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Volatility and vehicle driveability performance of ethanol/gasoline blends: a literature review

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Volatility and vehicle driveability performance of ethanol/gasoline blends: a literature review

Prepared for the CONCAWE Fuels and Emissions Management Group by its Special Task Force FE/STF20:

- R. Stradling (Chair)
- F-J. Antunez Martel
- J. Ariztegui
- J. Beeckmann
- S.D. Bjordal
- P. Blosser
- J. Canovas
- A. Clark
- N. Elliott
- J. Farenback-Brateman
- P. Gomez-Acebo
- P.M. Martinez Sanchez
- P. Scorletti

J.S. McArragher (Consultant) P.J. Zemroch (Consultant)

K.D. Rose (Technical Coordinator)

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ABSTRACT

The effect of blending ethanol (up to 20% v/v) into gasoline on the volatility of the ethanol/gasoline blend and on the hot and cold weather vehicle driveability performance of these blends has been assessed from published literature. This literature review covers major fuel blending and vehicle driveability studies that have been completed over the past 20 years.

Volatility of Ethanol/Gasoline Blends

The percentage of an ethanol/gasoline blend that evaporates at $70^{\circ}C$ (E70) substantially increases when ethanol is blended into gasoline. The corresponding E100 (the percent of the blend that evaporates at $100^{\circ}C$) also increases but less substantially than the E70 value. The increase in these two volatility parameters with ethanol addition is usually smaller as the volatility of the gasoline increases. Interestingly, "Blending E70" values for ethanol tend to decrease with increasing ethanol content while "Blending E100" values increase. This difference is due to the formation of an azeotrope that affects the volatility behaviour of the ethanol/gasoline blend at different temperatures. Simple predictive models have been developed based on analytical data from the published studies that describe the change in Blending E70 and Blending E100 values with the base gasoline's E70 and E100 and with ethanol contents in the range of 5 to 20% v/v.

Vehicle Driveability Performance of Ethanol/Gasoline Blends

Published studies on the impact of ethanol and gasoline volatility on vehicle driveability performance have also been evaluated. These included seven studies on Hot Weather Driveability (HWD) and eleven studies on Cold Weather Driveability (CWD). These studies show that modern vehicles are much less susceptible to HWD performance problems than are older vehicles. Some early model Direct Injection Spark Ignition vehicles tested by CONCAWE/GFC (2003) showed some HWD problems but only on high volatility fuels. Current specification properties appear to be adequate to control HWD but some increases in the E70 maximum limits allowed by the European EN228 gasoline specification may be needed in order to allow ethanol blending into gasoline at 10% v/v and higher.

CWD vehicle performance is affected by mid-range gasoline volatility (E100) and is an issue for modern vehicles because it is linked to exhaust emissions performance under cold starting conditions. CWD is degraded by the use of ethanol/gasoline blends at the same volatility level as hydrocarbon-only gasolines. To reduce the impact of ethanol, new Driveability Indices (DI) have been developed and applied in some extensive US studies. These DIs generally include ethanol offset terms in order to control the impact of volatility on CWD performance. Although current E100 volatility class limits are fixed in the European EN288 gasoline specification, the published literature indicates that the minimum E100 limits should ideally vary with ambient temperature and should include an ethanol offset term in order to control CWD performance. Based on these results, a European DI including an ethanol offset term should be considered in order to account for the performance of European vehicles under European climatic conditions.

KEYWORDS

Gasoline, ethanol, volatility, vapour pressure, DVPE, E70, E100, vehicle driveability, blending, predictive models, light-duty passenger cars, driveability index, HWD, CWD, DI

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SUMMARY

The blending of bio-components into European gasoline has been mandated by the Renewable Energy Directive (2009/28/EC). Ethanol and ETBE manufactured from renewable ethanol are the only widely available bio-components today for gasoline blending. Ethanol is currently allowed at levels up to 5% v/v in the EN228 specification and up to 10% v/v in some countries due to Member State initiatives. With growing concerns related to climate change and energy security, there is considerable interest in increasing the amount of renewable fuels in road transport, especially by increasing the ethanol content of standard grade gasoline above its current 5% v/v level.

The combustion and antiknock benefits of ethanol as a neat fuel or as a blending component have been known for a long time. When used as a blending component in gasoline, however, ethanol impacts other fuel properties, especially the vapour pressure and distillation profile, due to the formation of azeotropes. Ethanol's effect at 5% v/v on Dry Vapour Pressure Equivalent (DVPE) is well known and a waiver to increase the summertime DVPE for ethanol/gasoline blends in some countries is included in the new EU Fuel Quality Directive (2009/30/EC). This Directive mandates the use of ethanol up to 10% v/v and the European Committee for Standardization (CEN) is already working to modify the EN228 gasoline specification to accommodate this increase. Much less is known, however, about the effect of blending even higher ethanol concentrations into gasoline, for example up to 25% v/v, on the distillation properties of the ethanol/gasoline blend, especially on the E70 and E100 distillation values. For this reason, this review of the published literature is intended to provide technical input to the CEN process specifically on the effect of ethanol on volatility and on vehicle driveability performance.

In order to evaluate the effect of ethanol in gasoline on E70 and E100 values, published analytical data on ethanol/gasoline blends up to 20% v/v ethanol were analysed. A total of 212 blends from 107 base gasolines were evaluated statistically. This evaluation included estimating E70 and E100 values from the distillation curves for fuels where these properties were not reported in the original publication.

When ethanol is blended into a hydrocarbon-only gasoline, the increase in E70 compared to that of the base gasoline (Δ E70) was found to be as high as 30% for blends containing up to 20% v/v ethanol. The Δ E70 values were found to decrease with increasing E70 of the base gasoline. The Δ E70 values also increased with ethanol content up to 10% v/v but then appeared to stabilise at higher ethanol contents up to 20% v/v. The corresponding Δ E100 levels were found to increase up to 10% for 10% v/v ethanol and up to 20% for 15-20% v/v ethanol/gasoline blends. The Δ E100 values were also found to decrease with increasing E100 of the base gasoline and increase with increasing ethanol content up to 20% v/v.

Simple models were developed from this analysis of Blending E70 and Blending E100 values. The Blending E70 decreased with increasing ethanol content while the Blending E100 increased with increasing ethanol content. This is due to the behaviour of azeotropes formed when ethanol is blended into a predominantly hydrocarbon mixture.

Published studies on the impact of ethanol and gasoline volatility on vehicle driveability performance were also evaluated. These included seven studies on Hot Weather Driveability (HWD) and eleven studies on Cold Weather Driveability (CWD) vehicle performance.

Hot Weather Driveability (HWD) of vehicles was found to be affected most strongly by the "front-end" volatility of gasoline, especially the DVPE and E70 values. In the USA, an alternative volatility parameter, TVL_{20} , is used, representing the temperature at which a vapour to liquid ratio of 20 is achieved for a liquid fuel sample.

According to the published literature, modern vehicles using multi-point injection (MPI) technology are much less susceptible to HWD problems than older vehicles. However, two early technology direct injection spark ignition (DISI) vehicles tested in a CONCAWE/GFC programme did show higher driveability demerits on high volatility blends. Extensive testing completed by the Coordinating Research Council (CRC) in the USA has derived alternative volatility properties for gasoline that correlate with HWD performance on ethanol/gasoline blends better than TVL_{20} but these have not yet been applied in US gasoline specifications. Current EN228 specification properties appear adequate to control HWD performance in European vehicles but some increase in the E70_{max} limits may be needed in order to produce ethanol blends of 10% v/v and higher.

Cold Weather Driveability (CWD) is affected most strongly by mid-range volatility, defined in Europe by the E100 value. CWD performance is an issue for modern vehicles because it is linked to exhaust emissions under cold starting conditions. For splash blends of ethanol in gasoline, CWD performance was found to improve somewhat due to the higher volatility of the ethanol/gasoline blend. CWD performance degrades, however, when the ethanol/gasoline blend is at the same volatility level as a hydrocarbon fuel because of the higher latent heat of ethanol and a leaning effect on the air-fuel ratio (AFR) due to ethanol under open-loop engine conditions.

Current E100 minimum and maximum limits in the European EN228 gasoline specification are fixed for all volatility classes. To properly control CWD, however, the minimum E100 volatility limits should ideally vary with ambient temperature and should include an ethanol offset. For example, the CRC in the USA has developed new fuel parameters, called "Driveability Indices" (DIs), that include ethanol offset terms, but these only apply to US vehicles. Ideally, a European DI should be developed on modern European vehicles and applied in future gasoline specifications.

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1. INTRODUCTION

Ethanol has been recognised to be a promising fuel for internal combustion engines almost as long as such engines have existed. This is because ethanol can easily be produced by fermenting sugar-containing crops to produce a liquid fuel having a high octane value and exhibiting high antiknock performance. Ethanol was first evaluated and promoted as a vehicle fuel by Tizard and Pye at Ricardo in 1919. In the 1920s, Henry Ford was quoted in the New York Times that ethanol was "the fuel of the future" and "there is fuel in every bit of vegetable matter that can be fermented. There's enough alcohol in one year's yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years."

The subsequent discovery, however, that very small amounts of tetra-ethyl lead (TEL) could increase the antiknock quality of gasoline effectively left alcohol fuels 'on the shelf' in most parts of the world for more than 50 years. The oil crises of the 1970s and the phase-out of TEL antiknock additives increasingly focused research on alternative fuels. A significant amount of work was carried out in the late 1970s and early 1980s leading to the widespread use of ethanol and methanol. More recently, interest has grown again for the use of ethanol in road fuels as a way to reduce Greenhouse Gas (GHG) emissions and improve energy security through the use of renewable fuels.

To encourage greater use of renewable fuels, especially ethanol, the European Union (EU) adopted the Fuel Quality Directive (FQD, 2003/30/EC) in 2003 on "the promotion of the use of biofuels or other renewable fuels for transport". This Directive required the increasing use of biofuels, including bio-ethanol, bio-methanol, bio-MTBE, bio-ETBE, and "synthetic biofuels" (hydrocarbons), in road transportation. This legislation, passed in April 2004, required each Member Country to set indicative targets for future biofuel use to reach a minimum of 5.75% v/v of all European automotive fuels by 2010. The Directive did not set mandatory targets, however, and the 5.75% v/v target by 2010 is not likely to be reached.

For this reason, the FQD was updated in December 2008 to increase the allowed ethanol limit in gasoline to 10% v/v (3.7% m/m oxygen). The legislation also requires that the current gasoline grade containing up to 5% v/v ethanol is made available in the marketplace until at least 2013 in order to protect the performance of older vehicles. For this reason, the EN228 gasoline specification is being updated by CEN to allow up to 10% v/v ethanol in the standard gasoline grade while retaining a second so-called 'protection grade' containing up to 5% v/v ethanol for older vehicles.

In December 2008, the EU also adopted the new Renewable Energy Directive (2009/28/EC) (RED) requiring a 20% share of total energy from renewable sources in the EU by 2020, including a 10% share by energy content in road transport fuels. A 10% share on an energy basis represents about a 14% share of road fuels on a volumetric basis and is likely to require the ability to blend ethanol into road fuels at levels higher than the 10% v/v level that is currently under CEN discussion.

Although the combustion and antiknock benefits of ethanol are well known, ethanol also affects other fuel properties, especially the DVPE and distillation of the resulting ethanol/gasoline blend. The effects on the gasoline's DVPE are well documented and models have been developed in USA to predict the change in DVPE for ethanol/gasoline blends. In the new EU FQD, countries having low summertime

temperatures and a 60 kPa DVPE limit can request a waiver to increase the DVPE of ethanol/gasoline blends by up to 8 kPa.

The addition of ethanol also changes other volatility and distillation properties of gasoline, especially the $E70^1$ and $E100^2$ values, but there are limited published data on the magnitude of these effects at 10% v/v ethanol contents and higher levels. In some studies, models have been developed, especially in the USA, to predict the $T50E^3$ values for ethanol/gasoline blends but these effects have not yet been modelled in Europe, where we prefer to specify E70 and E100 values.

The use of ethanol in gasoline and the changes in the blend's DVPE and distillation curve are known to affect both the HWD and CWD performance of vehicles. These effects have been studied in some detail but do not always follow simple volatility changes so there may be a need to adopt different or modified volatility specifications when ethanol is used.

In response to the new FQD discussed above, CEN is now reviewing the European EN228 gasoline specification, especially for blending ethanol at up to 10% v/v in gasoline. As an input to this review and at the request of DG-TREN, this technical report assesses published data on the effect of ethanol blending on E70 and E100 values, as well as the effect of gasoline volatility on HWD and CWD performance. In order to anticipate higher ethanol levels in the future, the report considers published data on gasoline blends containing up to 20% v/v ethanol.

¹ The percent of the gasoline sample that evaporates at 70°C

² The percent of the gasoline sample that evaporates at 100°C

³ The temperature at which 50% of the gasoline sample has evaporated

2. LITERATURE ASSESSMENT

The effect of ethanol on gasoline vapour pressure is well documented but there are very little published data on the effect of ethanol on the other distillation properties of the ethanol/gasoline blends. The most comprehensive study was completed by the California Air Resources Board (CARB) in which a CARBOB (California Reformulated gasoline Blendstock for Oxygenate Blending) model was developed to predict RVP, T50E, T90E⁴ and other properties of finished ethanol/gasoline blends [1] (see also **Appendix 1**). Other work has been published recently on the effects of ethers and other solvents on the properties of ethanol/gasoline blends [2-6].

HWD performance of light-duty vehicles has been studied in some detail over many years. In the USA, the CRC has evaluated HWD many times and recently completed several studies of HWD with ethanol/gasoline blends. The CRC work represents the most comprehensive set of data on vehicle driveability performance [7-11]. In Europe, an "Inter-Company Volatility Working Group" was set up by the oil industry and operated for many years in the 1980s and 90s. Results from this Working Group were generally not published but were used as the basis for one CONCAWE report [12]. More recently, CONCAWE conducted a study with the French GFC on HWD and CWD performance on ethanol/gasoline blends [13,14]. A study on evaporative emissions from gasoline vehicles was also carried out by the EU's Joint Research Centre (JRC) in collaboration with CONCAWE and the European Council for Automotive R&D (EUCAR) [15,16]. A recent review of ETBE data [17] reported some HWD tests completed in the early 1990s on gasolines containing ETBE and ethanol using CEC test procedures on two vehicles.

