [Figure 3](#) shows the carbon monoxide (CO) emissions, [Figure 4](#) the total hydrocarbon (HC) emissions, [Figure 5](#) those for non-methane hydrocarbons (NMHCs) and [Figure 6](#) those for oxides of nitrogen (NOx).

From the results of [Figures 3, 4, 5, 6](#) it can be seen that the vehicle had no problem delivering legal emissions when operated on the four ternary GEM fuels as well as gasoline, i.e. that the EAT system functions equally well regardless of the fuel used. This is to be expected given the basic mode of operation of three-way catalysis. Also, an outlying fuel consumption result (and related tailpipe CO₂ and energy utilization) seen when the vehicle was operated on Blend A on the second day and reported in [\[6\]](#) is also seen in the results for the regulated emissions reported here, giving credence to disregarding those results in that work because they are not in line with the rest of the values for the alcohol blends. The reasons for this difference in results is unknown since the vehicle performed with exactly the same driveability for all tests and no MILs were illuminated during testing at all; however, it should be noted that a human driver and not a robotic one was used and this is known to increase test-to-test variation (even though the same driver drove all tests).

Specifically, CO emissions are broadly comparable across all of the fuels tested. For HC emissions, and disregarding the

⁵Note that the limits for Euro 5 stated in [Table 2](#) also apply at Euro 6; the major difference for spark-ignition engines at Euro 6 level is that there are additional particulate number limits. Euro 5 came into effect in September 2009 and Euro 6 will come into effect in September 2014. The only difference between the primary pollutant emissions limits in [Table 2](#) and those for the earlier Euro 4 emissions level is that at Euro 4 the NOx emissions limit was 0.08 g/km.



Fig. 2. Photograph of Saab 9-3 BioPower test vehicle on the dynamometer rolls during emissions testing

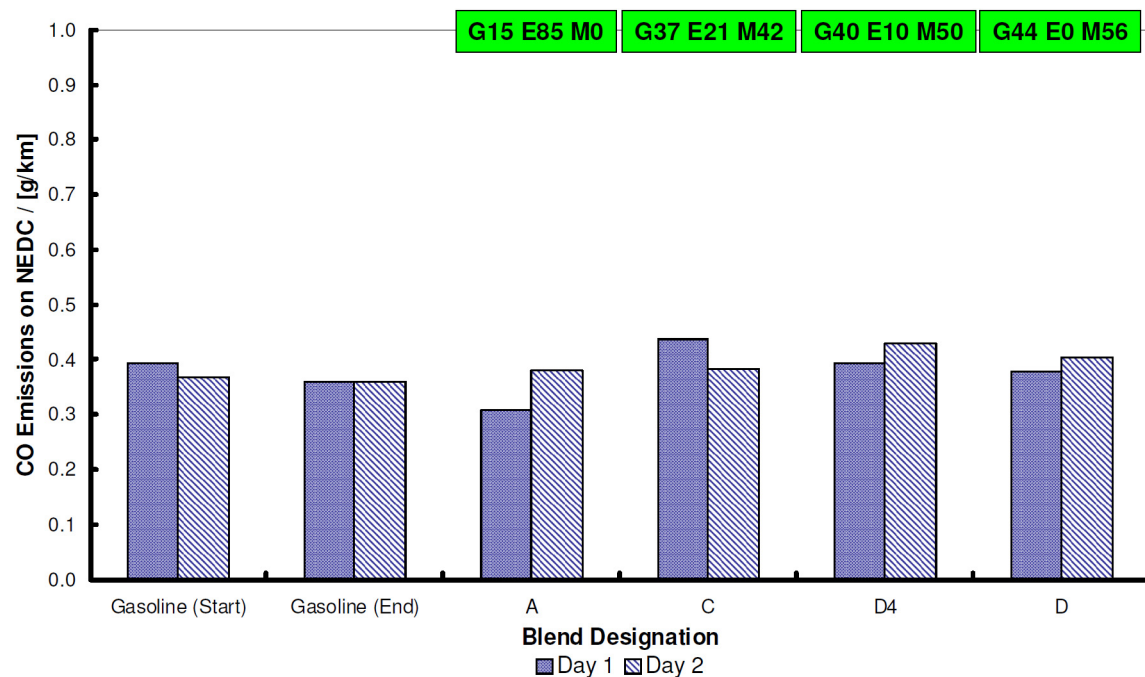


Fig. 3. Drive cycle tailpipe carbon monoxide emissions for the control gasoline and four GEM blends tested during NEDC tests.

