Evolution of alcohol fuel blends towards a sustainable transport energy economy

J.W.G. Turner and R.J. Pearson
Lotus Engineering

E. Dekker
BioMCN

B. Iosefa
Methanex Corporation

G.A. Dolan
Methanol Institute

K. Johansson and K. ac Bergström
Saab Automobile Powertrain AB

ABSTRACT

Work undertaken by Lotus Engineering and partners has shown that the miscibility of the low-carbon-number alcohols with gasoline provides a powerful tool to enable the introduction of methanol as a transport fuel in a wholly evolutionary manner. This is primarily facilitated by the fact that the CAFÉ regulations in the US (together with other incentives in other countries, such as Sweden) have created a situation in which there are 7-8 million E85/gasoline flex-fuel vehicles on the roads there, for which insufficient E85 can be provided at an affordable price. This paper will show that the introduction of methanol (which can be made extremely simply and cheaply from natural gas) into gasoline-ethanol mixtures, can be used to create drop-in fuels equivalent to E85 and can bring the price of an alcohol-based fuel for spark-ignition engines down to less than that of gasoline (on a per-unit-energy basis, before tax is applied). It can thus more than compete with that fuel. This opens up the possibility of using the US's reserves of naturally gas (be it conventional or unconventional types such as shale) immediately to manufacture methanol to displace gasoline, as a bridge to a broader energy economy based on higher concentrations of methanol made from renewable sources.

The vehicle work conducted has shown the possibility of realizing this state of affairs, and related laboratory tests on some of the potential fuel blends have similarly demonstrated that they possess some of the necessary characteristics to be truly 'drop-in' alternatives to E85. These necessary characteristics are considered to be equal volumetric energy content (to enable compliance with on-board diagnostics requirements), equal octane numbers and latent heat (to provide invisibility to the combustion and air handling systems), and inherent miscibility with gasoline (to avoid the requirement to change the fundamental nature of the vehicle fuel system). A further requirement in practice is that the vehicles still be of adequate performance with regard to tailpipe emissions standards using the existing exhaust after treatment systems fitted to them. In the present work this is demonstrated by reporting data for oxides of nitrogen emissions (NOx) taken from a standard production Saab 9^3

certified to the EU5 emissions standard using ternary blends (such NOx emissions being especially important from a human health point of view in built-up areas), which shows that generally such emissions are significantly lower for all of the alcohol blends than for gasoline. All results are found to be well within the EU5 limits, with the gasoline results showing that the after treatment system was indeed functioning correctly.

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

The conversion of fossil hydrocarbons to carbon dioxide (CO_2) causes atmospheric levels of greenhouse gas to increase, which, due to the fact that much of the world's oil supply comes from areas outside of those of the main consumer regions, gives rise to a further concern with respect to security of energy supply.

The European situation is complicated by the facts that diesel penetration in the vehicle pool is high (at approximately 50% in the light-duty sector) and the volume of bio components in diesel which it is practical to include in the fuel is limited to approximately 7% by volume if future emissions standards are to be met. Together these imply that the proportion of ethanol blended into gasoline in Europe will have to be approximately 13% *by energy*, which equates to ~20% by volume as a result of the lower volumetric lower heating value (LHV) of ethanol versus gasoline. Although most current vehicles fitted with spark-ignition (SI) engines can accept 10% by volume ethanol as standard (a situation essentially initiated by the presence of 10% ethanol in gasoline in wide areas of the US), 20% is beyond their capability. Realization of this fact, coupled to the impending fines on the fuel suppliers if they do not meet their legal obligations under the RED, has prompted calls by one oil major to give vehicle OEMs credits in terms of tailpipe CO_2 for any E85[1]/gasoline flex-fuel vehicles that they manufacture, in order to produce a larger market for high-blend-concentration ethanol fuels [3].

This situation is desirable since selling large volumes of ethanol is probably the most pragmatic way for the fuel suppliers to comply with the requirements of the RED and the related Fuel Quality Directive (FQD) (which defines minimum standards before a fuel can be considered a biofuel). In actual fact, the EU vehicle tailpipe CO_2 fines system does presently allow a 5% reduction in tailpipe CO_2 to be claimed for any flex-fuel vehicle that an OEM sells, provided one-third of the fuel forecourts in the country in which it is sold has at least one E85 pump [4]. It could be said, therefore, that the potential remedy to the RED impasse for the fuel suppliers is in fact in their own hands. Furthermore, for a theoretical vehicle at the 2011 EU average of 145.1

---

[1] Throughout this paper, the use of E followed by a number refers to the proportion *by volume* of ethanol in a blend. The same applies for M (methanol) and G (gasoline). Thus E85 is nominally 85% ethanol in bulk gasoline (a high blend rate), and E10 is 10% ethanol in bulk gasoline (a low blend rate).

gCO_2/km, and at the highest proposed fine rate in 2015 of €95/gCO_2, this represents a saving to the OEM of €689 per car, which the authors contend is significantly greater than the costs of modifying a standard gasoline-fuelled vehicle to be flex-fuel with E85 in the first place. Thus all of the notional prerequisites are in place for ethanol to become a major transport fuel, which begs the question as to why this should not already be so.

Ethanol as a minor blend component in gasoline has two main benefits: firstly, there is the renewability and energy security factor, and secondly it is an excellent octane enhancer, in part because of its high heat of vaporization [5]. This latter fact means that even at low blend rates of 5-10% it can provide a significant uplift in octane number, which concomitantly means that a fuel supplier can reduce the volume of other octane enhancers in the bulk gasoline [6], reducing its net price and increasing profits. Unfortunately this low blend effect means that the price of ethanol is kept high and is closely tied to the price of gasoline. Thus, when it is used at high blend rates to make E85, there is little decontenting possible in the gasoline comprising the remaining 15% of the fuel; in fact, in commercial E85, the bulk gasoline often has to have its composition altered to facilitate cold starting, ethanol being a difficult fuel in this respect[2].

Hence, any mechanism to offset the high price of ethanol while still permitting its use in large volumes across the fuel pool will be of benefit to the fuel suppliers and, if they are encouraged to put pumps with the necessary capability on sufficient fuel station forecourts it would also be of benefit to OEMs selling in the EU, providing fuel renewability factors as mandated by the RED and FQD are adhered to. If the resulting fuel was cheaper than gasoline to use in terms of operating cost the consumer would readily move to its use. Approached in terms of taxation per unit energy, migration to this situation could be achieved without a reduction in tax take for governments, together with no requirement for direct subsidies, which are necessary in the case of electrification of the vehicle fleet. Hence all stakeholders could benefit if a suitable introduction mechanism could be found.

At the same time, the biomass limit for ethanol production has been used by some as a reason not to pursue alcohol fuels for transport, since only about 27% of the energy required can be gathered within it (this figure varies country by country)[3]. The biomass limit only applies to fuels made using biological processes (such as bioethanol and biodiesel). In fact, using thermochemical processes, it is possible to manufacture liquid fuels from anything containing carbon and hydrogen via Fischer-Tropsch chemistry or a syngas-to-methanol-to-gasoline (or similar) process. Thermochemical routes therefore open up the possibility of using more waste as a carbon feed stock, meaning that the amount of renewable fuel which could be manufactured moves beyond the biomass limit and prevents more conventional biofuels from being regarded as a strategic dead end. As an end game, in order to cover the full amounts of energy necessary for transport, atmospheric CO_2 and

---

[2] Note that commercial E85 is often not configured with 85% ethanol; US limits are 51-83% by volume. Generally, in winter months ethanol concentration is often reduced to 70% to aid cold starting, and even in summer months the ethanol component may only comprise 77%.

[3] It is interesting to contrast this with the fact that even in optimistic scenarios electric vehicles are not expected to penetrate to more than 10% in the short term, yet that is *not* seen as a reason not to pursue them vigorously.

molecular hydrogen could be used as the physical ingredients to carry renewable energy either in liquid or gaseous form [7-9].

Thus there exist various possibilities to increase renewable fuel supply as a result of the miscibility between gasoline and the alcohols, the fact that a liquid fuel infrastructure already exists, that the necessary vehicles also exist and are cheap to manufacture, and that the feed stocks required are not limited if the necessary technologies can be developed. The only thing missing is to construct a route to enable this scenario to play out, with the necessary fuel and vehicle specification changes linked to it. A first step along this road to energy security and sustaianability would be to employ ternary (three-component) blends of gasoline, ethanol and methanol.