CWD performance of light-duty vehicles has also been studied over many years by the CRC, including the performance of vehicles operating on ethanol/gasoline blends [18-26]. The Intercompany Working Group in Europe also tested CWD and the results were published [27] before this Working Group was disbanded. The CONCAWE/GFC programme [13,14] also investigated CWD. In addition, Shell has actively investigated CWD performance of European vehicles, developing a fundamental "enthalpy requirement" (ER) parameter [27-30] for ethanol/gasoline blends.

The Australian Government has sponsored the Orbital Engine Company to carry out two major studies on the use of ethanol/gasoline blends in Australian vehicles. The first, in 2002, was an investigation of the impact of 20% v/v ethanol in gasoline, carried out for the Environment Australia project "Market Barriers to the Uptake of Biofuels - Testing Petrol Containing 20% Ethanol (E20)". The program comprised a paper and an experimental study [31-34]. In July 2003, however, the Australian Government decided to limit the amount of ethanol in gasoline to 10% v/v and announced a new experimental programme in 2005 to test the performance of vehicles on 5% v/v (E5) and 10% v/v (E10) blends. This programme was completed and reported by the Orbital Company in 2007 [35,36]. Both studies included an analysis of vehicle driveability under normal ambient, hot, and cold temperature conditions. However, the work was completed using Orbital's in-house test procedures and did not specifically look at the effect of ethanol on fuel volatility. Results on fuels prepared by splash blending ethanol into a hydrocarbon-only gasoline were evaluated without correcting for the change in volatility upon ethanol addition.

⁴ The temperature at which 90% of the gasoline sample has evaporated

There are little data available on ethanol/gasoline blends containing ethanol higher than 10% v/v. The first Australian study described above looked at 20% v/v blends as did a more recent study completed by the US State of Minnesota [37]. Minnesota has legislated that by August 30, 2013, gasoline sold in Minnesota shall contain at least 20% v/v ethanol (E20), provided that the US EPA certifies E20 by December 31, 2010 as a motor fuel through a waiver under section 211(f) (4) of the Clean Air Act. In pursuit of this EPA waiver, Minnesota contracted the University of Minnesota (UMN) to conduct a driveability evaluation of a vehicle test fleet comprising 40 pairs of similar 2000–2006 vehicles with similar driving patterns. Vehicle drivers were asked to complete daily log sheets indicating any driveability problems that occurred. In addition, trained vehicle driveability raters were contracted to conduct industry standard driveability tests on a subset of the vehicle fleet, with a test series for each season (fall, winter, spring, and summer). Thus, the results covered both HWD and CWD vehicle performance.

One additional study [38] by Lubrizol looked specifically at CWD performance using an artificially cooled test bed engine. The engine was instrumented so that the cylinder pressure could be recorded for each cylinder and used to calculate the area under the Indicated Mean Effective Pressure (IMEP) curve, as well as misfires and "nimps" (did NOT reach threshold IMEP cycles). Since this study was conducted on a single bench engine and not on a vehicle, the results are constructive but extrapolating the conclusions to CWD performance in vehicles is difficult. Toyota also published a fundamental review [39] of the effect of ethanol on combustion, especially under cold temperature conditions. A recent review of ETBE data [17] also reported some CWD tests completed in the early 1990s on gasolines containing ETBE and ethanol using CEC test procedures. Two vehicles were tested at -5, -15 and -25°C.

3. EFFECT OF ETHANOL BLENDING ON GASOLINE VOLATILITY

In this report, the following abbreviations are used to describe different volatility properties of ethanol/gasoline blends:

- [EtOH] % Ethanol/100
- E70(base) The percent of the base gasoline that evaporates at 70°C
- E70(blend) The percent of the ethanol/gasoline blend that evaporates at $70^{\circ}C$
- Δ E70 The increase in the E70 of the blend compared to that of the base gasoline (E70(blend) E70(base))

The blending performance defined by the following equation:

• BlendE70(EtOH) <u>E70(blend) - (1 - [EtOH]) x E70(base)</u> [EtOH]

Similar abbreviations apply for E100 and E150 values.

3.1. BEHAVIOUR OF ETHANOL IN HYDROCARBON SOLUTIONS

As a pure chemical, ethanol boils at about 78°C, significantly higher than the initial boiling point (IBP) of gasoline (\sim 30°C) but also lower than the mid-range of the gasoline distillation curve (\sim 100°C). The DVPE of pure ethanol (about 16 kPa) is also much lower than that of gasoline. Consequently, one would expect that blending ethanol into gasoline at low concentrations would lower the DVPE of the ethanol/gasoline blend and increase somewhat the mid-range volatility.

This is not the case, however, because ethanol forms azeotropes with the hydrocarbons typically comprising gasoline. An azeotrope is a mixture of two or more liquids in such a ratio that the composition of the mixture cannot be changed by simple distillation. This means that the azeotropes of ethanol and hydrocarbons distil at a nearly constant temperature. This phenomenon results in an essentially flat distillation curve in the standard ASTM distillation measurement until the azeotropes of ethanol has distilled completely from the liquid, the distillation curve rapidly returns to that of the hydrocarbon-only gasoline, as shown in **Figure 1**. See **Appendix 3** for typical properties of gasoline and ethanol, including ethanol-hydrocarbon azeotropes.

Figure 1



Impact of 10% ethanol on the distillation curve of a typical gasoline [41]

Although this is the case in the distillation measurement, the behaviour in an engine's fuel inlet system is quite different. In the engine, a rapid or flash distillation of the fuel mixture occurs without sufficient time to achieve equilibrium conditions. Especially in cold weather or cold engine conditions, the engine heat needed to facilitate volatilization will be limited, leaving a liquid fuel "puddle" in the inlet system whose composition will vary during transient driving conditions as the engine warms up. In addition, ethanol's higher latent heat of vaporization, compared to that of hydrocarbons, means that it is more difficult to vaporise the ethanol/hydrocarbon azeotropes under cold conditions, even though the ASTM volatility of the azeotropes is higher. This will result in a leaner mixture, leading to misfires and poorer vehicle driveability performance.

In modern vehicles, the Engine Management System (EMS) will "learn" the stoichiometry of the ethanol-gasoline blend, but the ethanol fraction of the fuel entering the cylinder during cold transients will vary from what is expected based on this "adaptive learning", Because the ethanol content will be higher in the "front end" of the fuel, i.e. the fraction that boils below the mid-point temperature, the transient mixture can still be leaner than expected by the EMS, leading to driveability malfunctions.

Azeotropes always deviate from Raoult's law, an equation that describes the vapour pressure of ideal solutions containing two or more liquid components. In the case of ethanol/gasoline blends, this results in a positive deviation from ideal behaviour, so that the vapour pressure of the blend will be higher than that of the base gasoline up to about 3% v/v ethanol and then will gradually fall again at higher ethanol levels (**Figure 2**). This increase in vapour pressure at low ethanol concentrations means that HWD problems can occur most frequently under hot weather conditions when sufficient heat is available to generate vapour in the liquid fuel inlet system leading to the combustion chamber. Higher DVPE levels of ethanol/gasoline blends can also

increase evaporative emissions unless they are properly controlled by the on-vehicle systems [15-16].

Figure 2

Vapour pressure of ethanol blends with two different gasolines [40]



3.2. US PREDICTIVE EQUATIONS

In the USA, most marketed ethanol/gasoline blends are "splash blends", that is, produced by adding ethanol to a base gasoline at terminal blending locations. This practice is used in order to avoid distributing gasoline containing ethanol through the multi-product pipeline system used to distribute fuels across the country [40]. In order to ensure that the ethanol/gasoline blend blended at the terminal meets the volatility specifications, a special Blendstock for Oxygenate Blending (or BOB) gasoline must be prepared and delivered to the terminal. For this reason, the blending performance of ethanol in hydrocarbon fuels of different composition must be accurately characterized in order for the splash blend approach to work. Alternatively, volatility specification waivers can be issued by the prevailing authorities.

In California, a legislated CARBOB model has been developed. This model incorporates a series of equations to predict the RVP, T50E and T90E, and other properties of finished gasolines (see **Appendix 1**). The fuel supplier must use the CARBOB model to estimate the finished properties of a blend of known ethanol content with his BOB, then enter these properties into the CARB Predictive Model to ensure that the final blend will meet the requirements of CARB Phase 2 or Phase 3 Reformulated Gasoline. These models were developed by statistical analysis of data from over 500 commercial fuel blends in California. These data were made available to CONCAWE and have been considered in the analysis described below.

3.3. DATA SOURCES AND INTERPOLATION OF MISSING VALUES

In order to estimate the increase in E70 and E100 values due to ethanol blending, CONCAWE have reviewed published literature for fuel analysis data on ethanol splash blends. Thus, published data were only analyzed where the study reported results for both the base hydrocarbon fuel and the splash blends of ethanol in that same fuel. These included the US AQIRP study [41], several CRC programmes [22], the CONCAWE/GFC driveability study [13,14], the JRC/EUCAR/CONCAWE (JEC) evaporative emissions programme [15,16], Australian studies completed by the Orbital Company [34,36], the AEAT fuel economy study [42], IDIADA work completed on behalf of Repsol [43], the Swiss EMPA report [44], the dataset used to derive the CARBOB models, and unpublished Shell data.

Many of the fuel analysis datasets were incomplete. Few had full compositional information (olefins, aromatics, etc.), some had nominal ethanol contents, while others reported measured values. Only one of the base fuels, from IDIADA, contained ethers, specifically ETBE at 4% v/v. This fuel and its one 5% v/v ethanol blend have been excluded from all subsequent plots and models. More data on the effects of ETBE/ethanol mixtures has recently become available [2-6], but these data were not included in our analysis on fuel composition. The few data that are available on gasolines containing both ethers and ethanol suggest that the use of higher concentrations of ETBE (2-6%) as a cosolvent for 5% v/v ethanol blends may reduce Δ E70 by 2-4%.

Most data from USA and Australian studies lacked E70 and E100 values which were essential for this analysis. This is because the USA and many other countries report the temperature required to reach a given percent of sample evaporated (TxxE values) as required by prevailing specifications. Temperatures are typically reported for 10% evaporated (T10E), 50% evaporated (T50E), and 90% evaporated (T90E).

Europe, on the other hand, reports the percent of sample evaporated at a given temperature, such as 70°C (E70), 100°C (E100), and 150°C (E150). Exx numbers have the advantage that they blend linearly, at least for hydrocarbon fuels, while TxxE values do not. Fortunately, all of the datasets analysed here provided full distillation information (i.e. T values), although only in 10% v/v or at best 5% v/v steps. Using the reported data, it was possible to interpolate the missing E70 and E100 values by fitting Piecewise Cubic Hermite Interpolating Polynomials [45,45] (*pchip*) to the distillation data using the *pchip* function in Matlab [47]. This function is appropriate for interpolating data points on distillation curves because the curves are monotonic, that is, the values on the curve are always increasing, as illustrated in **Figure 3** for a base fuel and various ethanol blends.

Such interpolations can never be as accurate as direct measurements of E70 and E100, based on the ISO 3405 distillation test method. For example, ISO 3405 requires the operator to "record temperature readings at intervals of 1% v/v or smaller over a range approximately 10°C below and 10°C above the desired temperature". Modern automated distillation apparatus can do this very accurately. There is further uncertainty in the exact position of interpolated E100 and especially E70 values because these are often found on a very flat portion of the distillation curve, as exemplified by the lower left- and right-hand plots in **Figure 3**. The interpolation problem is exacerbated in such cases by measurement error.

Figure 3 Fitted distillation curves (temperature in °C vs. %v/v evaporated) using "Piecewise Cubic Hermite Interpolating Polynomials (pchip)" for:

(A)	a base gasoline
(AS5)	a 5% v/v ethano

5)	a 5% v/v ethanol splash blend in base
10)	a 10% v/v ethanol splash blend in bas



e gasoline (A) se gasoline (A)





The interpolation procedure was carried out on all samples, including those where measured E70 and E100 values had already been reported in the original study. For these fuels where measured values were known, the values from the interpolation procedure agreed well with the measured values, generally within 1% v/v although a few fuels had higher errors.

After the interpolations had been completed, E70 and/or E100 values from a total of 212 ethanol/gasoline blends splash blended from 107 base fuels were available for subsequent analysis. Most of these data covered 5% and 10% v/v ethanol/gasoline blends, but there were some Australian and US data obtained on 15% and 20% v/v blends as shown in Table 1. The measured and interpolated E70 and E100 values are shown in Figure 4.

Table 1 Ethanol contents of gasoline blends reported in published literature studies

Nominal ethanol content (% v/v)	Range in ethanol content (in % v/v)	Total number of samples at this ethanol content
5	1–6%	91
10	8–11%	80
15	15–17%	16
20	19–22%	27
Total	1–22%	214

Notes:

- 1. In **Figures 5, 6, 8, 9, 13** and **14**, the ranges of ethanol content have been narrowed to 4-6%, 9-11%, 14-16% and 19-21% and blends that were outside of these narrower ranges are not shown.
- 2. Two of these 214 blends were not used in the subsequent analyses because there were insufficient distillation data to estimate the E70 and E100 of the base gasoline.





3.4. EFFECT OF ETHANOL ON E70

Figure 5 shows the E70(blend) values for 5%, 10%, 15% and 20% v/v ethanol splash blends (within \pm 1% of the indicated ethanol content; blends at other concentrations are not shown) plotted against the E70(base) of the hydrocarbon-only gasoline. There is a clear linear increase in E70(blend) compared to E70(base) for 5% v/v ethanol/gasoline blends and to a lesser extent for 10% v/v ethanol/gasoline blends. A somewhat weaker correlation is observed for 15 and 20% v/v ethanol/gasoline blends where there are also fewer data points.



Figure 5

E70(blend) versus E70(base) at four different ethanol concentrations

NOTE: In this chart, the actual ethanol concentration ranges are 4-6%, 9-11%, 14-16%, and 19-21% v/v.