Note: height of y-axis represents Euro 5 legal limit (see Table 2)

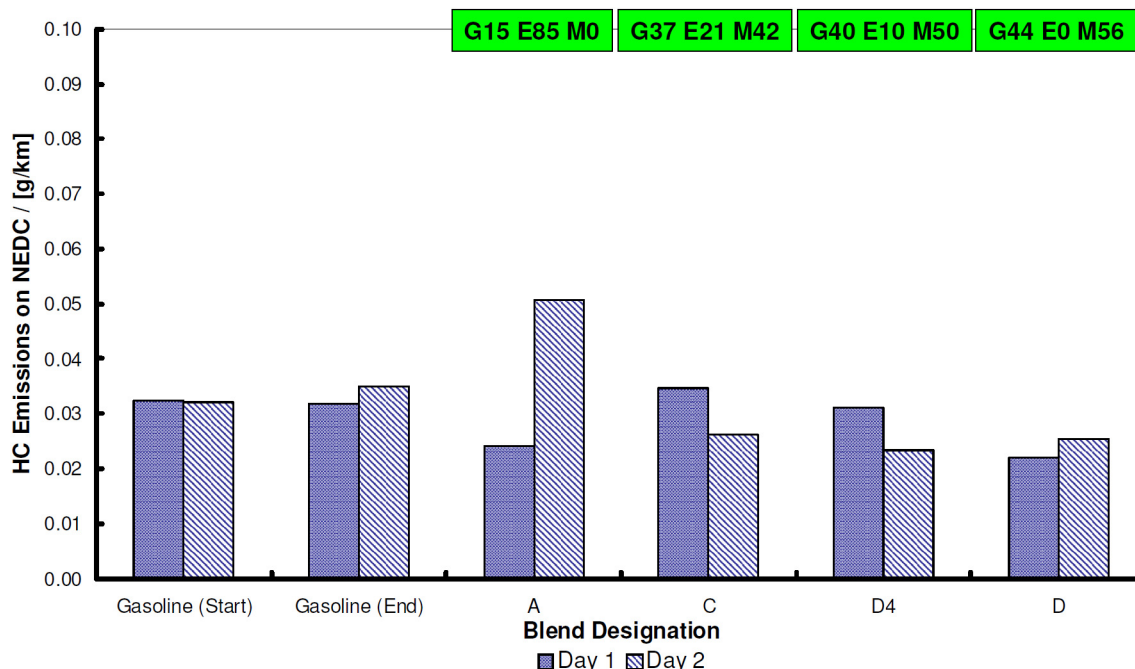


Fig. 4. Drive cycle tailpipe hydrocarbon emissions for the control gasoline and four GEM blends tested during NEDC tests.
Note: height of y-axis represents Euro 5 legal limit (see Table 2)

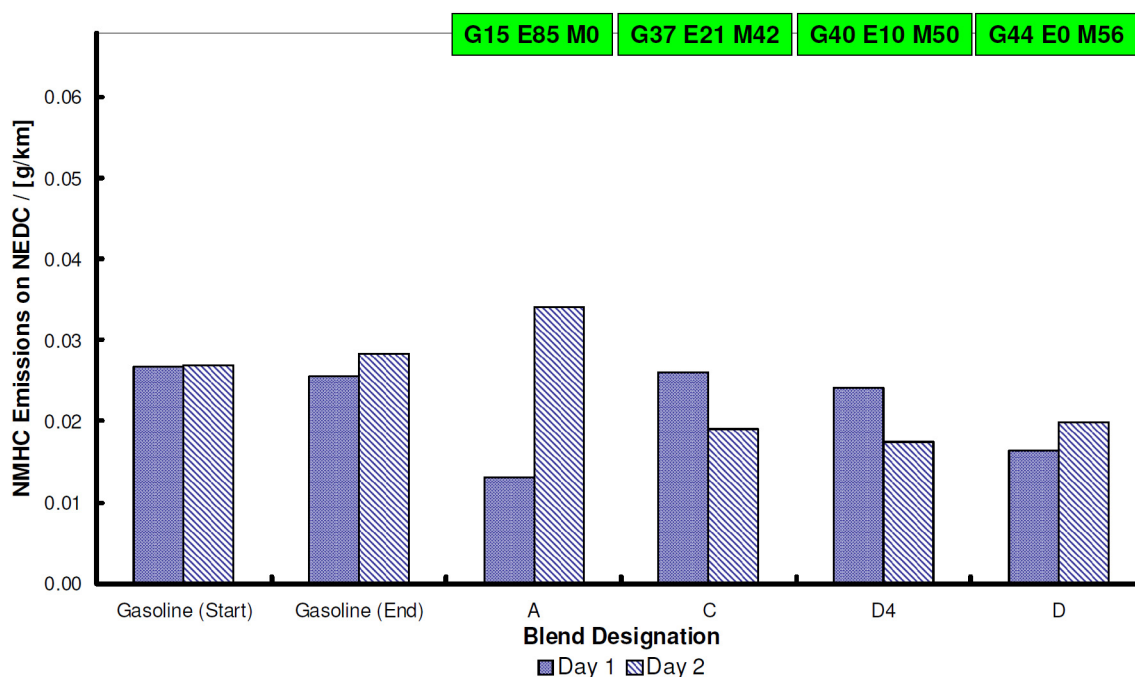


Fig. 5. Drive cycle tailpipe non-methane hydrocarbon emissions for the control gasoline and four GEM blends tested during NEDC tests.
Note: height of y-axis represents Euro 5 legal limit (see Table 2)

Blend A (G15 E85 M0) emissions results from the second day, one can say that when a ternary blend is used, the vehicle behaves in a broadly identical way regardless of the alcohol fuel it is operated on; in fact, the HC emissions are lower than gasoline (see later). NMHC emissions follow a

similar trend. As would be expected, NO_x emissions are extremely low when the engine is operated on the alcohol fuels. Finally, note that aldehyde speciation was not available for this series of tests; this is planned for later work.