TERNARY BLENDS OF GASOLINE, ETHANOL AND METHANOL

Gasoline, ethanol and methanol are all miscible together and ternary (i.e. three-component) blends can be configured to have the same target stoichiometric air-fuel ratios (AFRs) as any binary gasoline-ethanol blend. In the present paper we concentrate on such 'GEM' ternary blends with a target stoichiometric AFR of 9.7, i.e. that of E85, but equally ternary blends targeted at E10, E22, etc. could be arranged. For a fixed stoichiometric AFR the relationship between them is defined by linear volumetric relationships and this has been discussed in detail in earlier publications [10,11]. Furthermore, when configured in an iso-stoichiometric manner, all such blends have near-identical volumetric lower heating value (LHV) and practically the same octane numbers when configured to constant stoichiometric AFRs; they also have extremely close enthalpies of vaporization (to +/- 2%). For the case of a stoichiometric AFR of 9.7:1 the volume relationship between the components is shown in Figure 1, as determined using the Lotus Fuel Mixture Database [12]. In this figure one can see that as the volume percentage of ethanol is reduced, so the rate of increase of the methanol proportion is faster than that of the gasoline proportion. This is because as one volume unit of ethanol is removed, a volume unit of the binary gasoline-methanol mixture with the same stoichiometric AFR as ethanol (i.e. 9:1) has to be used to replace it, and the necessary volume ratio of gasoline:methanol is 32.7:67.3, as discussed in detail in [10].

Several points of interest arise from Figure 1: firstly (and most obviously) is that E85 contains no methanol; secondly, that the binary equivalent of E85 for a gasoline and methanol mixture occurs at volume percentages of 44 and 56, respectively (i.e. the left hand limit, where no ethanol is present); and thirdly, the ratio where the proportion of gasoline and methanol are equal occurs at approximately 42.5 volume percent ethanol. Aspects related to this will be returned to later.

Initial experimental results using four such GEM blends in a production vehicle showed that, provided a certain minimum level of cosolvent was present, the blends were invisible to the vehicle's on-board diagnostics (OBD) system [10]. Ethanol performs the cosolvency function in gasoline-methanol mixtures, and the minimum level of ethanol concentration in a GEM blend was further investigated in a car certified to a higher emissions standard and using a different alcohol concentration sensor technology (actually a physical sensor as opposed to the virtual sensor the first vehicle used). Here, no such minimum requirement for ethanol was identified, despite repeated cold soaks to -20°C and cold start tests [11]. From these pieces of work it is presumed that a minimum ethanol concentration is needed to ensure satisfactory operation of all of the vehicles in the fleet, since they do not all use the same alcohol sensing technology.

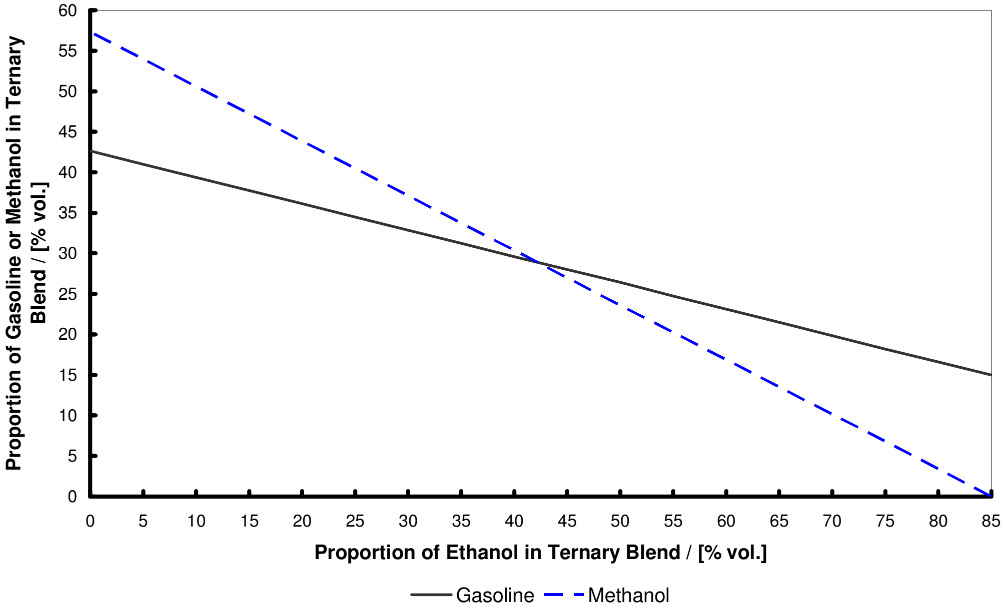

Fig. 1: Relationship between blend proportions of gasoline, ethanol and methanol in iso-stoichiometric ternary blends configured with a stoichiometric AFR of 9.7. Blend ratios determined using the Lotus Fuel Mixture Database [12]

Note 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. It is intended to investigate blend ratios of these in a later publication [13].

TEST FUELS, VEHICLE AND EXPERIMENTAL RESULTS

Test Fuels

The fuel blends used were as described in Table 1. Note that the terminology used to describe the blends from this point hence in this paper is as follows: G, E and M refer to gasoline, ethanol and methanol, and the percentage proportion by volume is given after each letter (i.e., GEM component ratios). Hence E85 would be G15 E85 M0 and from Figure 1 the binary equivalent using gasoline and methanol only would be G44 E0 M56. The blends were given the names shown in the table.

Several points of interest arise from the choice of these fuel blends. Blend C takes the same amount of ethanol as was used to make one volume unit of Blend A (the commercial E85 surrogate) and spreads it across four times the volume of fuel. Similarly, Blend D4 takes the same volume of ethanol and spreads it across 8.5 times the volume of fuel. Thus, if the amount of ethanol that can be supplied is constrained for any reason – by feed stock supply, a desire to avoid interference with the food chain, or concern over indirect land use change (ILUC), for example – one can extend how far the limited amount of ethanol can reach into the fuel pool by introducing methanol in a ternary blend with it. The situation is improved if the methanol used is better, from an energy security or carbon intensity perspective, than gasoline. It should be pointed out that this is effectively the situation in the US, if one considers that the Energy Independence and Security Act mandates the production of a specified amount of ethanol. This can be coupled to the recent shale gas finds and the ease with which methane can be turned into methanol, and is synergistic with the fact that there exist many more vehicles which can take high-alcohol blend fuels than currently use them. The subjects of gasoline displacement and cost will be returned to in the Discussion.

Table 1: GEM ternary blend fuels used in the vehicle tests described. Properties calculated using Lotus Fuel Mixture Database [12] or measured to the relevant ASTM standards where applicable

Original Blends				
Fuel	**Blend A**	**Blend C**	**Blend D4**	**Blend D**
GEM Component Ratios	G15 E85 M0	G37 E21 M42	G40 E10 M50	G44 E0 M56
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

Test Vehicle and Facility

A production flex-fuel Saab 9[3] BioPower station wagon was used for these tests. This vehicle was fitted with an automatic gearbox and was certified to Euro 5 emissions standards. It was tested on the rolling road dynamometer at Lotus Engineering and was operating with the standard production flex-fuel calibration and OBD system. The drive cycle used was the New European Drive Cycle (NEDC). Two gasoline baseline results were taken before and after the tests, and the order in which the fuels were tested was gasoline, Blends A, C, D, D4 and then the repeat of the gasoline tests.

The same procedure was followed for each test fuel, in line with the requirements for testing vehicles on the NEDC. Each fuel was tested twice on sequential days, and on each day a hot NEDC test was conducted after the cold test. Only the cold test results will be reported here, since this is what is used to determine the emissions compliance of a vehicle. The Euro 5 oxides of nitrogen (NOx) emissions limit is 0.06 g/km [14][4].

---

[4] Note that the NOx limit for Euro 5 regulations stated also applies 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.

Experimental Results

Figures 2 and 3 show the fuel consumption (in miles per US gallon[5]) and tailpipe CO_2 emissions (in terms of gCO_2/km, which is the parameter used to establish a manufacturer's total tailpipe CO_2 emissions for the purposes of establishing any fiscal penalties in Europe, weighted by sales volume [4]), respectively. Figure 4 shows the energy utilization of the vehicle, calculated using the data in Table 1.