Figure 6 shows Δ E70 (that is, E70(blend)–E70(base) versus E70(base). For 5, 10, and 20% v/v ethanol blends, there is a clear trend of decreasing Δ E70 for higher E70(base) levels. For 15% v/v ethanol, there is no clear trend but there are also very few data points. For 10, 15, and 20% v/v ethanol blends, Δ E70 values up to 30% v/v can be seen at lower E70(base) values (20–30% v/v).

Figure 7 shows Δ E70 versus ethanol content (including data points at all ethanol concentrations). This figure shows that Δ E70 increases rapidly up to 10% v/v ethanol and then levels off at higher ethanol levels. The Δ E70 exhibits a wide range of values between 2-15% v/v at 5% v/v ethanol and 9-31% v/v at ethanol concentrations of 10% v/v or higher. This confirms that ethanol blending is not a simple Linear by Volume (LBV) process and may also be sensitive to the properties of the base fuel into which the ethanol is blended.



Figure 6 ΔE70 versus E70(base) at four different ethanol concentrations



Figure 7 ΔΕ70 versus ethanol concentration



NOTE: In this chart, reported data for all ethanol concentrations have been evaluated.

3.5. EFFECT OF ETHANOL ON E100

The E100 data have been plotted in the same format as for E70. Figure 8 shows the E100(blend) of 5%, 10%, 15% and 20% v/v ethanol splash blends (each \pm 1%) plotted against E100(base).

Figure 8 shows much stronger linear relationships between E100(blend) and E100(base) at all ethanol levels than those seen between E70(blend) and E70(base) in **Figure 5**.

Figure 9 shows Δ E100 versus E100(base). The Δ E100 values are considerably smaller than the Δ E70 values plotted in **Figure 6**, particularly at the lower ethanol concentrations. Values of Δ E100 up to 20% v/v can be seen for 15 and 20% v/v ethanol blends and again Δ E100 gets smaller as the E100(base) increases.

Figure 10 suggests that Δ E100 continues to increase with increasing ethanol content up to 15% v/v. Because the data at higher ethanol contents come from several different sources, it is not entirely clear whether Δ E100 levels off between 15% and 20% v/v. The spread of Δ E100 values, however, is generally less than that seen for Δ E70, except at 20% v/v, indicating that blending may be more predictable at 100°C than it is at 70°C. This is not surprising because the distillation curve for ethanol blends is very flat at 70°C while the curve is much steeper at 100°C. As was seen in **Figures 1** and **3**, the azeotrope formed by ethanol and gasoline components generally distils over the range 50–70°C. Thus, the E70 of ethanol/gasoline blends will always be more variable than the higher distillation points, such as E100 or E150.



E100(blend) versus E100(base) at four different ethanol concentrations



NOTE: In this chart, the actual ethanol concentration ranges are 4-6%, 9-11%, 14-16%, and 19-21% v/v.



Figure 9 ΔE100 versus E100(base) at four different ethanol concentrations



Figure 10

ΔE100 versus ethanol concentration



NOTE: In this chart, reported data for all ethanol concentrations have been evaluated.

3.6. EFFECT OF ETHANOL ON E150

A detailed analysis of E150 values was not included in this review because the effects of ethanol were expected to be small at this higher distillation value. For this reason, any E150 values that were not reported in the datasets were not interpolated. However, for fuels where E150 data were reported, the Δ E150 values were as shown in **Table 2**.

Table 2

 $\Delta E150$ at different ethanol concentrations for ethanol/gasoline blends included in published literature studies

	ΔE150 Values			
Ethanol Contents	Minimum	Maximum	Mean	Predicted by LBV
5% v/v blends (± 1%)	-0.2	2.0	0.6	0.7
10% v/v blends (± 1%)	0.4	3.0	1.4	1.3
20% v/v blends (± 1%)	1.2	3.1	2.3	2.6

The mean values of Δ E150 tabulated above are very similar to those that would be expected from the following LBV blending rule:

E150(blend) = (1 – EtOH) x E150(base) + EtOH x BlendE150(EtOH)

where EtOH is the fractional ethanol content (=%Ethanol/100). This is not surprising because 150°C is well above the azeotrope region (see **Figure 1**) and all of the ethanol in the mixture will have distilled from the sample before reaching this temperature. The values in the LBV column in **Table 2** were calculated with E150(base) assumed to be equal to its average value 86.8% and BlendE150(EtOH) set equal to 100% v/v (its boiling point being 78.4°C).

3.7. PREDICTIVE MODELS FOR E70 AND E100

The blending performance of ethanol can be expressed in terms of "Blending E70" (**BlendE70(EtOH)**) and "Blending E100" (**BlendE100(EtOH)**) values. These are used in the following equations:

- E70(blend) = (1 [EtOH]) x E70(base) + [EtOH] x BlendE70(EtOH)
- E100(blend) = (1 [EtOH]) x E100(base) + [EtOH] x BlendE100(EtOH)

to predict the E70 and E100 of simple gasoline/ethanol splash blends.

Observations of BlendE70(EtOH) can be obtained from measured (or interpolated) pairs of E70(blend) and E70(base) values using the inverse equation:

• BlendE70(EtOH) =
$$\frac{\text{E70(blend)} - (1 - [\text{EtOH}]) \times \text{E70(base)}}{[\text{EtOH}]}$$

Similarly, observations of BlendE100(EtOH) can be calculated from:

• BlendE100(EtOH) =
$$\frac{E100(blend) - (1 - [EtOH]) \times E100(base)}{[EtOH]}$$

Figure 11 shows the observed values of BlendE70(EtOH) and BlendE100(EtOH) plotted against ethanol content. It can be seen from this figure that BlendE70(EtOH) decreases with ethanol content while BlendE100(EtOH) increases.

Figure 11a BlendE70(Et







Figure 11b BlendE100(EtOH) versus ethanol concentration

NOTE: In this chart, reported data for all ethanol concentrations have been evaluated.

If ethanol/gasoline blending were a true LBV process, then the BlendE70(EtOH) and BlendE100(EtOH) values would be expected to be 0 and 100% v/v, respectively, consistent with the boiling point of pure ethanol (78°C). In both cases, therefore, the volatility of ethanol blends in the 70-100°C range is higher than would be predicted by LBV blending due to the azeotrope formation.

When ethanol is present in gasoline at low concentrations, it is less likely to form persistent hydrogen bonds with other ethanol molecules due to their low concentration. Hydrogen bonding interactions between ethanol and hydrocarbon molecules will be very weak but azeotropes will form between ethanol and the hydrocarbon molecules in the gasoline. For these reasons, ethanol can readily escape from the liquid phase to the vapour phase in ethanol/gasoline blends and this can be seen in the higher than expected DVPE for low concentration ethanol/gasoline blends (**Figure 2**). The azeotrope formation also results in higher Δ E70 and BlendE70(EtOH) values at low concentrations of ethanol but the Δ E100 and BlendE100(EtOH) values are relatively low because most of the azeotropes distil by about 70°C.

As the concentration of ethanol in gasoline increases, hydrogen-bonding interactions between ethanol molecules are more likely due to their higher concentration. This makes it easier for the ethanol to remain in the liquid phase at temperatures higher than 70°C. Thus the BlendE70(EtOH) will decrease towards that of pure ethanol. This transition is not necessarily linear with ethanol content and will depend on azeotropic interactions of ethanol with different hydrocarbon species in the gasoline mixture. As the distillation temperature increases above 70°C, the ethanol concentration will drop in the remaining mixture fuel. This will lead to a

disproportionate increase in E100 and higher than expected BlendE100(EtOH) values.



Figure 12 Distillation curves for a base gasoline and 5, 10, and 20% v/v ethanol/gasoline blends

This behaviour can be seen in **Figure 12**, which shows distillation curves (measured in 1% v/v steps) for a base gasoline and 5, 10, and 20% v/v ethanol blends. The 5 and 10% v/v ethanol blends show a similar increase in volatility up to about 60°C, at which point the 5% v/v ethanol/gasoline blend begins to approach the base gasoline distillation curve. On the other hand, the 10% v/v ethanol/gasoline blend shows azeotropic distillation and higher volatility up to about 70°C. The 20% v/v ethanol/gasoline blend shows a smaller volatility increase up to 70°C, while azeotropic distillation continues up to almost 80°C.

Empirical models have been fitted relating the observed values of BlendE70(EtOH) and BlendE100(EtOH) shown in **Figure 11** to the concentration of ethanol and the values of E70 or E100 for the corresponding base fuel. These models can then be used to predict the E70 and E100 values of the final ethanol/gasoline blend. Data on compositional variables (for example, aromatics, olefins, etc.) were very limited and detailed analysis showed little apparent impact of gasoline composition on blending values. There were also no fuels containing ethers in this dataset and ethers are known to affect DVPE and most probably distillation. Consequently, empirical models were developed only with ethanol content and E70(base) or E100(base) as variables. The models were fitted using weighted multiple regression analysis, as described in **Appendix 2**.

The empirical models derived from this analysis are:

- BlendE70(EtOH) = 289 754 x [EtOH] 0.384 x E70(base)
- E70(blend) = (1 [EtOH]) x E70(base) + [EtOH] x BlendE70(EtOH)

- BlendE100(EtOH) = 142 + 247 x [EtOH] 1.066 x E100(base)
- E100(blend) = (1 [EtOH]) x E100(base) + [EtOH] x BlendE100(EtOH)

where [EtOH] is the fractional ethanol content (=%Ethanol/100). The models shown here should not be used for ethanol concentrations higher than 20% v/v ethanol.

As can be seen, the coefficient for the ethanol content ([EtOH]) is negative for E70 but is positive for E100. Thus, the Blending E70 (BlendE70(EtOH)) decreases with increasing ethanol content while the Blending E100 (BlendE100(EtOH)) increases with increasing ethanol content, as was shown in **Figure 11**.

Figures 13a and **13b**, respectively, show the observed values of BlendE70(EtOH) plotted versus the E70(base) and BlendE100(EtOH) plotted versus the E100(base) of the gasoline. For BlendE70(EtOH), we see a strong negative correlation at 5% v/v ethanol which weakens at higher ethanol concentrations. This indicates that the blending performance of ethanol depends not only on the ethanol concentration but also on the composition of the mixture into which the ethanol is blended. There is also evidence of a negative relationship between BlendE100(EtOH) and the E100(base) of the gasoline but the patterns are less clear.





NOTE: In this chart, the actual ethanol concentration ranges are 4-6%, 9-11%, 14-16%, and 19-21% v/v.



Figure 13b BlendE100(EtOH) versus E100(base)

NOTE: In this chart, the actual ethanol concentration ranges are 4-6%, 9-11%, 14-16%, and 19-21% v/v.

Figures 14a and **14b**, respectively, show the observed (that is, either the measured or interpolated) values of E70 and E100 plotted against the fitted values calculated from the models shown above. For E100, there is a very good fit except for the limited data at the 15% v/v ethanol content. For E70, there is a good fit for 5% v/v blends but the fit is less good for 10% v/v and higher ethanol concentrations. This could be because the distillation curve is very flat around the 70°C temperature, particularly at higher ethanol concentrations, so that the interpolated values may be less accurate. There may also be problems associated with the various sources of analytical data. For example, the empirical model fits the CONCAWE data very well but the CARBOB and Shell data very poorly. As was already shown in **Figure 13a**, the E70(base) may have a stronger impact at lower ethanol concentrations and **Appendix 2** describes how this might be taken into account in order to improve the empirical models.



Figure 14a Modelled versus observed E70(blend) values for ethanol/gasoline blends





Figure 14b Modelled versus observed E100(blend) values for ethanol/gasoline blends

NOTE: In this chart, the actual ethanol concentration ranges are 4-6%, 9-11%, 14-16%, and 19-21% v/v.

3.8. CONCLUSIONS ON THE VOLATILITY OF ETHANOL/GASOLINE BLENDS

The addition of ethanol into a hydrocarbon-only gasoline is well known to impact the physical, chemical, and combustion properties of the resulting blend. For the purposes of this report, the impact of ethanol on the physical properties, especially distillation, is the primary focus.

Considerable work has been reported in the published literature to understand and account for the effect of ethanol on the vapour pressure and distillation of the resulting ethanol/gasoline blend. The effect of ethanol on vapour pressure in particular is well documented and models have been developed to predict the change in DVPE for ethanol/gasoline blends.

Ethanol also changes the distillation properties of gasoline, especially the E70 and E100 values, but there are limited published data on the magnitude of these effects at 10% v/v ethanol contents and higher. In some studies, models have been developed to predict the T50E values for ethanol/gasoline blends but these effects have not yet been modelled in Europe, where we prefer to specify E70 and E100 values. There are also limited data on the impact of the base gasoline composition on volatility changes when ethanol is introduced, especially the impact of other oxygenates, such as ethers, in gasoline.

In order to evaluate these effects, published analytical data on ethanol/gasoline blends containing up to 20% v/v ethanol were analysed. The published data were only analyzed where the study reported data for both the base gasoline and the splash blends of ethanol in that same fuel. This evaluation included interpolating the E70 and E100 values from the distillation curves for fuels where these properties were not reported in the original publication. Where the measured E70 and E100 values were reported, the same interpolation procedure was used in order to validate the statistical approach. A total of 212 blends from 107 base gasolines were evaluated statistically.

When ethanol is blended into a hydrocarbon-only gasoline, the increase in E70 compared to that of the base gasoline (Δ E70) was found to be between 2-15% v/v for 5% v/v ethanol blends and between 10-30% v/v for 10-20% v/v ethanol blends. The Δ E70 values were found to decrease with increasing E70 of the base gasoline. The Δ E70 values also increase with ethanol content up to 10% v/v but then appear to stabilise at higher ethanol contents up to 20% v/v.

The corresponding Δ E100 values were found to be 1-5% v/v for 5% v/v ethanol blends, 2-10% v/v for 10% v/v ethanol blends, and 10-20% v/v for 15-20% v/v ethanol blends. The Δ E100 values were also found to decrease with increasing E100 of the base gasoline and increase with increasing ethanol content up to 20% v/v.

The blending performance of ethanol can be expressed in terms of Blending E70 and Blending E100 values which are, of course, strongly non-linear. Using the published data validated by the previous analysis, predictive models for Blending E70 and Blending E100 were developed. These included distillation and ethanol terms only, because very little composition data on the base gasolines were available. The Blending E70 is observed to decrease with increasing ethanol content while the Blending E100 increases with increasing ethanol content. This difference is due to the formation of an azeotrope that affects the distillation behaviour of the ethanol/gasoline blend at different temperatures for different ethanol contents.

From this analysis, there are some indications that the blending performance of ethanol also depends on the composition of the base gasoline into which the ethanol is blended. However, more consistently collected analytical data on a well-designed fuel matrix with widely varying composition are needed in order to better understand these effects. Fortunately, a project of this sort for ethanol contents from 5 to 25% v/v is in progress⁵.

⁵ Ethanol/Petrol Blends: Volatility Characterisation in the Range 5-25 vol% Ethanol (DG-TREN Contract TREN/D2/454-2008-SI.2.522.698)

4. EFFECT OF ETHANOL ON HOT WEATHER DRIVEABILITY

In this section, published studies are reviewed on the effect of gasoline volatility and oxygenate content on HWD performance. With some exceptions, most of the studies report on the effect of ethanol on HWD performance. These studies include:

- CRC Studies (Section 4.1)
- CONCAWE/GFC Studies (Section 4.2)
- Australian Orbital Studies (Section 4.3)
- State of Minnesota Studies (Section 4.4)
- Other Work (Section 4.5)

Only the CONCAWE/GFC Studies were conducted on vehicles that are representative of the European market.

4.1. CRC STUDIES

The CRC in the USA conducted HWD test programmes in 1999 [8], 2001 [9], 2004 [10] and 2006 [11] using a new test procedure developed in 1998 [7]. The main test programmes evaluated 11 multi-point injection (MPI) vehicles on 14 test fuels in 1999 [8] and 20 MPI vehicles on 12 test fuels in 2001 [9].

The 1999 programme used 7 hydrocarbon-only fuels and 10% v/v ethanol splash blends from each of these base fuels. The two parameters most commonly used to describe hot driveability behaviour of US MPI vehicles had been RVP (now DVPE) and the temperature needed to achieve a vapour-liquid ratio of 20 (TVL₂₀). These parameters showed poor correlation with HWD performance (as measured by Total Weighted Demerits (TWD)) for both hydrocarbon-only fuels and 10% v/v ethanol blends. A new parameter developed by General Motors (GM), the temperature needed to achieve a vapour-liquid ratio of 1 at a 500kPa pressure (TVL₁₋₅₀₀) showed the best correlation with both sets of fuels:

Ln(TWD) regressed against TVL1-500	adjusted R2 = 0.92
Ln(TWD) regressed against DVPE	adjusted R2 = 0.25
Ln(TWD) regressed against TVL20	adjusted R2 = 0.37

The vapour-liquid ratio of 1 at a 500kPa pressure was considered to be a condition representative of modern MPI fuel delivery systems. This TVL_{1-500} parameter, however, is not a standard measurement (for example, there is no ASTM test method) and it cannot be easily measured by most laboratories. Therefore, efforts were made to develop several indices using more conventionally measured parameters, such as DVPE and TVL_{20} . Two indices showed good correlation with TWD, giving the following correlations with linear ethanol offsets:

Ln(TWD) regressed against DVPE + 0.234 × [Ethanol in %v/v]

adjusted
$$R^2 = 0.87$$

• Ln TWD regressed against $TVL_{20} - 1.01 \times [Ethanol in \%v/v]$ adjusted $R^2 = 0.87$ It was thought, however, that these models would be specific to the set of fuels used in the study so additional studies were proposed to broaden the applicability of the indices.

To do this, the 2001 CRC test programme used three sets of 4 fuels (hydrocarbononly gasolines and 3, 6, and 10% v/v ethanol blends) at three different volatility (TVL₁₋₅₀₀) levels giving a total of 12 test fuels. These fuels were tested in 20 vehicles whose driveability performance was found to be sensitive to volatility changes. The results showed that TVL₁₋₅₀₀ was the best single volatility parameter, confirming the 1999 results, but once again TVL₂₀ or DVPE in combination with an ethanol offset term were as good as TVL₁₋₅₀₀ for predicting the HWD TWD. This time, the correlations were:

0.863
(

- Ln(TWD) = -0.0325 x (TVL₂₀ 1.27 × [Ethanol in % v/v]) + 6.4187 adjusted R² = 0.879
- $Ln(TWD) = 0.1383 \times (DVPE + 0.338 \times [Ethanol in \% v/v]) + 0.9612$ adjusted R² = 0.880

As an example, **Figure 15** shows the correlation of Ln(TWD) with DVPE and Ethanol (in %v/v).



Figure 15 Mean corrected TWD versus (DVPE +0.338 * Ethanol %v/v) [9]

The 2001 programme also developed a correlation to calculate TVL₁₋₅₀₀ from TVL₂₀ or DVPE and ethanol content. The 2004 programme extended this correlation to lower vapour pressure fuels and developed improved equations as below. The equation based on TVL₂₀ was the best to predict TVL₁₋₅₀₀.
•
$$TVL_{1-500} = 44.38 + 0.565^{*}TVL_{20} - 0.880^{*}$$
 (R² = 0.986)

or

• $TVL_{1-500} = 147.44 - 2.851*DVPE$ (in psi) -1.259*%Ethanol (R² = 0.941)

The 2006 programme [11] tested 23 pre-screened late-model and 4 older MPI vehicles on 12 fuels comprising 0, 5, 10 and 20% ethanol blends at three volatility levels. However, few tests showed significant driveability problems so no conclusions were drawn from this work and no correlations developed with fuel properties. This suggests that vehicle manufacturers have developed more robust fuel systems over the years, including variable pressure systems, and EMS strategies.

In view of the lack of perceived HWD problems in the field, no ethanol offset was applied to the TVL_{20} specification in ASTM D4814 and no changes were made to the limits.

4.2. CONCAWE/GFC STUDY

In Europe, an oil industry group called the Intercompany Volatility Working Group carried out both HWD and CWD vehicle testing for many years in the 1970s ending in about 1996. This work used test procedures developed by the Coordinating European Council (CEC). Although CONCAWE had previously completed driveability studies [48,12], it was considered appropriate to begin new testing in 2003 because vehicles had changed. This was especially due to the introduction of DISI gasoline engines and there was growing interest in the use of ethanol in gasoline. Because the European CEC test procedures had not been updated recently, CONCAWE contacted Groupement Français de Coordination (GFC) who had developed new test procedures for both HWD and CWD but had not used them for detailed fuel effect studies. CONCAWE and GFC began a joint test programme to evaluate the impact of gasoline volatility and ethanol content on the driveability performance of modern European vehicles using these procedures [13,14].

Eight vehicles, three with DISI fuel systems and five with MPI systems, were tested for HWD performance at 20, 30 and 40°C. A matrix of four hydrocarbon test fuels (A,B,C,D) at two levels of vapour pressure (DVPE) and E70 was used, as shown in **Figure 16**. For each hydrocarbon fuel, two other fuels containing 10% v/v ethanol were made, one "splash" blend and one having a volatility matched to that of the hydrocarbon-only base fuel. Some tests were also carried out using 5% v/v ethanol blends, made from 50/50 mixtures of the hydrocarbon and 10% v/v ethanol blends.

The GFC HWD procedure required a trained driver to follow a specific set of driving sequences, comprising a motorway hot-soak test, a mountain climbing test and a "canister loading" test designed to simulate stop-and-go driving in heavy traffic. Driveability malfunctions (stall, hesitation, loss of acceleration performance, stumble, surge, and roughness) were recorded by the trained driver and given demerit ratings using pre-defined demerit and severity scales, as described in [13].



Three of the MPI vehicles showed good HWD performance on all fuels tested, with \leq 24 demerits. Another vehicle showed <24 demerits in all tests, except for fuel AS10 (10% v/v ethanol splash blend) at 30°C (34 demerits). In view of these low demerit levels, three vehicles were also tested at 40°C on Fuel A, the highest volatility hydrocarbon-only fuel. Even though this was an extreme combination of temperature and fuel volatility, all results were \leq 20 demerits, confirming the excellent HWD performance of modern MPI vehicles. In general, the highest demerits were observed on Fuel A at 30 or 40°C, showing a slight sensitivity to fuel volatility. Vehicle 4 had an MPI fuel system but varied the inlet valve lift to control engine power rather than the throttle. This vehicle showed low demerits (<12) under all test conditions except at 30°C for the highest volatility fuels, where demerit levels of 16–95 were seen.

One of the DISI vehicles showed good HWD performance in all test conditions, similar to the four MPI vehicles. The other two DISI vehicles showed much poorer HWD performance as shown in **Figure 17**, with several tests giving 100–500 demerits. The DISI Vehicle 2 showed high demerits on high volatility fuels, with the highest demerits of 471 occurring in a test on Fuel A at 30°C. Vehicle 3 also gave many results with high demerits (270-314) on high DVPE Fuels A and C at 30°C and on Fuel BS at 40°C. These high demerits were accompanied by an engine warning message that the fuel pressure was out of range, indicating that vapour lock was taking place somewhere within the fuel system. For both of these vehicles, tests on volatility class D fuels gave low demerits (\leq 17) at all temperatures.



Figure 17 HWD demerits for two sensitive DISI vehicles tested at 30°C and 40°C

For the five vehicles exhibiting low overall demerits, no analysis of volatility effects was possible. The other three vehicles showed clear effects of increasing volatility. For example, in **Figure 18**, results on Vehicles 2 and 3 at 30°C are plotted against volatility as "bubbles", with the area of the bubble being proportional to the number of demerits and the colour of the bubble indicating the severity rating. For Vehicle 2, increasing the DVPE at 30°C (and E70 at 40°C, not shown) gave a clear increase in demerits, while Vehicle 3 at 30°C only showed an increase in demerits on the most volatile Fuel A.

Figure 18 Effect of DVPE and E70 on HWD for Vehicles 2 and 3 and hydrocarbon-only fuels



Bubble area represents total demerits.



Statistical modelling indicated that the three sensitive vehicles, that exhibited substantial HWD problems and variations with volatility, were more sensitive to fuel DVPE than they were to E70. The effect of DVPE over the range 60-100 kPa was more than twice that of the effect of E70 over the range 40-55% v/v. In all cases, substantial increases in demerits were only seen at high temperatures on fuels having volatilities beyond the summertime volatility class limits within EN228. This shows that manufacturers have validated their vehicles on fuels at the extremes of the EN 228 volatility limits, as would be expected to ensure driveability performance.

Only four vehicles exhibited sufficient HWD demerits to perform a meaningful analysis of ethanol effects. Two examples of the effects of ethanol in the sensitive vehicles are shown in **Figure 19**. In general, the effects are only evident with high volatility fuels and at high temperatures. In these cases, ethanol splash blends increased demerits and, in some cases, the overall severity rating. Matched volatility

ethanol blends gave similar HWD performance to the equivalent hydrocarbon fuels. This suggests that the effects seen are not due to the presence of ethanol *per se* but are a consequence of the increase in volatility that is caused by the addition of ethanol.



Figure 19 Effect of ethanol on Vehicles 3 and 4

4.3. AUSTRALIAN ORBITAL STUDIES

Two major test programmes on ethanol/gasoline blends were completed in Australia by the Orbital Engine Company. The first in 2002 was an investigation of the impact of 20% v/v ethanol in gasoline, carried out for the Environment Australia project "Market Barriers to the Uptake of Biofuels – Testing Petrol Containing 20% Ethanol (E20) [31-33]. In July 2003, however, the Australian Government limited the amount of ethanol in gasoline to 10% v/v and, in 2005, announced a programme to test vehicles on E5 and E10 blends. This programme was completed and reported by Orbital in 2007 [35].

Both of these test programmes looked at a range of vehicle issues covering emissions, material compatibility and performance, and including both HWD and CWD performance. The HWD testing was carried out as follows. Vehicles were fully warmed up by driving them on a Chassis Dynamometer until the engine oil temperature had reached 120°C. The vehicles were then soaked in an environmental chamber at 40°C with extra infrared lamps to simulate solar loading for 30 minutes. Hot start times and idle quality were assessed after 10 and 30 minutes. An extended idle test was also performed over 40 minutes after warm-up. After this, the vehicle was stopped, soaked for an additional 20 minutes, then restarted and rated again. A no-load acceleration test (throttle "blip") was carried out, followed by an HWD test after a further 20 minute soak. This final HWD test was a road test at ambient temperature involving idle, cruise, and acceleration, as shown in **Figure 20**. HWD performance was rated on a scale from 1 to 10 as shown in **Table 3**. A rating of 7 was defined as a typical production target.



Figure 20 Driveability test cycle used in the Orbital study

Table 3Orbital driveability rating scale

10	Excellent	Excellent driveability. No defects, user is truly impressed.
9	Very Good	No trace of defects, solid/responsive
8	Good	No noticeable defects, less responsive or flat performance. User is pleased
7	Satisfactory	One or more slight defects present barely noticeable. All minor in nature
6	Agreeable	One or more defects present, very noticeable, not objectionable. User does not consider objectionable. User is generally satisfied
5	Mediocre	Obvious defects present, irritating, will probably generate complaints. User not particularly happy with car operation and is likely to seek corrective action
4	Poor	Disturbing defects present, but still confident of continual operation. User would seek corrective action
3	Very poor	Undermines driver confidence, not reliable
2	Bad	Failure to stay running, will not operate consistently
1	Very bad	Uncontrollable, unpredictable operation

4.3.1. E20 Programme

For this programme, tests were completed in 2002 on 5 new and 4 older (1986-93) vehicles using a 70 kPa base gasoline and E20 splash blended gasolines at 40°C. Hot start times for the new vehicles are shown in **Figure 21**.

Clearly some vehicles showed significantly longer hot start times, especially the Ford Falcon and similar results were seen for the older vehicles. Orbital concluded that some vehicles may experience increased starting times of up to three seconds under hot conditions while idle stability may be degraded such that it will be noticed by the average driver.



Hot start and restart times for new Australian vehicles

Note: Start time Re-start time after 30 mins soak Re-start time after 120 mins extended idle.