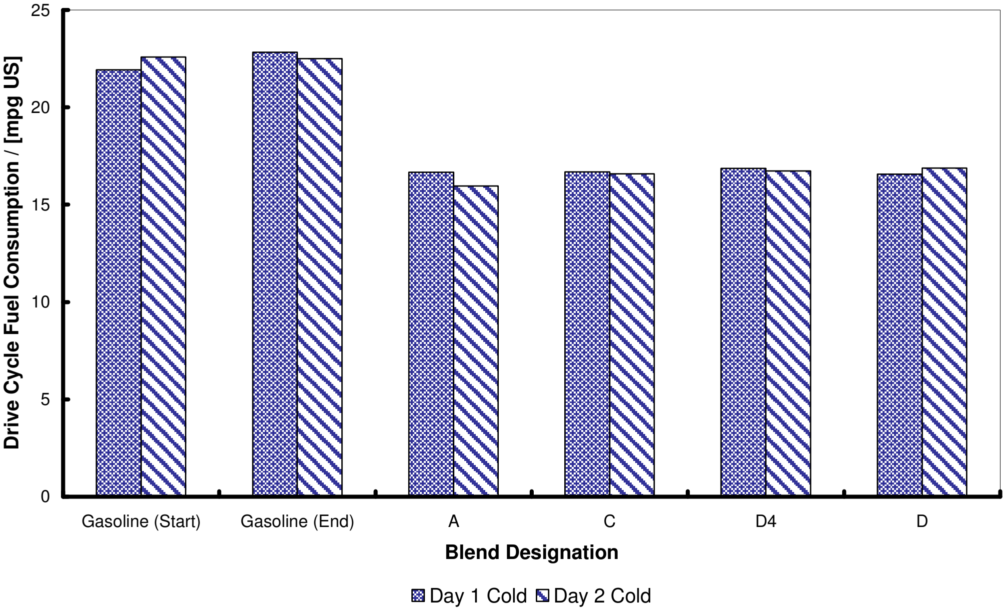

Fig. 2: Production flex-fuel vehicle fuel consumption (in terms of miles per US gallon) when operated on four GEM blends and gasoline on the New European Drive Cycle. Vehicle certified to Euro 5 emissions level

From the data in Figure 4 one can see that the vehicle was energetically more efficient when operated on the alcohol blends than it was when operated on gasoline. The result for the second cold test on Blend A (G15 E85 M0) is considered a slight outlier, but nevertheless (and disregarding the Blend A result from the second day) the improvement in energy utilization across all of the alcohols was 2.8-4.9% for the first day and 2.0-3.4% for the second day [15]. This improvement in energy utilization was echoed in a higher result when the vehicle was hot in earlier work with a car with a different alcohol sensing system and certified to an earlier emissions level (Euro 4), where 3-5% improvement was seen when the vehicle was warm [10]. The implications are that there would be a reduction in energy consumption from a fleet of vehicles using such alcohol blends versus gasoline, with obvious advantages if those fuels were to have to be synthesized in the future from another feed stock, e.g. from shale gas.

---

[5] In order to convert miles per US gallon to miles per Imperial gallon, divide the data in Figure 2 by 0.833.

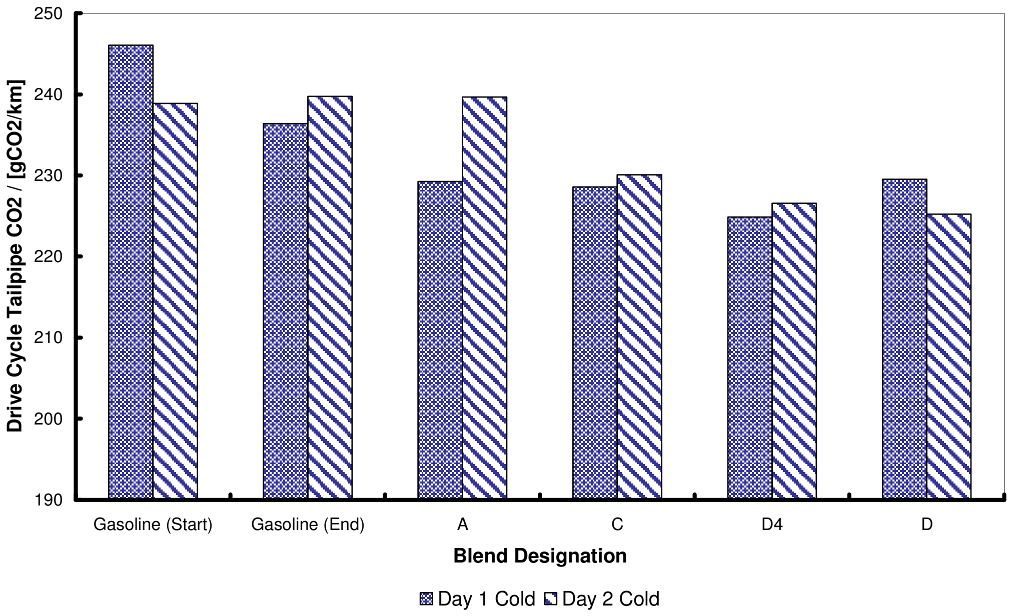

Fig. 3: Production flex-fuel vehicle tailpipe CO_2 emissions (in terms of gCO_2/km) when operated on four GEM blends and gasoline on the New European Drive Cycle. Vehicle certified to Euro 5 emissions level

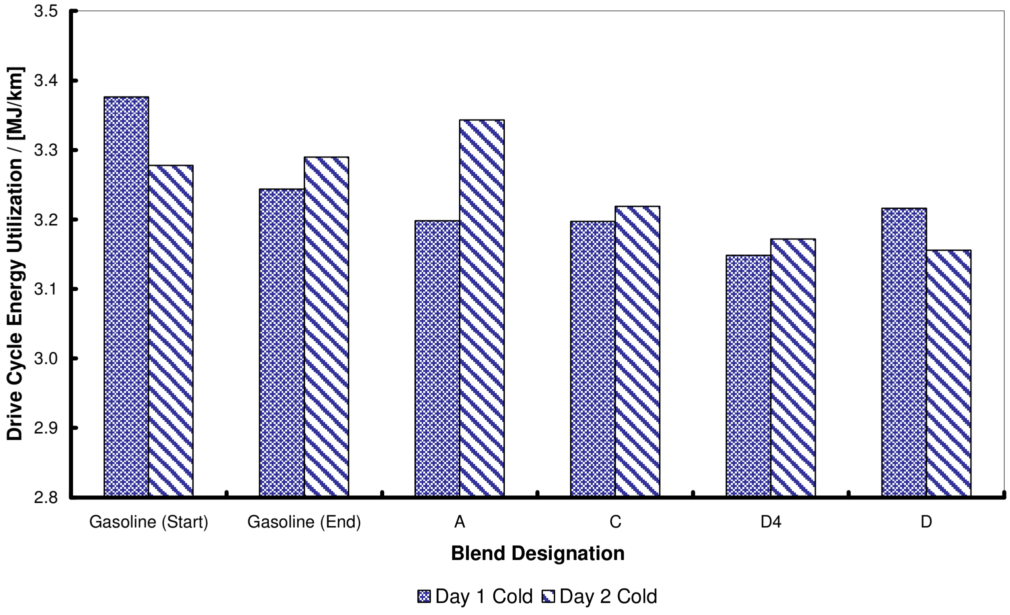

Fig. 4: Production flex-fuel vehicle drive cycle energy utilization (in terms of MJ/km) when operated on four GEM blends and gasoline on the New European Drive Cycle. Vehicle certified to Euro 5 emissions level. Data calculated from tailpipe CO_2 emissions shown in Figure 3 using the Lotus Fuels Mixture Database [12]

Results for NOx emissions are shown in Figures 5(a) and 5(b), in absolute terms and as an average percentage of the regulated maximum of 0.06 g/km, respectively.

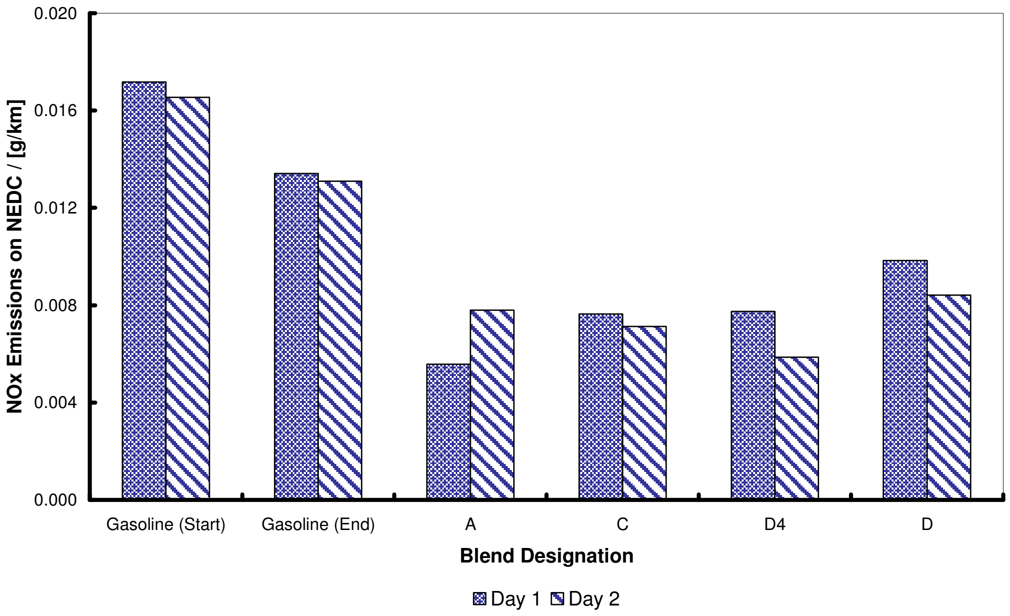

Fig. 5(a): Production flex-fuel vehicle tailpipe NOx emissions in g/km when operated on four GEM blends and gasoline on the New European Drive Cycle. Vehicle certified to Euro 5 emissions level