> The driveability assessments are summarized in Table 4, for normal ambient temperature, plus Hot and Cold Weather. The Hot Weather assessments showed that the average driveability for new vehicles was generally slightly worse on E20, while the worst rating was sometimes significantly worse. This is also true for three of the older vehicles, but one of them (Ford Falcon) was much worse. Orbital concluded that:

- All of the new vehicles tested for HWD were found to operate in a similar way on hydrocarbon-only gasolines and when operating on E20 splash blended gasolines.
- Some older vehicles may display stalling and rough running to such a degree that the driver will think that the vehicle will stop running. The startability of other vehicles may degrade, but the driver would still be confident of continued operation and would seek corrective action. Idle quality may also degrade so that the driver would seek corrective action.
- Significant hesitation at Wide Open Throttle (WOT) demand may be experienced in older vehicles along with hesitation at cruise speeds of 50 to 70 km/h. Some vehicles may experience sufficient hesitation that the driver will seek corrective action.

Table 4

New and older Australian vehicle driveability assessment on gasoline and E20 fuels

		Ambient Driveability		Hot Driveabi	lity	Cold Driveability	
New Vehicles		Gasoline	E20	Gasoline	E20	Gasoline	E20
Holden	Average	7.7	7.7	7.8	7.4	7.9	7.8
CommodoreVXII AENHO01	Maximum	8.5	8	8	8	8	8
	Minimum	6.8	7.2	7.3	6	7.3	7
Ford Falcon	Average	7.4	7.3	7.6	7.2	7.8	7.4
AU III AENFO02	Maximum	8	7.9	8	8	8	8
	Minimum	6.1	6.8	6.8	5.8	7.3	6.3
Toyota Camry	Average	7.6	7.8	7.9	7.7	7.9	7.6
Altise AENTO03	Maximum	8.3	8	8	8	8	7.8
	Minimum	7	7.3	7.8	7	7.5	7.3
Hyundai	Average	7.8	7.5	7	7.3	8	7.5
Accent AFNHY04	Maximum	8	8	8	8	8	8
	Minimum	7.5	6.6	4.7	6.5	7.9	7.2
Subaru	Average	7.8	7.8	7.6	7.4	7.7	7.4
Impreza WRX AENSU05	Maximum	8.3	8.3	8	8	8	8
	Minimum	7	7.3	7	6	6.8	4
Older Vehicles		Gasoline	E20	Gasoline	E20	Gasoline	E20
AENFO11 1985 Ford Falcon	Average	6.6	6.1	6.1	3.9	6.7	6.2
XF	Maximum	7.3	7	7.3	4.5	7.3	7.1
	Minimum	5.6	4.3	5	3.5	5.5	5
AENHO12 1985 Holden	Average	7.1	6.6	6.9	6	5.8	4.2
Commodore	Maximum	8	7.8	8	7.3	7.4	6
	Minimum	6.2	4.6	4.8	4.5	1	1
AENMI13 1986 Mitsubishi	Average	7	6.7	6.5	5.9	6.5	7.1
Magna TM	Maximum	7.8	7.5	7.8	7.8	7.3	7.8
	Minimum	5.5	7.5	5	2.5	5	5.5
AENTO14 1993 Toyota Camry	Average	7.6	7.5	7.9	7.3	8	7.9
Ultima	Maximum	8	8	8.3	8	8.3	8.3
	Minimum	6.5	6.8	7.5	3	7.5	7.4

4.3.2. E5 and E10 Programme

In the second Orbital study completed in 2007, sixteen vehicles were tested to assess their suitability for use with E5 and E10 ethanol/gasoline blends. All of these vehicles had not been identified by the Australian Federal Chamber of Automotive Industries (FCAI) as suitable for use with E10 fuels. Eight pre-1986 vehicles were included in the test fleet in order to assess their suitability for use with E5, but not

E10. Five of the sixteen vehicles were fuel injected and the rest had carburettors. A single batch of commercial summer-grade Australian fuel was used for the HWD tests and blended to a level of 5 and 10% v/v ethanol. The same HWD test procedure and ratings scale were used as in the previous E20 study described above. This time, however, the hot-start and idle performance was rated using the scale shown in **Table 5**. The overall ambient, hot and cold starting and driveability ratings for all vehicles are shown in **Table 6**. This shows the "worst case" difference in rating between hydrocarbon-only gasoline and the E5 and E10 ethanol blends, i.e. the most significant degradation in driveability/performance that was evident when comparing an ethanol/gasoline blend with its corresponding hydrocarbon-only gasoline.

Table 5

Orbital startability and idle quality rating table

	Startability Rating	Idle Quality Rating
7	Normal	Normal
5	Rough	Rough
3	Start and Stall	Surge
1	No start	Engine Stall

Table 6

New and older Australian vehicle driveability assessment on gasoline, E5, and E10 fuels

	"Worst	rst Case"		E5	E5 compared to Petrol		l to	to E10 compared to Petrol				Over worst					
De-rating for each Assessment Group		Vehicle		Ambient Driveability	Hot Start and Driveability	Cold Start and Warm-up	Snap test	Ambient Driveability	Hot Start and Driveability	Cold Start and Warm-up	Snap test		E5	E10			
			GOV5-01	Hyundai Excel	-0.2	-0.1	-0.5	if nap	-0.3	-0.3	-0.5	-0.2		-0.5	-0.5		
	s	fed	GOV5-02	Nissan Pulsar	-0.5	-0.3	-0.1	lired 10 s	0.0	0.0	-0.2	0.0		-0.5	-0.2	led –	ş
	arc	-ue ect	GOV5-03	Ford Festiva	-1.0	-0.1	-0.5	лш	-0.4	-1.0	-0.5	-0.5		-1.0	-1.0	-ue ect	arc
	Ň	l nj	GOV5-04	Honda Civic	-0.3	0.0	-1.5	ully Jes o	-0.3	0.0	-2.0	-0.3		-1.5	-2.0	ц Г	Ň
	Q		GOV5-05	Nissan Patrol	-0.5	-3.0	-0.5	0 issu	-0.8	-0.5	-0.3	0.0		-3.0	-0.8		Q
	986		GOV5-06	Toyota Hilux	-1.0	-3.0	-1.5		-0.5	-3.5	-2.5			-3.0	-3.5		986
	10		GOV5-07	Mazda 323	-1.3	-0.3	-3.5		-2.3	-0.6	-2.3			-3.5	-2.3		16
			GOV5-08	Toyota Corolla	-0.5	-2.3	-1.0		-1.0	-2.0	-0.3			-2.3	-2.0		
Γ		2	GOV5-09	Holden Commodore	-1.5	-1.0	DNS	ble			ble		-1.5		'n		
		ette	GOV5-10	Ford Falcon	-0.3	-1.0	-0.5	ica				ica		-1.0	ss	ette	
	92	un	GOV5-11	Ford Laser	-1.5	-1.8	-0.9	bpl			bpl	ppl	-1.8	oroj	nu	8	
	198	arb	GOV5-12	Toyota Corolla	-0.3	-1.5	-0.3	ťΑ	nroie	n pan	ne to	pe to To	-1.5	ofpoas	arb	198	
	ė	U U	GOV5-13	Mitsubishi Magna	-0.8	-1.3	-1.0	Ž	pioje				-1.3	e to	U U	ė	
	ā		GOV5-14	Toyota LandCruiser	-0.5	-1.0	-1.0			10000	,			-1.0	op op		•
			GOV5-15	Nissan Bluebird	-0.8	-1.0	-3.0							-3.0	Sc		
			GOV5-16	Holden Camira	-1.0	-0.5	-2.0							-2.0	_		
										* Ratings a	re "worst						
Legend											case", color	ur coaing					
		bold	/white //black	Petrol rated as poor, therefore	e delta	not bia								after review	of		
n/a		n/a	Result not available										specific res	ults.			
		C	NS	Did Not Start (on any fuel) in	10secs	allocat	ed										
				Of interest and potentially not	iceable										Of interest and	potentially no	oticeable
		DNS Did Not Start (on E5) in 10secs		cs alloc	ated									Serious and	l of potential i	issue	

Surprisingly the worst HWD performance was seen for some of the more modern vehicles. However, only one of these (the Nissan Patrol) was fuel injected, and this vehicle showed little HWD performance loss on the E10 fuel, but significant performance loss on E5 fuel, which is even more surprising. Orbital concluded that:

Figure 22

- For vehicles 1986-onwards, the use of E5 had an adverse impact on hot-start and driveability for the Corolla, Hilux, and Patrol, while the use of E10 had an adverse impact on the Corolla and Hilux only.
- For the pre-1986 vehicles, the use of E5 had no major adverse impact of concern for hot-start and driveability, although the Laser, Corolla, and Magna all showed poor hot startability after soaking for various periods of time. While unsatisfactory from an operator's perspective, these would not pose a safety risk.

4.4. STATE OF MINNESOTA STUDY

In the State of Minnesota Study [37], vehicle owners (also called untrained raters) were asked to complete daily log sheets indicating any driveability problems that occurred. In addition, trained raters for vehicle driveability performance were contracted to conduct industry standard driveability tests on a subset of the vehicle fleet, with a test series in each season: fall, winter, spring, and summer. The E0 fuel was commercially available hydrocarbon-only, regular octane grade gasoline. The E20 fuel was commercially available E10 up-blended with ethanol to E20. Throughout the nominal one-year vehicle driveability study, the UMN Fleet Services Facility received 24 deliveries of E0 gasoline and 10 deliveries of E20 ethanol/gasoline blends. Fuel properties were not controlled, and the E20 fuel is not directly comparable with the E0 fuel.

Figure 22 shows the results from untrained raters (lay drivers) for all seasons, covering both HWD and CWD performance. The left-hand figure shows results weighted by the number of reports; this weighting gives greater emphasis to vehicles that repeatedly reported problems. In the right-hand figure, the average demerits for each vehicle are calculated and statistics are based upon performance of individual vehicles.

The report-weighted figure does show significant degradation of driveability in Fall and Spring, but not in winter or summer. Perhaps this is due to changes in fuel volatility classes occurring during these seasons. The vehicle weighted analysis shows no significant effects.



Demerit scores from untrained raters from the Minnesota Study

To assist in scientifically validating the test, trained driveability raters evaluated a subset of a nominal twelve pairs of vehicles over four separate seasons, using CRC test procedures. Logistical problems meant that not all vehicles were tested in all seasons. HWD testing was carried out in summer in the ambient temperature range of $90-98^{\circ}F(32-37^{\circ}C)$ and the results are shown in **Figure 23**.



Average TWD reported by trained raters by season and on individual vehicles during the summer season





In the summer test session, about 62% of the observations fell within the data noise level, defined as 20 TWDs or less. Idle quality contributed heavily to the malfunctions, but there were some occurrences of manoeuvring malfunctions that would be noticeable to average drivers. These malfunctions however were split evenly (50% each) between E0 and E20. The study concluded that:

"Analysis of vehicle driveability evaluations performed by the trained raters showed that seasonal performance differences between E0 and E20 were not statistically significant at the 95% confidence interval".

4.5. OTHER WORK

Table 7

A recent review of ETBE data [17] reported some HWD tests on gasoline blends containing ETBE and ethanol that had been completed by Neste in the early 1990's using CEC test procedures.

Two vehicles were tested, both with 1.3L engines, a Japanese car with a carburettor and no catalyst and a German MPI car with an oxidation catalyst. Six fuels were tested that had been blended to the then-current EN specifications containing ETBE from 13–20% m/m and ethanol from 7.2–12.3% m/m. The properties of these fuels are shown in **Table 7**. Clearly, the blends containing ethanol had much higher oxygen contents and volatility levels.

				Fuel I	Blends		
Property	Unit	ES13	ES17	ES19	AS7	AS9	AS12
ETBE Content	% m/m	13.0	16.7	19.4			
Ethanol Content	% m/m				7.2	9.4	12.3
Oxygen content	% m/m	2.04	2.57	3.05	2.50	3.26	4.27
DVPE	kPa	79	70	71	82	84	85
E70	% v/v	29.4	28.3	29.2	39.6	43.7	45.5
VLI		996	898	914	1097	1146	1169

HWD study on gasoline blends containing ETBE and ethanol [17]

In this study, Car A with the carburettor had major HWD demerits on the ethanol blends at 30°C giving a Category 3 Fail for the 9.4 and 12.3% m/m blends. Surprisingly, similar problems were not observed at the higher test temperatures of 35 and 40°C however. On the ETBE blends, demerits increased slightly at the higher temperatures but were always less than 10 demerits.

The MPI Car B showed no major problems on either ETBE or ethanol fuels. Again demerits increased at the higher test temperatures but were less than 10 demerits with the exception of one test at 40°C on Fuel AS9 where 18 demerits were recorded. All demerits were from the acceleration phase of the test, either "jerk" (Car A) or "hesitation" (Car B).

4.6. CONCLUSIONS ON HOT WEATHER DRIVEABILITY

Modern EFI vehicles are much less susceptible to HWD problems than are older vehicles, as shown in the CRC, CONCAWE/GFC, Orbital Engine, and State of Minnesota studies. This is due to the continued development of EFI systems that operate at relatively high pressure, and electronic EMS to control fuelling and adjust for changes in fuel composition. Even the move to "returnless" EFI systems where

hot fuel from the injector rail is not returned to the fuel tank has not created new HWD performance problems. In particular, the most recent CRC programme found so few demerits that it was not possible to analyse the data.

DISI vehicles operate at higher injection pressures and are expected to have better HWD performance. However some early European DISI vehicles were clearly sensitive, as shown in the CONCAWE/GFC programme, where problems were seen with two out of three DISI vehicles tested at 40°C on 60kPa fuels having an E70>55. Although the move to DISI engines has slowed in Europe since the early 2000s, it is expected that this trend may reverse and that improvements will have been made in HWD performance based on the earlier experience.

The State of Minnesota study in particular showed that most HWD problems occurred in the "Intermediate" seasons of spring and autumn. This is when high volatility fuels may be in the marketplace and could cause problems on unseasonably hot days. It is understood that manufacturer warranty claims relating to poor starting and rough idle are highest in these seasons. This should be taken into account in any future test programmes.

The use of ethanol splash blends without DVPE control degrades the HWD performance of some vehicles under extreme conditions. This appears to be mainly due to the changes in DVPE and distillation properties of the ethanol/gasoline blend, rather than the specific use of ethanol *per se*.

For modern EFI vehicles, US CRC data suggested that HWD demerits correlate favourably with a parameter proposed by GM, TVL_{1-500} or the temperature required to achieve a vapour-liquid ratio of 1 at 500kPa pressure. These temperature and pressure conditions are considered to be representative of those in modern MPI fuel delivery systems although equally good correlations were found with DVPE or TVL_{20} including an ethanol offset term. This may not apply, however, to DISI systems that operate at higher pressures.

Limited statistical analysis of CONCAWE/GFC data for the few European vehicles where significant demerits were found suggested that DVPE was a more important parameter than E70 for ensuring acceptable HWD performance.

5. EFFECT OF ETHANOL ON COLD WEATHER DRIVEABILITY

In this section, published studies are reviewed on the effect of gasoline volatility and oxygenate content on CWD performance. With some exceptions, most of the studies report on the effect of ethanol on CWD performance. These studies include:

- CRC Studies (Section 5.1)
- Shell Studies (Section 5.2)
- CONCAWE/GFC Studies (Section 5.3)
- Australian Orbital Studies (Section 5.4)
- State of Minnesota Studies (Section 5.5)
- Other Work (**Section 5.6**)

The Shell, CONCAWE/GFC, and Neste Oil (in **Section 5.6**) studies were conducted on vehicles that are considered to be representative of the European market.

5.1. CRC STUDIES

In addition to their extensive HWD studies, the CRC in the USA has also evaluated CWD performance over many years. The original ASTM Driveability Index (DI) was developed in the 1980s [18] to describe fuel effects better than the single distillation parameters (T50E or E100) that had been used up till then. This was applicable to hydrocarbon fuels, but did not cover oxygenates, which were known to have substantial effects on CWD. Consequently, a major programme was completed during the 1990s to investigate the effects of both MTBE and ethanol on CWD performance [19-23] at test temperatures between -8 and 84°F (-22 and 29°C). A total of 135 EFI vehicles and 87 fuels were tested using the latest CRC test procedures in this very comprehensive study. A detailed statistical analysis was carried out on these data and the resulting equations checked against older programmes that had used different test procedures.

CWD demerits were correlated with a number of different DI models. These included Evaporative DIs based on Exx numbers (EDIs), the older DI developed by ASTM, and new versions of the ASTM DI equation, called the New Driveability Index (NDI). The fuels contained only 0 or 10% v/v ethanol, or 0 or 15% v/v MTBE, so that only fixed oxygenate offsets could be calculated and not coefficients for the % v/v MTBE or EtOH. The best models evaluated (with Exx numbers in °C) were:

	Models	Adjusted R ²
•	DI = 1.50 x T10 + 3.00 x T50 + 1.00 x T90	0.78
•	NDI = 1.50 x T10 + 3.00 x T50 + 1.00 x T90 + 43.2 x (15%MTBE) 86.2 x (10%EtOH)) + 0.88
•	NDI = 1.23 x T10 + 2.95 x T50 + 1.00 x T90 + 42.5 x (15%MTBE) 86.6 x (10%EtOH)) + 0.88
•	EDI = E70 + 1.44 x E100 + 1.57 x E140 – 14.9 x (15%MTBE) - 41.1 x (10%EtOH)	0.88

- EDI = 2.75 x E93 + E149 -17.6 x (15%MTBE) 32.2 x (10%EtOH) 0.76
- EDI = E70 + 2.08 x E121 12.1 x (15%MTBE) -38.3 x (10%EtOH) 0.86

The Shell DI (see **Section 5.2**) was also evaluated and shown to provide a good fit but one that was not quite as good as the Celsius-based EDI shown above. The CRC work generally showed that higher distillation values (T90, E150) were less important than front-end and mid-range distillation values.

To extend this work, additional studies were completed between 2000 and 2003, using fuels with three ethanol concentrations: 3, 6, and 10% v/v. The 2000 programme [24] found no conclusive effect of either DI or ethanol on CWD performance (cold start and warm-up) and drew no conclusions. For the 2003 programme [25,26], CRC decided to screen vehicles for CWD sensitivity before starting the main test programme. As a result of this screening process, 27 sensitive vehicles were selected and tested at -1 to +6°C. As before, a statistical analysis was carried out and various models developed which were equally good at predicting the data. The best models included variable ethanol terms and had high correlation coefficients, as below quoted for temperatures in °C.

	Models	Adjusted R ²
•	NDI = 1.5 x T10 + 3 x T50 + T90 – 1.33 x (%EtOH)	0.944
•	EDI = E70 + 2.08 x E121 - 2.046 x (%EtOH)	0.956
•	EDI = E70 +1.354 x E93 - 3.123 x (%EtOH)	0.964

The NDI model shown above is plotted in **Figure 24**, using Fahrenheit temperatures.

Other models using fixed offsets for 10% ethanol were also developed. A model based on the ASTM DI with fixed offset of 21 was as good as the NDI with ethanol concentration model. EDI models developed with a fixed offset however were not as good.

Model	Adjusted R ²
DI = 1.50 x T10 + 3.00 x T50 + 1.00 x T90 +21 x (10% EtOH)	0.949

Because the models gave similar correlations and there was little added benefit from the EDI models, the New Driveability Index (NDI) equation above was adopted in the latest version of the ASTM D4814 gasoline specification with no change in the DI limits.



Figure 24 Relationship between TWD and DI with ethanol offset in °F [25]

5.2. SHELL STUDIES

Shell has studied CWD performance for many years primarily from a fundamental viewpoint. The hypothesis for these studies is that the standard distillation test does not accurately simulate the process of evaporation in an engine because the fuel is heated slowly and the liquid fuel and air-fuel vapour remain in equilibrium throughout. Evaporation in an engine, however, is controlled by the amount of engine heat that is available and does not reach equilibrium. This means that a flash evaporation occurs in which only a fraction of each fuel component evaporates. For low boiling point compounds, this fraction is large but for higher boiling components, less is flash-vaporised. The "enthalpy requirement" of a gasoline can then be defined as: "the amount of heat required to evaporate sufficient fuel to form an ignitable air-fuel-vapour mixture".

In the 1980s Shell developed a computer program to calculate the "enthalpy requirement" (ER) of a fuel based on a GC analysis [27]. The ER varied according to air-fuel ratio, fuel and air temperature, manifold pressure, and vehicle-dependent effects. Nevertheless, one particular combination of parameters correlated well with chassis dynamometer test results. The Standard Enthalpy Requirement (SER) was defined as "the amount of heat required to form an air-fuel vapour ratio (AFVR) of excess air ratio (λ) of 1.4 with a metered air-fuel ratio (AFR) of 11:1 at 100 kPa pressure and with fuel and air starting at 0°C".

The ER concept was used in a later study [30] to develop a DI for European vehicles, similar to work done by the US CRC. One hundred "model fuels" were developed using the computer programme to calculate their distillation properties and ER at different AFRs. Three DIs were compared: the US ASTM DI, one of the CRC DIs (E93+E149 in SI units), E100+E150 and E100 alone, and the correlation between the DIs and ER at different AFRs plotted, as shown in **Figure 25**.

Figure 25

From this analysis, it was found that all DIs were better than E100 alone. As can be seen, there was little difference between the three indices at rich AFRs (~11:1). The E100+E150 DI is clearly better, however, as the AFR approaches stoichiometric, which is where modern engines mostly operate. Further work was done using inhouse driveability test programmes carried out between 1992-97 on fuel-injected vehicles and a Shell developed test cycle [29]. This work showed that all three DIs gave similar correlations and all were better than single distillation parameters. Some of the fuels contained MTBE (but not ethanol) so a method of adapting the driveability indices to allow for the effects of MTBE was evaluated. The best MTBE offset was found to be 1.2, so DI = E100+E150-1.2x(%MTBE). However subsequent unpublished work using the same approach, but a much larger driveability working Group for 1997-98 [27] showed a lower mean value for the MTBE offset coefficient of 0.7, so:

• Shell DI = E100 + E150 - 0.7 x (%v/v MTBE)

Correlation coefficients of three different DIs with ER versus AFR



Comparison of this work with the US CRC DI equations and ethanol offsets available at that time [22] support the value of 0.7 for MTBE offset. No European tests on ethanol fuels were available at that time, but again comparison with the CRC work suggested that a value of 2.0 would be appropriate, so:

• Shell DI = E100 + E150 - 2.0 x (%v/v EtOH)

5.3. CONCAWE/GFC STUDY

As described in **Section 4.2**, the European Intercompany Volatility Working Group carried out CWD testing during the 1970s to 1990s using CEC test procedures. That work stopped, however, in 1996 and no further work has been done since that time. Thus, by 2003, CONCAWE thought that it was appropriate to look again at CWD performance using newly-developed GFC test procedures in order to evaluate the

impact of gasoline volatility and ethanol content on the CWD performance of modern European vehicles [13,14].

Because the CWD tests were only intended to be used as a screening exercise, no attempt was made to separate the effects of different volatility parameters. Three fuels were blended with essentially parallel distillation curves of high, medium and low volatility, with E100 targets of 76, 56 and 46% v/v, respectively. In addition, 10% v/v ethanol splash blends and matched volatility blends were made from these three hydrocarbon fuels. The eight test vehicles were first screened by testing on the lowest volatility fuel at -10°C, and four of the vehicles selected (2 MPI and 2 DISI) for further testing on the full fuel set.

Surprisingly, the vehicles showed similar demerit levels at both +5 and -10°C. One vehicle showed consistently high demerits (250-450) on all fuels at both temperatures. The other three were in the range 20-150 demerits. Clear fuel effects however were only seen at -10°C, as shown in Figure 26. Three of the vehicles showed an increased level of demerits at -10°C on fuels with E100 below about 50% v/v. In several cases, higher demerits were largely due to difficult cold starting. Statistical analysis of the four vehicles as a fleet showed a significant effect of E100 but no specific evidence for an ethanol effect. Splash ethanol blends generally (but not always) improved CWD due to their higher E100 but matched volatility blends generally showed similar demerit levels to the hydrocarbon-only gasolines. Only Vehicle 7 showed clearly that matched volatility blends (AE, GE, and EE) gave higher demerits than HC fuels (A, G, E).



CWD demerits for four CONCAWE/GFC test vehicles at -10°C

5.4. AUSTRALIAN ORBITAL STUDIES

As described in Section 4.3, two major studies on ethanol/gasoline blends were completed in Australia by the Orbital Engine Company. The first in 2002 was an investigation of the impact of E20 [31-33] followed by a programme in 2007 to test vehicles on E5 and E10 blends [35]. Both of these comprehensive test programmes looked at CWD performance.

The CWD testing was carried out as follows. Vehicles were soaked in an environmental chamber at -10°C overnight (at least 8 hours). Cold start times were then measured and idle quality rated. This was followed by a CWD road test using the same cycle as for the HWD test, at ambient temperature involving idle, cruise and acceleration, as shown in **Figure 20**. Driveability was rated on a scale from 1 to 10 as shown in **Table 3** above. A rating of 7 was defined as a typical production target.

For the first E20 programme, tests were carried out on 5 new and 4 older (1986-93) cars. The fuels were a winter grade gasoline with E70 of 34 %v/v and T50E of 95 °C and a 20% ethanol splash blend with this fuel, with E70 47 %v/v and T50E 72 °C. E100 values were not determined.

Cold start times for new and older vehicles are shown in **Figure 27**. As can be seen, cold start times increased for all of the older vehicles and for most of the new ones as well. For several vehicles, the increase was substantial: 2–5 seconds, for one vehicle (Holden Commodore – AEN-HO12) cold starting was poor anyway: 22 sec on HC fuel which increased to 65 sec on E20. This vehicle also had poor idle quality.



Cold start times after a -10°C soak for new and older vehicles



Table 8



CWD ratings are given in **Table 4** above along with the HWD ratings. This shows that CWD was degraded slightly on E20 for most new vehicles, but not generally to a significant extent. The same was true for the older vehicles, again except for the Holden Commodore which suffered from severe full throttle hesitation on both normal and E20 fuels.

The second 2007 programme for E5 and E10 blends followed a similar format. Five fuel-injected and 11 carburettor cars, which had not been identified by the FCAI as suitable for use with E10, were tested for HWD and CWD using the same test procedures and rating scales. Eight pre-1986 vehicles were included in the test fleet in order to assess their suitability for use with E5, but not E10. Single batches of regular unleaded and premium unleaded fuel (for the older vehicles) were used and blended with ethanol at 5 and 10% v/v. Fuel properties are shown in **Table 8**.

Fuel	ULP	ULP-E5	ULP-E10	PULP	PULP - E5
DVPE kPa	70	76.3	75.6	73.9	80.3
T10E °C	48	46	46	47	45
T50E °C	93	90	68	97	94
T90E °C	172	167	167	158	153
E70 %v/v	33.4	40	50.7	29.8	38.6
E93 %v/v	49.9	51.9	56.4	-	-
E100 %v/v	54	-	-	-	-
E149 %v/v	80.5	82.5	83.2	-	-

Distillation properties of CWD test fuels used in the 2007 Orbital programme

Cold start times were not tabulated separately in this study, and the overall CWD ratings are given in **Table 6** with the HWD ratings. Of the fuel injected vehicles, only the Honda Civic showed poorer driveability on E10 due to cold starting. Most of the carburettor vehicles however showed some level of degradation on E5 and/or E10,

and several had serious issues with loss of rating >2. This was mostly due to poor cold starting although one vehicle experienced severe hesitation while another vehicle stalled.

5.5. STATE OF MINNESOTA STUDIES

The State of Minnesota study [37] covered driveability performance throughout one year, including a cold winter period. Untrained raters (i.e., the vehicle owners) were asked to complete daily log sheets indicating any driveability problems that occurred, and these were collected weekly. In addition, raters previously trained on CWD procedures were contracted to conduct CRC driveability tests on a subset of the vehicle fleet, with a test series in each season: fall, winter, spring, and summer. Fuels at E0 and E20 (prepared from commercial gasohol plus extra ethanol) were replenished with many deliveries over the year so they are not directly comparable.