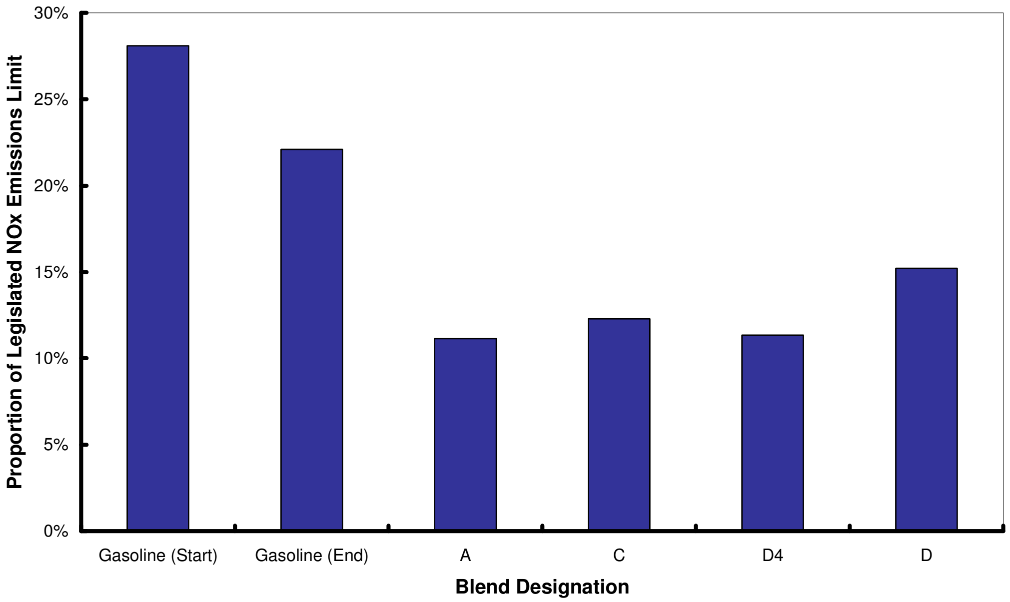

Fig. 5(b): Production flex-fuel vehicle averaged tailpipe NOx emissions as a proportion of the maximum permitted value when operated on four GEM blends and gasoline on the New European Drive Cycle. Vehicle certified to Euro 5 emissions level

From the results of Figure 5 it can be seen that the vehicle has no problem delivering legal NOx emissions when operated on the four ternary GEM fuels. The average of the four alcohol blend fuels is 0.0075 g/km, and is over 50% less than the average of the two gasoline tests (0.0151 g/km). Additionally, the results of all the fuels are less than 30% of the legislated maximum for NOx of 0.06 g/km, which is significantly lower than the normal engineering target of 50% to ensure compliance of the whole fleet over the lifetime of the vehicles. (Note that after catalyst light-off there will be virtually zero emissions anyway due to the conversion efficiency of three-way-catalysts.) Therefore, from these results there is likely to be little concern with regard to NOx emissions when existing flex-fuel vehicles are operated on any of the GEM ternary blends. Results for hydrocarbon and carbon monoxide emissions will be reported in a later publication.

Finally, the vehicle exhibited no driveability problems when using any of the ternary blends, and the on-board diagnostics were not upset, as shown by the fact that there was no malfunction indicator lamp (MIL) activity on the dashboard, regardless of fuel blend used. Approximately 1500 km were covered on a wide range of the GEM fuels (both as specific blends and as general tankfuls of one blend following another) and it always started well and has done so ever since as far as the authors are aware. For more details of this, plus the cold-temperature operation testing that was carried out, see [11].

DISCUSSION

The results presented here suggest that ternary blends can be true drop-in alternatives to E85, and that the NOx exhaust emissions important to human health will be lower than those for gasoline. This is important when considering how they can help with energy security in countries where they can be manufactured from indigenous feed stocks, such as is the case with the recent shale gas finds in the US [16], which create an opportunity for it to become more energy independent. The scale of the opportunity was illustrated by Moniz *et al.* [16], who estimated that with recent finds the total US reserves of natural gas equal 92 times the current annual consumption, and thus these resources can provide a bridge to a low-carbon future. From this work, the issue of how to apply this opportunity to increase energy independence to transport (which is especially reliant on imported oil) is one that can be addressed by two routes in terms of making liquid energy carriers: full Fischer-Tropsch (FT) synthesis of liquid hydrocarbon fuels, or conventional methanol synthesis from natural (shale) gas.

While full FT synthesis produces drop-in fuels for all vehicles (including ships and aircraft), direct methanol synthesis is a more efficient means of converting methane to a liquid fuel, and furthermore, requires less investment in plant and is economical on a smaller scale. An extension of this could see small, economical methanol plants feeding the fuel pool with their products directly (via ternary blending) or providing methanol as a feed stock for larger methanol-to-synfuels (MtSynFuels) plants. This might help to open up some more of the stranded shale gas fields because of the relative ease of transporting energy dense liquids over distance.

If the methanol produced in this manner is introduced in the near-term via the ternary blending approach discussed above, one can extend the available ethanol significantly and displace more gasoline. For illustrative purposes, there follows an assessment of how much methanol fuel could be used. Of the 36 billion US gallons of ethanol which the US Energy Independence and Security Act mandates for 2022, some can be blended into gasoline. Currently the permitted level is 10%, although EPA is moving towards 15% in the future for 2001 and newer light-duty motor vehicles (subject to certain conditions) [17]. Assuming that 140 billion US gallons of gasoline are used for light-duty vehicles from 2016 onwards[6], and that ~12% of it by volume is ethanol (most in E10 but some in E15), let us assume that there will be 19 billion US gallons available for flex-fuel vehicles, which, at an E85 blend rate of 85% (disregarding the fact that less ethanol is typically used in commercial E85 in the winter months), implies that 22.4 billion gallons of E85 could be supplied.

These 22.4 billion gallons of E85 are equivalent in energy terms to 16.1 billion gallons of gasoline, although they do contain 3.4 billion gallons of gasoline themselves (the 15% gasoline in E85). Effectively, 19 billion gallons of ethanol is equivalent to 12.7 billion gallons of gasoline (i.e. the ratios of the volumetric LHVs of gasoline and ethanol, 31.6 MJ/l for and 21.2 MJ/l respectively) Thus, 140 billion gallons are reduced to 140-12.7 = 127.3 billion gallons of gasoline, and there is a reduction in gasoline usage of 9.1%.

Consider now that the 19 billion gallons of ethanol instead be used to manufacture a ternary blend such as Blend C (G37 E21 M42). As mentioned earlier, it is possible to show that the methanol displaces gasoline if the total ethanol volume in the fuel pool is held constant. Figure 6 shows this relationship; on the left-hand side of the figure one supplies four units of energy as three units of gasoline and one unit of E85, and on the right-hand side all four units are supplied as Blend C instead. Note that there is effectively the same volume of ethanol on both sides of the figure – which is the case when ethanol supply is constrained. Summing the gasoline volume on both sides one arrives at 231 volume units on the left (i.e. the traditional approach) and 148 on the right, i.e. 35.9% extra gasoline has been displaced *over and above that already supplied by the ethanol.* Put another way, 168 volume units of methanol have displaced 83 units of gasoline.

Because of the blend proportions then for ternary Blend C one would require twice as much methanol – i.e. 38 billion gallons (from a total of 90.5 billion gallons of Blend C that can be made from 19 billion gallons of ethanol). The situation compared to the traditional E85 approach is that the 38 billion gallons of methanol have been used to displace 18.8 billion gallons of gasoline (i.e. 38 x 83/168, which again is the ratio of the volumetric LHVs of gasoline and methanol, 31.6 MJ/l for and 15.7 MJ/l respectively).