The winter test session was completed on one day with soak and test temperature varying between -8 and +7°F (-22 to -14°C). The fall test was between 34–36°F (1–2°C) but the spring temperature range was not reported.

CWD results from untrained raters over all periods are shown in **Figure 22**. The lefthand figure shows results weighted by number of reports, but this gives greater emphasis to vehicles that repeatedly reported problems. In the right-hand figure the average demerits for each vehicle are calculated and statistics are based upon performance of individual vehicles. The report-weighted figure does show significant degradation of driveability in fall and spring, but not in winter. Perhaps this is due to changes in fuel volatility classes occurring during these seasons. The vehicle weighted analysis showed no significant effects

Trained rater demerit scores for the fall and winter sessions are shown in **Figure 28**. As expected, demerits were highest during the winter period, but still below 50 demerits. The report states that differences of 20 demerits or less lie within the "test noise" range so are not considered significant. Thus none of the fall tests showed significant differences. In fact, of the 8 vehicles tested on both fuels, five had higher demerits on E20 while three had higher demerits on E0. For the winter session, around one third of the data observations fell within the noise level. Nine vehicles showed higher demerits on E20 versus only two worse on E0. The main problems reported were degraded idle quality, with 62% of poor idle quality observations from cars running on E20.

Statistical analysis of the results over all four seasons showed (**Figure 22**) that none of the differences between fuels was significant at the 95% confidence level. The report states that:

"A review of the raw data for all four test seasons reveals that the fleet operated satisfactorily on both fuels. Relatively few objectionable malfunctions were detected, and there were no obvious differences between the fuels. The highest raw demerit scores for the fleet occurred in the winter which, as mentioned above, is not unexpected."



Figure 28 Minnesota study trained rater demerits during fall and winter testing on E0 and E20 fuels

5.6. OTHER WORK

5.6.1. Intercompany Emissions Group Study

The European Intercompany Emissions Group (IEG, formerly the Intercompany Volatility Group) measured driveability and emissions from ten 1994-97 European vehicles over the CEC Driveability test cycle [27]. The 6 test fuels varied volatility properties and MTBE (but not ethanol) as single step changes from a base fuel, but did not allow a correlation between fuel properties and demerits. Fleet mean demerits increased at -5°C with reducing volatility, especially fuels F4 and F5 with E100 ~42, and use of 15% MTBE (fuel F3) as shown in **Figure 29**.

There was a clear correlation ($R^2 = 0.79$) between increasing HC emissions and increasing demerits at -5°C, and a similar correlation with NOx emissions ($R^2 = 0.74$), as shown in **Figure 30**. The increase in HC emissions is to be expected, as driveability malfunctions are the result of misfires or partial burns which will increase unburned HC emissions. This was also shown in work by General Motors [49] in which a clear correlation between hydrocarbon emissions and driveability malfunctions was observed. However, the increase in NOx emissions with demerits is surprising and unexplained. CO emissions showed no clear correlation with demerits.

Figure 29 Mean driveability demerits for 10 European vehicles on individual fuels



Figure 30 Normalised HC and NOx emissions vs. average driveability demerits



5.6.2. Lubrizol Bench Engine Study

Lubrizol [38] have looked at the effect of fuel volatility (as ASTM DI), ethanol content and engine deposits on cold driveability using a test bed engine. A 2L 4-cylinder US engine was used; the engine was motored at 1000 rpm with no fuel to a coolant temp of 25°C. Then three accelerations to 2800 rpm were performed, allowing the engine to coast back to idle after each one:

- 20% throttle open loop fuel control
- 20% throttle closed loop fuel control
- 50% throttle open loop fuel control

During each acceleration, the cylinder pressure was recorded for each cylinder and used to calculate the IMEP curve. These data were processed to give:

- IMEP during the first 15 seconds
- Area under the IMEP curve (total work output)
- Peak IMEP
- Number of misfires and partial burns.

Misfires are defined as cycles when IMEP <103 kPa, or <690 kPa and 69 kPa less than previous cycle. Partial burns or "nimps" are cycles which did not meet a threshold Normalised IMEP.

A test programme was run using four fuels of varying DI from 1202 to 1317 and 10% Ethanol splash blends of the three highest DI fuels, with clean valves before an IVD build-up study. Results of this are shown in **Figure 31** for "area under the IMEP curve" and "nimps". This shows that ethanol blends do not perform as well as the HC only fuels, the area under the IMEP curve is lower and nimps are higher. Also a simple 2.5% energy content reduction applied to the hydrocarbon fuels does not accurately describe the ethanol response. The paper concludes that there are significant differences in cold start engine performance between hydrocarbon fuels and ethanol blends, and these cannot be described by simple ethanol offsets.

Figure 31 Lubrizol study – Effect of DI and ethanol content on the area under the IMEP curve and NIMPS



While this work was an interesting way to compare fuels in some detail, the study did not include cold start and idle conditions where customers are known to be sensitive to driveability performance.

5.6.3. Toyota Study

Toyota [39] also carried out a fundamental study of engine performance on ethanol and gasoline. They showed that neat ethanol takes around 20 engine cycles before combustion starts while gasoline or iso-octane take only a few cycles. This behaviour could not be explained by boiling point or latent heat effects, they found that the relationship between saturated vapour pressure and excess air ratio must be considered. Optimising valve timing for higher compressed gas temperature was shown to improve combustion at low temperatures and hence cold startability.

5.6.4. Neste Oil Study

As was reported in **Section 4.5**, a recent review of ETBE technical data [17] also reported a CWD study on gasoline blends containing ETBE and ethanol. This work was completed by Neste in the early 1990's using CEC test procedures with CWD measurements completed at -5, -15 and -25°C.

Two vehicles were tested, both with 1.3 litre engines, a Japanese car (Car A) with a carburettor and no oxidation catalyst and a German MPI car (Car B) with a catalyst. Six fuels were tested that had been blended to the then-current EN specifications containing ETBE from 13–20% m/m and ethanol from 7.2–12.3% m/m. The properties of these fuels are shown in **Table 9**.

				Fuel I	Blends		
Property	Unit	EW13	EW17	EW20	AW7	AW10	AW12
ETBE Content	% m/m	13.0	17.4	19.9			
Ethanol Content	% m/m				7.2	9.8	12.3
Oxygen content	% m/m	2.04	2.73	3.12	2.50	3.40	4.27
E70	% v/v	33.9	33.2	32.4	41.8	48.8	49.7
E100	% v/v	59.1	61.8	62.7	53.2	58.5	60.3
US DI (no oxygen offset)	°C	489	482	485	502	439	433

Table 9CWD study using gasolines containing ETBE and ethanol [17]

With the exception of AW7, all fuels had high E100 levels around 60, which would not be expected to show CWD problems. For the carburettor Car A, CWD was much worse at lower temperatures, with up to ~250 demerits recorded, but there was no clear difference between fuels. The MPI Car B, however, gave very low demerits (<20) on all fuel and temperature combinations. The ethanol blends generally gave lower demerits (<10) than the ETBE blends, though this is unlikely to be significant at these low demerit levels.

5.7. CONCLUSIONS ON COLD WEATHER DRIVEABILITY

E100 increases by up to 25% v/v when ethanol is blended into gasoline in the range 15-20% v/v ethanol. For this reason, CWD performance may be improved slightly for splash blended gasolines. CWD performance is poorer, however, for ethanol/gasoline blends at the same volatility level as a hydrocarbon-only gasoline.

This is due to a combination of the higher latent heat of vaporization for ethanol and a leaning effect on the air-fuel ratio under open-loop and some transient engine conditions.

Extensive CRC work has shown that the CWD performance of US vehicles operating on ethanol/gasoline blends can be predicted by any of several DIs, based on a combination of distillation terms and an ethanol offset. This is supported by separate Shell work. In the USA, ASTM has selected an NDI of the following form:

• NDI = 1.5 x T10 + 3 x T50 + T90 - 1.33 x (%EtOH) (in SI units)

The CONCAWE/GFC CWD test programme on European cars showed no clear effect of ethanol above the change in distillation properties due to ethanol addition. Indeed, no clear fuel effects on CWD demerits were seen except at -10°C on fuel blends having E100 less than about 50. It is important to note, however, that almost all of the CONCAWE fuels met the DI limits for the most volatile ASTM Class E. (In the CONCAWE/GFC study, the least volatile Fuel E was Class B while some fuel blends of Fuel E with ethanol were Class D.)

The Australian Orbital studies on E20 and later on E5 and E10 fuels showed some loss in CWD performance on splash blended fuels, especially cold starting of older vehicles.

The Minnesota study that covered extreme low temperatures showed slightly higher CWD demerits on E20 fuels, but the differences were not significant. Idle quality was the biggest problem.

A bench engine study completed by Lubrizol showed that ethanol blends do not perform as well as hydrocarbon fuels of equivalent DI under cold-start conditions but the difference in performance was not predicted by including a simple ethanol offset term.

Most of these studies, with the notable exception of some CRC "Intermediate Temperature" work, have looked at driveability at low ambient temperatures. There is also a case to investigate the effect of ethanol at intermediate temperatures around 25°C, because this is where emission tests are usually carried out. At this temperature, engines tend to have less cold start mixture enrichment and hence may be more sensitive to ethanol, especially during transient operation.

6. CONCLUSIONS

Blending ethanol into gasoline at levels up to 20% v/v ethanol increases the DVPE, E70, and E100 values of the final blend and the effects are generally higher as the ethanol content increases above 5% v/v. Based on published data and the analyses completed in this report, the increase in E70 compared to that of the base gasoline (Δ E70) was found to be 2-15% v/v for 5% v/v ethanol blends and 10-30% v/v for 10-20% v/v ethanol blends. The corresponding Δ E100 values were found to be 1-5% v/v for 5% v/v ethanol blends.

At the maximum E70 values allowed by the current EN228 gasoline specification (48 or 50% v/v depending upon volatility class), the Δ E70 values are only about 2-6% v/v at 5% v/v ethanol but 12-18% v/v at 10% v/v ethanol. At the maximum E100 value allowed by the current EN228 gasoline specification (71% v/v for all volatility classes), the impact of ethanol on the Δ E100 values is much smaller: only about 1-3% v/v at 5% v/v ethanol and 2-5% v/v at 10% v/v ethanol. For 15 and 20% v/v ethanol/gasoline blends, however, the Δ E100 values are 10-15% v/v. For this reason, the current E70 and E100 limits do not significantly impact the production of 5% v/v ethanol/gasoline blends but they are likely to constrain the base gasoline composition when blending ethanol at 10% v/v and higher.

To achieve good HWD performance, the objective is not to vaporize fuel in the fuel supply system and this is a challenge when there is sufficient heat from ambient conditions or from the engine itself. For this reason, the gasoline's lower distillation properties (DVPE and E70) are generally more important to good HWD performance than are the higher distillation properties (E100 and E150). Changes in E70 values appear to be less important to HWD performance than are changes in DVPE.

This literature review has shown that modern fuel-injected vehicles are much less sensitive to gasoline volatility than are older carburettor vehicles. For this reason, HWD problems are relatively rare today although two early model European DISI vehicles tested in one study were clearly sensitive.

Ethanol-containing gasolines can impact the HWD performance of some vehicles but only under extremes in temperature and fuel volatility. When these effects are observed, they appear to be due to the impact of ethanol on DVPE and E70 and not due to the chemical properties of ethanol *per se*. Work completed by the CRC has shown that an ethanol offset on the TVL_{20} term may be a good way to capture the impact of ethanol but this approach has not been incorporated into the USA gasoline specification.

To achieve good CWD performance, the objective is to vaporize sufficient fuel in the fuel system to achieve combustion even though there is not much heat available from the ambient conditions and engine. This process will be limited by the available heat and by the rate of heat transfer to the injected fuel. For this reason, the higher distillation properties (E100, E150) are generally more important than the lower distillation properties (E70).

CWD performance can still be an issue for some modern vehicles and is linked to higher exhaust emissions under cold operating conditions when malfunctions occur. CWD malfunctions are principally due to misfires, or partial misfires (slow burns), which increase hydrocarbon emissions. Although the CWD performance of modern fuel-injected vehicles is much better than it was on older carburetted vehicles, there are indications that drivers expect a higher level of performance from their cars today and could be more sensitive to mild driveability malfunctions.

The effect of ethanol in gasoline on CWD is perhaps clearer than it is for HWD. For splash blends of ethanol in gasoline, CWD performance is often improved slightly by the increased volatility of the ethanol/gasoline blend after ethanol addition. The CWD performance can be degraded, however, by the use of ethanol/gasoline blends at the same volatility level as a hydrocarbon-only gasoline. This is due to the combination of a higher latent heat of vaporisation for ethanol and its leaning effect on the air-fuel ratio under transient and open-loop engine conditions. Including an ethanol offset term in driveability index (DI) equations can improve the predictability of CWD performance, as has been shown by CRC studies.

Ideally, a European DI would be desirable but there are not enough published data available on modern European vehicles to develop a new DI equation. Although the E100 limits in the current EN228 are fixed at 46 to 71% v/v for all volatility classes, the limits should vary with ambient temperature in order to more effectively control CWD performance. The E100 maximum limit is not likely to be a constraint unless much higher ethanol levels (~20% v/v ethanol) are used. A change in the lower E100 limits would be appropriate, however, that varies with ambient temperature and compensates for higher ethanol levels either by means of a DI equation or an ethanol offset to E100 limits.