Now one can see that in addition to the 12.7 billion gallons of gasoline displaced by the ethanol, there is an additional 18.8 billion gallons displaced by the methanol, and the gearing on the ethanol is considerable. Effectively, instead of the 140 billion gallons of gasoline needed, the new volume required is 140-12.7-18.8 = 108.5 billion gallons, or a reduction of 22.5% by volume of gasoline in the entire fuel pool *with the same volume of ethanol being supplied.*

---

[6] Based on the actual 2007 consumption of 134.8 US gallons, with an assumption that vehicle fuel economy improves on the one hand and that there are more vehicles on the road on the other.

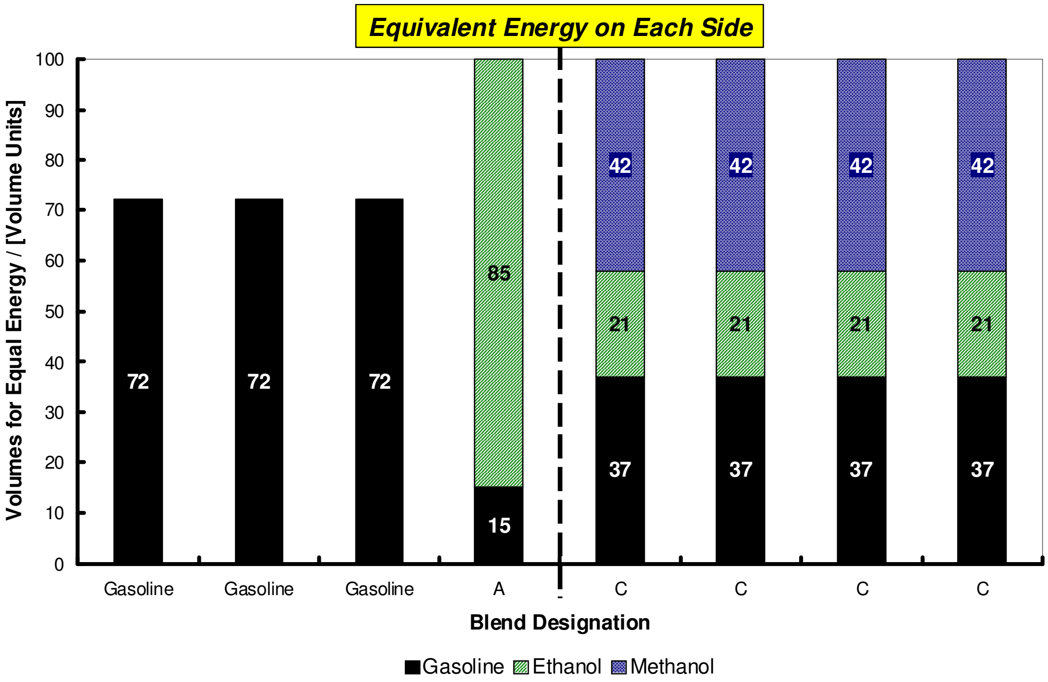

Fig. 6: Example of enhanced gasoline displacement by the introduction of methanol into ternary Blend C equivalent to E85 (for explanation, see text)

Note that the above argument is not extended to the 17 billion gallons of ethanol going into the remaining gasoline. In fact an iterative approach must be taken as the displacement of more gasoline (containing ethanol) implies more of it being available for a ternary blend. Furthermore, a ternary blending approach can be adopted at any blend rate, so assuming that methanol can be introduced via this method into E10 or E15 equivalents, a significant further proportion of gasoline could perhaps be replaced. This mechanism and overall system of displacement is perhaps worthy of further investigation and modelling.

Such an approach is academic if the vehicles do not exist to take the fuel (which can be easily rectified since the cost of making a flex-fuel vehicle is very low, and the CAFÉ regulations in the US are forcing this anyway) or if the blends are too expensive for the vehicle owner to use. Fortunately the low price of methanol means that the cost of ternary blend fuels can be lower than gasoline, on a per-unit-energy basis. As previously mentioned E85 is more expensive than gasoline in energy terms because the twin benefits of ethanol being renewable and a significant octane enhancer at low blend ratios drive its price up. It is interesting to illustrate the potential in cost reduction in ternary blends due to the introduction of the methanol blend component using assumed prices for gasoline, ethanol and methanol. We shall take these to be 3.21, 2.30 and 1.11 dollars per US gallon respectively, which was the case in September 2011 (before tax). Figure 7 shows how the price per unit energy relative to gasoline changes as the proportion of methanol in the ternary blend is increased. Only 24% methanol is required for the blend to be on a par with gasoline; at this point the user would see a reduction in operating costs anyway because of the reported higher efficiency with an alcohol blend fuel. Blends A to D are shown on Figure 7; specifically Blend D4 (G40 E10 M50), considered a practical fuel in terms of low-temperature phase separation, would be approximately 9.3% cheaper than gasoline on an energy basis.

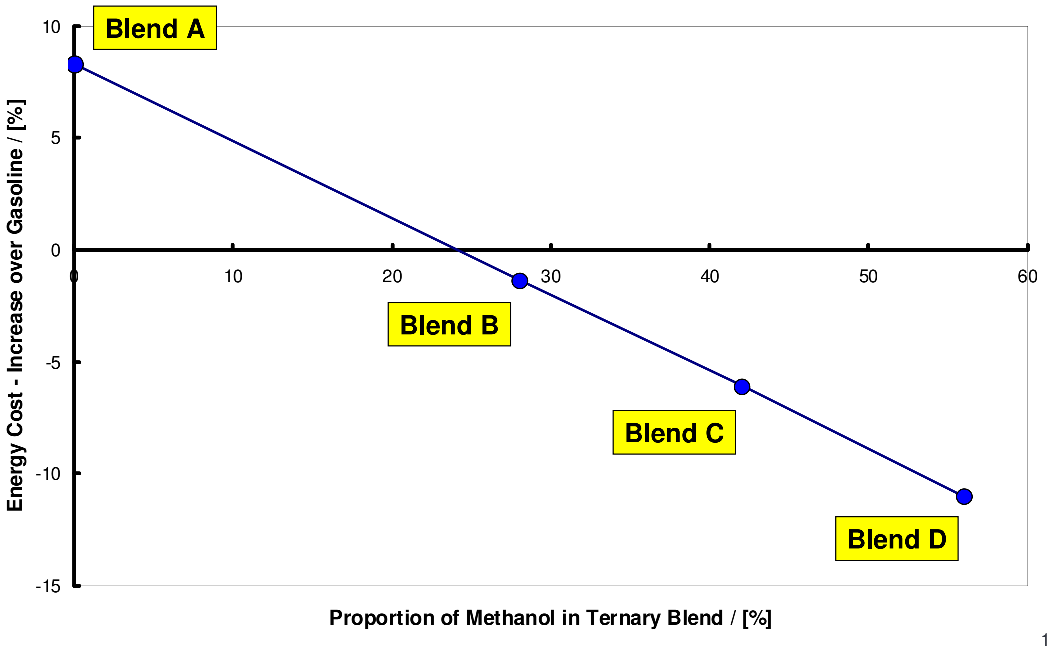

Fig. 7: Variation in energetic cost of GEM ternary blends versus that of gasoline as a function of the methanol concentration. Assumed costs per US gallon: gasoline $3.21, ethanol $2.30 and methanol $1.11. Ternary blends equivalent to E85

It should be remembered that a proportion of the gasoline required can be also made by either the FT or a MtSynFuels process (using methanol synthesis as an intermediate step). This will help with the gradual balancing of the two fuel products against the introduction of the necessary E85/gasoline flex-fuel vehicles. Given that the necessary fuel energy can be supplied in this manner, and that eventually a practical limit will be reached in terms of utilization in the existing vehicle technology (and that heavy-duty vehicles will otherwise continue to need diesel-type fuels, with the attendant energy losses from their onward synthesis from methanol) the remainder of this paper will discuss a pathway from ternary blends to the supply of fuels in full amounts to the light- and heavy-duty markets.

Having shown that the ternary blend approach produces functionally invisible drop-in blends suitable for E85/gasoline flex-fuel vehicles, further work will investigate the effect of such blends on fuel systems materials. The production flex-fuel vehicle used for these tests exhibited no problems in this regard, and has not done so ever since as far as the authors are aware. It is hoped that since many flex-fuel fuel system components are (it is believed) tested with methanol as a default that there will be no danger to existing vehicles through moving to an E85-equivalent blend containing methanol as well; even so, any potential issues can be mitigated by a phased introduction, which will be discussed in the following section.

Potential Rollout of the GEM Fuels and Possiblel Future Scenarios

From the work conducted to date it is entirely possible that methanol can be introduced into the fuel pool for existing flex-fuel vehicles (blended at E85-equivalent stoichiometry of 9.7:1) or for normal vehicles at blends equivalent to E10 or E15 in the near future. It is suggested that initial rollout be for E85/gasoline flex-fuel vehicles, since their smaller number automatically keeps the number of cars using the fuels down. Obviously some form of fleet test and further validation in-vehicle needs to be carried out before any rollout can be fully imagined, and it is hoped to do this with a small number of vehicles. Following successful conclusion of fleet trials, the release of the blends can be carried out in a manner controlled by both geography and blend ratio (obviously a blend containing much less methanol than Blend B can be created – such a blend is discussed later). This will allow the evolutionary change of the fuel and vehicles to gradually-increasing amounts of methanol in a steady and controllable manner. It is imagined that the ramp-up in plants converting shale methane to methanol would effectively mirror this, making the whole process complimentary.

Given that the existing light-duty fleet can start to use methanol by its incorporation as a blend component in a GEM fuel compatible with E85/gasoline vehicles, at some point the number of suitable vehicles able to take the fuel will become a limiting factor. It is suggested that early on in the process of GEM fuel introduction, given its successful implementation, government would enact legislation to encourage the wider production of the number of flex-fuel cars necessary so that the demand side is not a limiting factor. It is suggested that the approach of shale gas to methanol and use in the fuel pool would, at this point, have been considered a success, and that more far-reaching strategies could be created at that point. This section will discuss some such options.

With minimal impact on the vehicle manufacturers, it could be made mandatory that all spark-ignition vehicles should be made E85/gasoline flex-fuel. Some extension of the CAFÉ regulations would help to offset any costs incurred by the vehicle OEMs in doing this. However, considering the longer term, it would perhaps be advantageous to encourage the engineering of vehicles for sale which could take more than the maximum proportion of the methanol blend component in a blend equivalent to E85. This limit is Blend D (G44 E0 M56), although the actual maximum methanol proportion may need to be lower than this due to the need to have a cosolvent; it is suggested that Blend D4 (G40 E10 M50) would represent some upper limit in vehicles with E85/gasoline flex-fuel technology, due to the desire to be sure of avoiding low-temperature phase separation [11].

Since M85 was very successfully used before in the California methanol trial [18], it might be considered to make sense to move to that blend rate of methanol and gasoline as the next step, but it may equally be considered desirable to move straight to M100, while maintaining flex-fuel capability. This has been shown to be straightforward in previous work by the authors [19] and has also been called for in [16], together with more support of the US Open Fuel Standard (OFS). The vehicle engineering costs are likely to be similar to just providing M85 flex-fuel capability, since new technologies to aid starting in the form of direct injection are becoming commonplace now, and the efficacy of such technologies in cold starting pure alcohols having been known for some time [20]. A significant secondary advantage of this larger step is that the ensuing demand for pure methanol would then permit the use and adoption of either direct methanol fuel cells (DMFCs), proton exchange membrane (PEM) fuel cells with a simple reformer or optimized solid oxide fuel cells (SOFCs). In separate work, Bromberg and Cohn have suggested that heavy-duty trucks could move to M100 with the fuel being supplied by the smaller infrastructure necessary for such vehicles, which would limit the expenditure necessary [21]. This infrastructure would also play its part in the gradual evolution towards a full alcohol-based energy economy, since the necessary modifications to the heavy duty infrastructure could lead those in the light-duty infrastructure.

That emissions compliance is possible to achieve with current technology even at very high methanol concentrations was demonstrated at Euro 4 emissions level in [19]. In line with the above comments regarding NOx emissions for the ternary blends tests described above, Figure 8 reproduces the NOx results from [19], with the approximate blend ratios in the tank for each different test shown on the bars. Note that in the work reported in [19], constant stoichiometry was not aimed for in the fuel blends tested; rather the mixtures tested in that work were arbitrary since it was aimed at showing that any blend of gasoline, ethanol and methanol in a single vehicle fuel tank could be automatically compensated for by a modern engine management system. The modified Lotus vehicle used for this work was fitted with the standard-specification gasoline catalyst and was certified to Euro 4 emissions level, for which the NOx limit was 0.08 g/km. Figure 8 shows that the working engineering limit of approximately 50% when operating on gasoline was achieved for NOx. However, from the changes in the alcohol concentrations it is clear to see that in general the higher the proportion of ethanol or methanol (or both) the lower the tailpipe NOx emissions. Test 3 in Figure 8 uses G12 E0 M88 which is close to the notional M85 blend used in [18], and represents a reduction in NOx of nearly 70% versus gasoline; furthermore, the calibration was being refined as the test numbers increased, so the final value for M100 could be expected to be lower (for more details of the other emissions and how these interact, together with potential trade-offs enabled by the extremely low NOx output, see [19]).

In parallel with the above, Cohn and co-workers have proposed using the direct injection (DI) of ethanol or methanol in SI engines employing port-fuel injection (PFI) of gasoline as way of increasing the knock limit due to the chemical octane of the fuel coupled to the physical octane effects due to the high latent heat [22]. This they proposed under the banner of Ethanol Boosting Systems and their work was continued by Stein *et al.* [23]. The gearing on gasoline displacement was found to be significant since the direct injection of low-carbon-number alcohols helps to offset enrichment fuelling and to permit higher boost pressures, and thus greater degrees of downsizing.

Importantly with regard to this approach of PFI gasoline with DI of alcohol, the ternary GEM blends equivalent to E85 discussed earlier in this paper could be used instead of E85. This is because, when calculated on basis the of their mass ratios, the latent heat of all such ternary blends is the same from Blend A to Blend D to within +/- 2% (see Appendix I of [11]). Functionally this would not be expected to adversely impact the EBS concept, and it also acts as another means of introducing methanol into the fuel pool, should any such concept be commercialized. It represents another aspect of the invisibility of the blends to E85-optimized combustion systems.

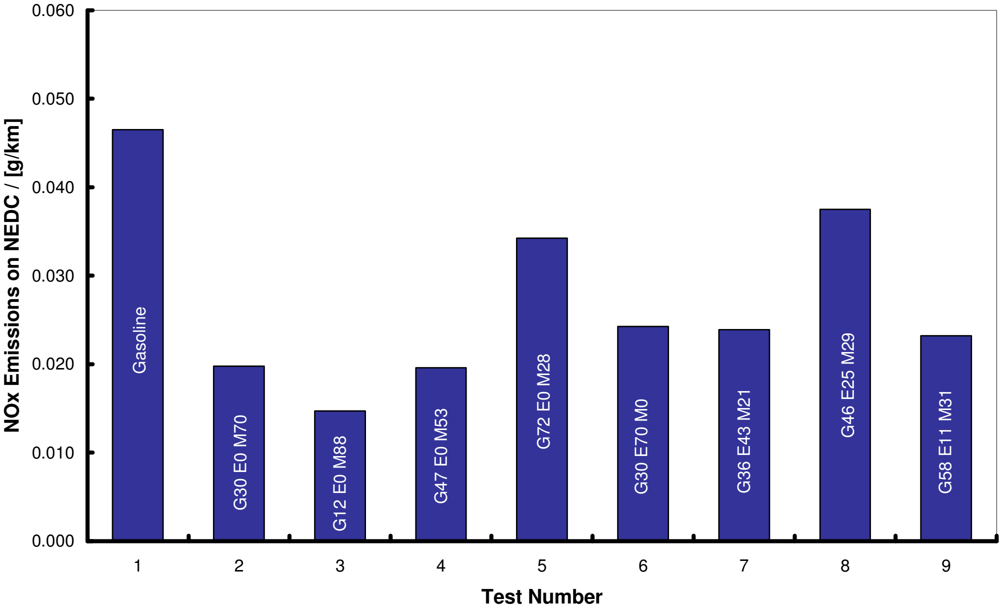

Fig. 8: Prototype gasoline-ethanol-methanol tri-flex-fuel vehicle tailpipe NOx emissions in g/km when operated on various blends of alcohol and gasoline on the New European Drive Cycle. Vehicle certified to Euro 4 emissions level. Calibration being developed from one test to the next; for more information see [19]. Note: fuel blend rates are not configured to a fixed, target stoichiometric AFR value (see text); limit = 0.08 g/km

Bromberg and Cohn discuss the use of DI of methanol in heavy-duty engines in general in [25] and Brusstar and co-workers have investigated alcohol fuels in very-high-compression ratio SI engines, showing that higher peak thermal efficiencies can be achieved with such concepts than the diesel engines on which they are based [26,27].

Thus high-blend alcohol fuels can offer the prospect of a future energy economy with increased energy security due to the high energy conversion efficiencies possible with these energy carriers. Furthermore, because of the miscibility with gasoline, flex-fuel approaches can ensure that the driver will not be left without a fuel to operate the vehicle on (although, as alcohol fuels become more commonplace, the engines may be biased towards operation on alcohols, and their may be a concomitant reduction in performance and range on gasoline; modern engine management systems will still permit safe operation despite the high compression ratios which such engines may adopt due to the superior characteristics of such high-blend alcohol fuels). A suggested time line for this process, showing how the fuels and their manufacturing processes interact with the vehicles, is shown in Figure 9, where it is proposed that the first ternary blend introduced contains only a relatively small percentage of methanol, and that this is ramped up in proportion and/or geographical area over time until all of the fuel is at Blend D4, which would represent saturation point for the vehicles was it not for mandating that all SI vehicles be capable of operating on E85 or similar (in

Figure 9 see the arrow moving from a potential introductory blend which we call Blend B1 (G20 E70 M10) to Blend D4 (G40 E10 M50)).

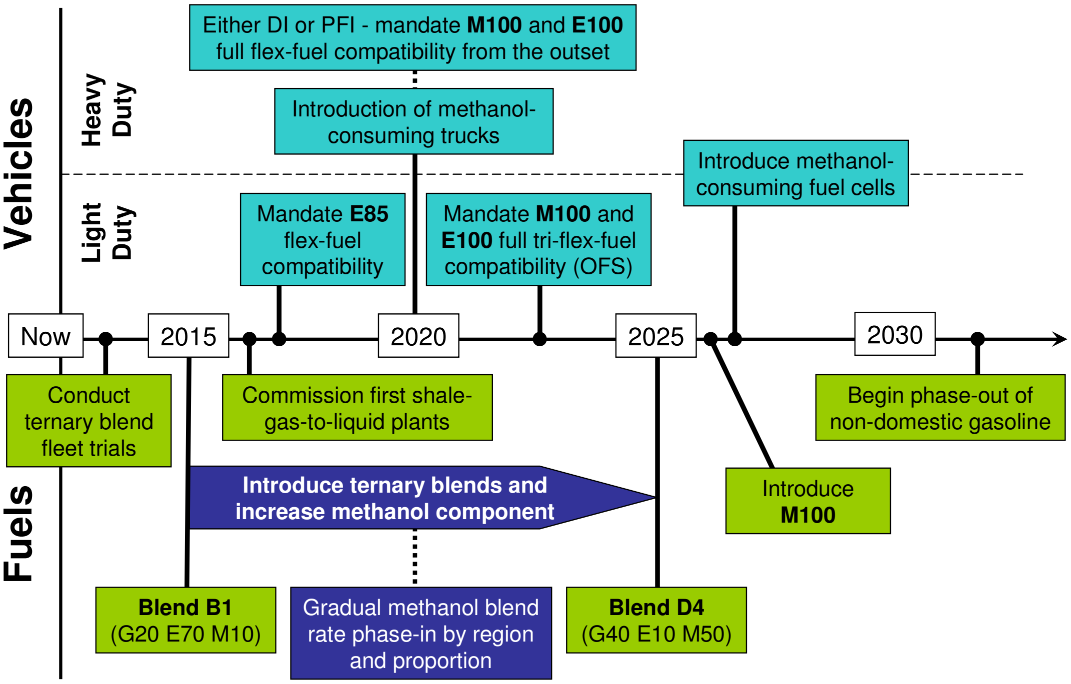

Fig. 9: Roadmap for introduction of increasing amounts of methanol into the US fuel pool via GEM ternary blends, eventually leading to M100. OFS = Open Fuel Standard

If the gasoline price does not increase further then the energy in Blend B1 (G20 E70 M10) would cost about 4.8% more than gasoline, which would likely be offset by the higher efficiency of the vehicles, so this blend could be expected to be cost neutral. However, it is not unreasonable to assume that the gasoline price will increase, and an increase of 10% would make Blend B1 2.3% cheaper (Blend D4: 12.7% cheaper). Thus Blend B1 would appear to be a practical target introduction blend; furthermore, since there would now only be 70% ethanol and both gasoline and methanol cold start more easily, it may be possible to stay with this blend ratio year-round (see [11] for the effect of the introduction of methanol on the cold startability of ternary blends).

Eventually, there will be supply side limitations even with methanol made from shale gas, and it must also be remembered that this is a finite resource. Many researchers have proposed that methanol (and higher hydrocarbons, albeit at an efficiency penalty) can be made using CO_2 extracted from the atmosphere, electrolytic hydrogen and renewable energy [7,28-32]. This has the potential to provide liquid transport fuels in full amounts, which fuels using biomass as a feedstock cannot do due to the biomass limit. It can be seen how the gradual introduction of such fuels would be facilitated by the vehicles and infrastructure having already moved in that direction. The high value of transport fuel will ensure that the investment necessary can be supported, and the volume used will help to bypass the issues faced by renewable energy in general, i.e. that the ability of the electricity grid to absorb renewable electricity is limited by the base load condition (which cannot be circumvented), and the fact that electricity cannot easily be stored. When the wind blows and the renewable energy output is above what the electricity grid can absorb, conversion to a hydrocarbon energy carrier is an excellent means of buffering such renewable energy [7,9].

Taking all of the foregoing into account, alcohol fuels therefore represent a pragmatic solution to future transport energy requirements for all stakeholders, since a continuous process of gradual evolution to a practical end game can be followed, with no quantum investment necessary at any stage by governments, OEMs, fuel suppliers or customers in either infrastructure or vehicles. This is because the alcohols are miscible with the gasoline that we use now, many flex-fuel vehicles already exist to use it, and it is feasible to make all future vehicles alcohol-compatible at minimal extra cost as the fuels become available in larger amounts.

REFERENCES

1. Energy Independence and Security Act of 2007, Public Law 110-140, 110th Congress, DOCID: f:publ140.110, 2007.
2. "On the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC," Directive 2009/28/EC of the European Parliament and of the Council, 23rd April 2009.
3. Cooper, J., "Future fuels for transport: Regulatory and supply drivers", Internal Combustion Engines: Improving Performance, Fuel Economy, and Emissions, Institution of Mechanical Engineers Conference, London, UK, 29th-20th November, 2011.
4. "Setting emission performance standards for new passenger cars as part of the Community's integrated approach to reduce CO_2 emissions from light-duty vehicles", Regulation (EC) 443/2009 of the European Parliament and of the Council, 23rd April, 2009.
5. Milpied, J., Jeuland, N., Plassat, G., Guichaous, S., Dioc, N., Marchal, A. and Schmerlzle, P., "Impact of Fuel Properties on the Performances and Knock Behaviour of a Downsized Turbocharged DI SI Engine - Focus on Octane Numbers and Latent Heat of Vaporization", SAE paper number 2009-01-0324, SAE 2009 World Congress, Detroit, Michigan, USA, 20th-23rd April, 2009.
6. Anderson, J.E., Kramer, U., Mueller, S.A., and Wallington, T.J., "Octane numbers of ethanol- and methanol-gasoline blends estimated from molar concentrations", Energy Fuels, Vol. 24, pp. 6576-6585, 2010.
7. Pearson, R.J., Eisaman, M.D., Turner, J.W.G., Edwards, P.P., Jiang, Z., Kuznetsov, V.L., Littau, K.A., di Marco, L., and Taylor, S.R.G., "Energy storage via carbon-neutral fuels made from CO_2, water, and renewable energy", Special Issue of Proc. IEEE: Addressing the intermittency challenge: Massive energy storage in a sustainable future. To be published Feb. 2012.
8. Olah, G. A., Goeppert, A. and Prakash, G.K.S., "Beyond Oil and Gas: The Methanol Economy", Second Edition, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009. ISBN 98-3-527-32422-4.
9. Sterner, M., "Bioenergy and renewable power methane in integrated 100% renewable energy systems", Dr.-Ing Thesis, University of Kassel, September 2009, ISBN 978-3-89958-798-2.
10. Turner, J.W.G., Pearson, R.J., Purvis, R., Dekker, E., Johansson, K. and Bergström, K. ac, "GEM Ternary Blends: Removing the Biomass Limit by

using Iso-Stoichiometric mixtures of Gasoline, Ethanol and Methanol", SAE paper number 2011-24-0113, The 10th International Conference on Engines and Vehicles, Capri, Naples, Italy, 11th-16th September, 2011.

11. Turner, J.W.G., Pearson, R.J., McGregor, M.A., Ramsay, J.M., Dekker, E., Iosefa, B., Dolan, G.A., Johansson, K. and Bergström, K. ac, "GEM Ternary Blends: Testing Iso-Stoichiometric mixtures of Gasoline, Ethanol and Methanol in a Production Flex-Fuel Vehicle Fitted with a Physical Alcohol Sensor", SAE paper number 2012-01-0113, SAE 2012 World Congress, Detroit, 24th-26th April, 2012.
12. Lotus Fuels Mixture Database, proprietary software of Lotus Engineering, 2008.
13. Pearson, R.J., Turner, J.W.G., Davy, M. and Stone, R., "Iso-stoichiometric ternary blends: Characterization of some physico-chemical properties of potential future transitional fuels", in preparation for submission to Proc. Instn Mech. Engrs Journal of Automotive Engineering, Part D.
14. "Worldwide Emissions Standards – Passenger Cars and Light Duty Vehicles 2011/2012", Delphi Corporation, Troy, Michigan, USA.; available on line at www.delphi.com/emissions-pc, last accessed 28th March, 2012.
15. Turner, J.W.G., Pearson, R.J., Dekker, E., Iosefa, B., Dolan, G.A., Johansson, K. and Bergström, K. ac, "Extending the role of alcohols as transport fuels using iso-stoichiometric ternary blends of gasoline, ethanol and methanol", submitted to Journal of Applied Energy, 2012.
16. Moniz, E.J., Jacoby, H.D., Meggs, A.J.M., Armstrong, R.C., Cohn, D.R., Connors, S.R., Deutch, J.M., Ejaz, Q.J., Kaufman, G.M., Kenderdine, M.A., O'Sullivan, F., Paltsev, S., Parsons, J.E., Perez-Arriaga, I., Reilly, J.M., Seto, C., Yang, Y., McRae, G.S., Ruppel, C., Fletcher, S., Hagerty, J.M., Kragha, O., Leung, T., Murphy, P., Rachokonda, A., Tapia-Ahumuda, K., Toukan, I., Ucok, D. and Yao, Y., "The Future of Natural Gas - An Interdisciplinary MIT Study", Massachusetts Institute of Technology, available at: http://web.mit.edu/mitei/research/studies/documents/natural-gas-2011/NaturalGas_Report.pdf, 2011, last accessed 28th March, 2012.
17. "E15 (a blend of gasoline and ethanol)", available at: http://www.epa.gov/otaq/regs/fuels/additive/e15/, last accessed 28th March, 2012.
18. Ward, P.F. and Teague, J.M., "Fifteen years of fuel methanol distribution", 11th International Symposium on Alcohol Fuels, Sun City, South Africa, 14th-17th April, 1996.
19. Pearson, R.J., Turner, J.W.G. and Peck, A.J., "Gasoline-ethanol-methanol tri-fuel vehicle development and its role in expediting sustainable organic fuels for transport", 2009 I.Mech.E. Low Carbon Vehicles Conference, London, UK, 20th-21st May, 2009, pp. 89-110.
20. Siewert, R.M. and Groff, E.G., "Unassisted Cold Starts to -29°C and Steady-State Tests of a Direct-Injection Stratified-Charge (DISC) Engine Operated on Neat Alcohols", SAE paper number 872066, 1987, doi:10.4271/872066.
21. Bromberg, L. and Cohn, D., "Alcohol Fueled Heavy Duty Vehicles Using Clean, High Efficiency Engines"
22. Cohn, D.R., Bromberg, L. and Heywood, J.B., "Direct Injection Ethanol Boosted Gasoline Engines: Biofuel Leveraging for Cost Effective Reduction of Oil Dependence and CO_2 Emissions", MIT report PSFC/JA-06-16, MIT Plasma Science and Fusion Centre, 20th April, 2005, available at:

http://www.psfc.mit.edu/library1/catalog/reports/2000/06ja/06ja016/06ja016_full.pdf, last accessed 28th March, 2012.

23. Stein, R.A., House, C.J. and Leone, T.G., “Optimal Use of E85 in a Turbocharged Direct Injection Engine”, SAE paper number 2009-01-1490, SAE Int. J. Fuels Lubr. 2(1):670-682, 2009, doi:10.4271/2009-01-1490.
24. Blumberg, P.N., Bromberg, L., Kang, H. and Tai, C., “Simulation of High Efficiency Heavy Duty SI Engines Using Direct Injection of Alcohol for Knock Avoidance”, SAE paper number 2008-01-2447 and SAE Int. J. Engines 1(1):1186-1195, 2009, doi:10.4271/2008-01-2447.
25. Bromberg, L. and Cohn, D., “Alcohol Fueled Heavy Duty Vehicles Using Clean, High Efficiency Engines”, SAE paper number 2010-01-2199 doi:10.4271/2010-01-2199.
26. Brusstar, M., Stuhldreher, M., Swain, D. and Pidgeon, W., “High Efficiency and Low Emissions from a Port-Injected Engine with Neat Alcohol Fuels”, SAE paper number 2002-01-2743, doi:10.4271/2002-01-2743.
27. Brusstar, M.J. and Gray, C.L., “High Efficiency with Future Alcohol Fuels in a Stoichiometric Medium Duty Spark Ignition Engine”, SAE paper number 2007-01-3993, doi:10.4271/2007-01-3993.
28. Steinberg, M., “Production of synthetic methanol from air and water using controlled thermonuclear reactor power – I. Technology and energy requirement”, Energy Conversion, vol. 17, pp. 97-112, 1977.
29. Bandi, A., Specht, M., Weimer, T. and Schaber K., “CO_2 recycling for hydrogen storage and transportation – electrochemical CO_2 removal and fixation”, Energy Conversion and Management, vol. 36(6-9), pp. 899-902, 1995.
30. Stucki, S., Schuler, A. and Constantinescu, M,. “Coupled CO_2 recovery from the atmosphere and water electrolysis: feasibility of a new process for hydrogen storage” , Int. J. Hydrogen Energy, vol. 20, 8, pp. 653-663, 1995.
31. Weimer, T., Schaber, K., Specht, M. and Bandi, A., “Methanol from atmospheric carbon dioxide: a liquid zero emission fuel for the future”, Energy Conversion and Management, vol. 37(6-8), pp. 1351-6, 1996.
32. Specht, M., Staiss., F., Bandi, A. and Weimer, T., “Comparison of the renewable transport fuels, liquid hydrogen and methanol, with gasoline – energetic and economic aspects”, Int. J. Hydrogen Energy, vol. 23, 5., pp. 387-396, 1998.

ACKNOWLEDGEMENTS

The authors from Lotus would like to thank the directors of Lotus Cars for permission to publish this paper and for encouragement to conduct the research. Mark McGregor and John Ramsay were heavily involved in the sequencing and conduct of the tests, and their rigour and enthusiasm is much appreciated.

The authors would also like to acknowledge the insights gained from discussions with, among others, the following people: Tony Marmont, Peter Harrison and Bob Jennings of Air Fuel Synthesis, Matt Eisaman of Brookhaven National Laboratory, Paul Wuebben of Carbon Recycling International, Steve Brueckner of Chrysler, Leon di Marco of FSK Technologies, Gordon Taylor of GT-Systems, Tim Fox and Philippa Oldham of the Institution of Mechanical Engineers, Martin Davy and Colin Garner of Loughborough University, Leslie Bromberg and Daniel Cohn of Massachusetts Institute of Technology, Frank Zeman of New York Institute of Technology, Arthur

Bell, Gareth Floweday and Andre Swarts of Sasol Technology, Karl Littau of Stanford University, Matt Brusstar of the United States Environmental Protection Agency, Chris Brace of the University of Bath, Peter Edwards and Richard Stone of the University of Oxford, and George Olah, Surya Prakash, and Alain Goeppert of the University of Southern California.

ABBREVIATIONS

AFR	Air-fuel ratio
CAFÉ	Corporate Average Fuel Economy
CO_2	Carbon dioxide
DI	Direct injection
DMFC	Direct methanol fuel cell
EBS	Ethanol Boosting Systems
EPA	Environmental Protection Agency
EU	European Union
FQD	Fuel Quality Directive
GEM	Gasoline, ethanol and methanol
ILUC	Indirect land use change
LHV	Lower heating value
MIL	Malfunction indicator lamp
MtSynFuels	Methanol-to-synfuels
OBD	On-board diagnostics
OEM	Original equipment manufacturers (i.e., vehicle manufactuers)
OFS	Open Fuel Standard
PEM	Proton exchange membrane
PFI	Port-fuel injection
NEDC	New European Drive Cycle
NOx	Oxides of nitrogen
RED	Renewable Energy Directive
SI	Spark-ignition
SOFC	Solid oxide fuel cell