7. GLOSSARY

ACEA	European Automobile Manufacturers Association
AEAT	AEA Technology plc (located in Oxfordshire, UK)
AFR	Air-Fuel Ratio
AFVR	Air-Fuel Vapour Ratio
AQIRP	Air Quality Improvement Research Programme
ASTM	American Society for Testing and Materials
BOB	Blendstock for Oxygenate Blending
CARB	California Air Resources Board
CARBOB	California Reformulated Gasoline Blendstock for Oxygenate Blending
CEC	Coordinating European Council
CEN	European Committee for Standardization
СО	Carbon Monoxide
CRC	Coordinating Research Council (USA)
CWD	Cold Weather Driveability
DG-TREN	Directorate-General for Transport and Energy
DI	Driveability Index or Indices
DISI	Direct Injection Spark Ignition
DVPE	Dry Vapour Pressure Equivalent
E70	% gasoline evaporated at 70°C
E100	% gasoline evaporated at 100°C
E150	% gasoline evaporated at 150°C
EDI	Evaporative Driveability Index, that is, a Driveability Index model based on Evaporative Distillation Numbers
EFI	Electronic Fuel Injection
EMPA	Swiss Federal Laboratories for Materials Testing and Research

EN228	European Norm 228
EPA	Environmental Protection Agency (USA)
ER	Enthalpy Requirement
ETBE	Ethyl t-Butyl Ether
EtOH	Ethanol
EU	European Union
EUCAR	European Council for Automotive Research & Development
EXX	Ethanol content in gasoline expressed as a volume percentage ethanol (for example, E5 is 5% v/v ethanol in gasoline)
FCAI	Federal Chamber of Automotive Industries (Australia)
FQD	Fuel Quality Directive
GC	Gas Chromatography or Chromatograph
GFC	Groupement Français de Coordination
GHG	Greenhouse Gas or Gases
HC	Hydrocarbon
HWD	Hot Weather Driveability
IBP	Initial Boiling Point
IDIADA	Applus+IDIADA Technology Centre, Santa Oliva, Spain
IEG	Intercompany Emissions Group
IMEP	Indicated Mean Effective Pressure
ISO	International Standards Organization
JEC	JRC-EUCAR-CONCAWE Consortium
JRC	Joint Research Centre of the European Commission
LBV	Linear by Volume Blending
MPI	Multi-Point Injection
MTBE	Methyl t-Butyl Ether

NDI	New Driveability Index
nimps	An engine test cycle that does not meet a threshold normalised IMEP, also called a partial burn
NOx	Nitrogen Oxides
PCHIP	Piecewise Cubic Hermite Interpolating Polynomials
RED	Renewable Energy Directive
RVP	Reid Vapour Pressure
SAE	Society of Automotive Engineers
SER	Standard Enthalpy Requirement
SI	International System of Units
STP	Standard Temperature and Pressure
TEL	Tetra-Ethyl Lead
T50E	The temperature at which 50% of the sample has evaporated
T90E	The temperature at which 90% of the sample has evaporated
TVL ₂₀	The temperature at which a vapour to liquid ratio of 20 is achieved for a given liquid sample
TVL ₁₋₅₀₀	The temperature at which an equilibrium vapour to liquid ratio of 1 is achieved under a pressure of 500kPa for a given liquid sample
TWD	Total Weighted Demerits
USA	United States of America
WOT	Wide Open Throttle

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APPENDIX 1 CARBOB MODEL EQUATIONS

The equations which constitute the CARBOB model are shown below:

A. RVP Model

• RVP_{FG} = 1.446 + 0.961 x RVP_{CARBOB}

Where:

- RVP_{FG} is the RVP of the finished gasoline, in psi
- RVP_{CARBOB} is the RVP of the CARBOB, in psi.

B. T50 Models

There are two CARBOB models for T50.

i. Model for $4\% \leq EtOH < 9\%$

The first T50 Model is for a finished gasoline having an ethanol content greater than or equal to 4.0% v/v but less than 9.0% v/v.

• T50_{FG} = 21.93 + 14.875 x [EtOH] - 10.238 x RVP_{CARBOB} + 0.672 x T50_{CARBOB} + 0.02579 x T90_{CARBOB} - 0.8313 x [EtOH]² - 0.3103 x RVP_{CARBOB} x [EtOH] + 0.06623 x T50_{CARBOB} x [EtOH] - 0.05519 x T90_{CARBOB} x [EtOH] + 0.03607 x RVP_{CARBOB} x T90_{CARBOB}

Where:

- T50_{FG} is the T50 of the finished gasoline, in degrees F,
- [EtOH] is the ethanol content of the finished gasoline, including the denaturant, in volume%,
- RVP_{CARBOB} is the RVP of the CARBOB, in psi,
- T50_{CARBOB} is the T50 of the CARBOB, in degrees F,
- T90_{CARBOB} is the T90 of the CARBOB, in degrees F.

ii. Model for $9\% \leq EtOH \leq 10\%$

The second T50 model is for a finished gasoline having an ethanol content greater than or equal to 9.0% v/v but less than or equal to 10.0% v/v.

T50_{FG} = 559.276 - 0.5431 x RVP_{CARBOB} - 4.1884 x T50_{CARBOB} - 0.3957 x T90_{CARBOB} + 0.01482 x (T50_{CARBOB})² - 0.05309 x T50_{CARBOB} x RVP_{CARBOB} + 0.02884 x T90_{CARBOB} x RVP_{CARBOB}

Where:

- T50_{FG} is the T50 of the finished gasoline, in degrees F,
- EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,
- RVP_{CARBOB} is the RVP of the CARBOB, in psi,
- T50_{CARBOB} is the T50 of the CARBOB, in degrees F,
- T90_{CARBOB} is the T90 of the CARBOB, in degrees F.

There is a T50 CARBOB model only for CARBOB ethanol contents greater than or equal to 4.0% v/v. If the ethanol content of the CARBOB is less than 4.0% v/v, then the CARBOB model cannot be used.

C. T90 Model

• T90_{FG} = 1.493 + 0.964 x T90_{CARBOB} + 0.0468 x T50_{CARBOB} - 0.473 x [EtOH]

Where:

- T90_{FG} is the T90 of the finished gasoline, in degrees F,
- T90_{CARBOB} is the T90 of the CARBOB, in degrees F,
- $T50_{CARBOB}$ is the T50 of the CARBOB, in degrees F,
- [EtOH] is the ethanol content of the finished gasoline, including the denaturant, in volume%.

D. Aromatic Content Model

• AROM_{FG} = ((1 - ([EtOH] x 0.01)) x AROM_{CARBOB}) + ([EtOH] x 0.01 x AROM_{EtOH})

Where:

- AROM_{FG} is the aromatic content of the finished gasoline, in volume%,
- [EtOH] is the ethanol content of the finished gasoline, including the denaturant, in volume%,
- AROM_{CARBOB} is the aromatic content of the CARBOB, in volume%,
- AROM_{EtOH} is the aromatic content of the ethanol, in volume%.

E. Olefin Content Model

• OLEF_{FG} = ((1 - ([EtOH] x 0.01)) x OLEF_{CARBOB}) + ([EtOH] x 0.01 x OLEF_{EtOH})

Where:

- OLEF_{FG} is the olefin content of the finished gasoline, in volume%,
- [EtOH] is the ethanol content of the finished gasoline, including the denaturant, in volume%,
- OLEF_{CARBOB} is the olefin content of the CARBOB, in volume%,
- OLEF_{EtOH} is the olefin content of the ethanol, in volume%.

F. Benzene Content Model

• BENZ_{FG} = ((1 - ([EtOH] x 0.01)) x BENZ_{CARBOB}) + ([EtOH] x 0.01 x BENZ_{EtOH})

Where:

- BENZ_{FG} is the benzene content of the finished gasoline, in volume%,
- [EtOH] is the ethanol content of the finished gasoline, including the denaturant, in volume%,
- BENZ_{CARBOB} is the benzene content of the CARBOB, in volume%,
- BENZ_{EtOH} is the benzene content of the ethanol, in volume%.

G. Sulfur Content Model

• SULF_{FG} = {((1- ([EtOH] x 0.01)) x SULF_{CARBOB} x 0.718) + ([EtOH] x 0.01 x SULF_{EtOH} x 0.788)} / {((1-([EtOH] x 0.01)) x 0.718) + ([EtOH] x 0.01 x 0.788)}

Where:

- SULF_{FG} is the sulfur content of the finished gasoline, in ppm,
- [EtOH] is the ethanol content of the finished gasoline, including the denaturant, in volume%,
- SULF_{CARBOB} is the sulfur content of the CARBOB, in ppm by wt.,
- SULF_{EtOH} is the sulfur content of the ethanol, in ppm by wt.

APPENDIX 2 STATISTICAL MODELING

The blending performance of ethanol can be expressed in terms of "Blending E70" (**BlendE70(EtOH)**) and "Blending E100" (**BlendE100(EtOH)**) values. These are used in the following predictive equations:

- E70(blend) = (1 [EtOH]) x E70(base) + [EtOH] x BlendE70(EtOH)
- E100(blend) = (1 [EtOH]) x E100(base) + [EtOH] x BlendE100(EtOH)

These equations can be used to estimate the E70(blend) and E100(blend) of simple splash blends of base gasoline and ethanol where EtOH is the fractional ethanol content (=%Ethanol/100).

BlendE70(EtOH) observations can be obtained from measured (or interpolated) pairs of **E70(blend)** and **E70(base)** values using the following inverse equation:

• BlendE70(EtOH) =
$$\frac{\text{E70(blend)} - (1 - [\text{EtOH}]) \times \text{E70(base)}}{[\text{EtOH}]}$$

Similarly, **BlendE100(EtOH)** observations can be calculated from the following inverse equation:

• BlendE100(EtOH) =
$$\frac{E100(blend) - (1 - [EtOH]) \times E100(base)}{[EtOH]}$$

Figures 11 and **13** in Section 3.7 showed that the BlendE70(EtOH) and BlendE100(EtOH) values depend not only on the concentration of ethanol but also on the properties of the base gasoline. These dependencies can be explored using multiple regression analysis to derive models of the form:

• BlendE70(EtOH) = a + b × [EtOH] + c × E70(base) + ...

and

• BlendE100(EtOH) = a + b × [EtOH] + c × E100(base) + ...

Terms in the base fuel's compositional variables (aromatics, olefins, etc.) were also considered but data were only available for a small number of base fuels and few clear trends emerged.

Care is needed when applying multiple regression techniques to observations of BlendE70(EtOH) and BlendE100(EtOH). Standard multiple regression analysis assumes that the error or uncertainty in the various measurements of BlendE70(EtOH) (or BlendE100(EtOH)) is "independently and identically distributed". This assumption does not hold in the present analysis. Measurements of E70 and E100 are divided by the ethanol concentration when calculating BlendE70(EtOH) or BlendE100(EtOH) values. Since [EtOH] in the above equations is a number between 0.01 and 0.22, it follows that, in absolute terms, the uncertainty in observations of BlendE70(EtOH) and BlendE100(EtOH) will be considerably higher at lower ethanol concentrations.

The data set used in the modelling exercise is an amalgam of subsets from many different sources. In many of these studies, splash blends were made at different concentrations in the same base fuel. Observations of BlendE70(EtOH) (or BlendE100(EtOH)) derived from such subsets will not be independent because the same measurement of E70(base) (or E100(base)) is used in the calculation of BlendE70(EtOH) (or BlendE100(EtOH)) for each blend. The uncertainty in the measurement of E70(base), E70(blend), E100(base) and E100(blend) also varies markedly between fuels and between different data sources. Automated E70 and E100 measurements based on T values at 0.1°C intervals will be more precise than manual measurements based on 1°C intervals. These in turn will be much more precise than values

based on interpolation between T values that are 5°C or 10°C apart. Interpolation is a particular problem in flat parts of the distillation curve (see **Section 3.3** and **Figure 3**). In addition, measurements that are averages of repeat tests from several laboratories will be more precise than single measurements.

The problem of differing ethanol concentrations and common base fuel measurements can be handled quite elegantly using generalized least squares regression [40]. Handling the differing levels of uncertainty in the various data subsets presents a more difficult problem because quantification is difficult. As a consequence, it was not possible to perform a statistically rigorous regression analysis.

In order to stabilize the variance of different observations of BlendE70(EtOH), these values were multiplied by the ethanol concentration [EtOH] giving measurements of δ (E70)⁶ defined as

• δ(E70) = BlendE70(EtOH) × [EtOH] = E70(blend) – (1 – [EtOH]) × E70(base)

The earlier regression model was then rewritten as:

• δ(E70) = a × [EtOH] + b × [EtOH]² + c × E70(base) × [EtOH] + ...

The rewritten model was then fitted by multiple regression with each observation assigned a weight of:

• weight = $\frac{1}{[EtOH]^2 - 2[EtOH] + 2}$

In practice, these weights were found to be fairly constant, varying between 0.526 and 0.610 at 5% v/v and 20% v/v ethanol concentrations, respectively.

The model produced by this approach was then converted back into the form:

• BlendE70(EtOH) = 289 - 754 x [EtOH] -0.384 x E70(base)

The effect of [EtOH] is much the stronger being significant at $P < 0.1\%^7$ while the effect of E70(base) is, perhaps surprisingly, only significant at P < 10%. This could be because the E70(base) effect is only really seen at 5% (see **Figure 13**).

The model fit can be improved a little by adding a cross-product term

• BlendE70(EtOH) = 376 - 1367x[EtOH] - 3.44xE70(base) + 21.4x[EtOH]xE70(base)

with all coefficients now significant at P < 0.1%. However, the improvement in fit is not great in practical terms.

The δ (E100) value was defined and modelled in the same way producing the model:

• BlendE100(EtOH) = 142 + 247 x [EtOH] -1.066 x E100(base)

The effects of [EtOH] and E100(base) are of similar importance, with both being significant at P < 0.1%.

⁶ Note that $\delta(E70)$ and $\delta(E100)$ are not the same as the simple differences $\Delta E70$ (= E70(blend) – E70(base)) and $\Delta E100$ (= E100(blend) – E100(base)) plotted in Figures 6, 7, 9 and 10.

⁷ P < 0.1% = the probability that such an event could be observed by chance when no real effect exists is less than 0.1%. In other words, we are 99.9% confident that the effect is real.

APPENDIX 3 PROPERTIES OF ETHANOL AND HYDROCARBONS

Property	Gasoline	Ethanol
Molecular Formula	C ₄ to C ₁₂ compounds	C₂H₅OH
Molecular Weight (g/mole)	100 - 105	46.07
Carbon Content	85 - 88	52.2
Hydrogen Content	12 - 15	13.1
Oxygen Content	0.0	34.7
Boiling Temperature (°C)	27 - 225	78.3 - 78.5
Density (kg/L)	0.72 - 0.78	0.792
Reid Vapour Pressure (kPa)	50 - 100	15 - 17
Heat of vaporisation (kJ/kg)	330 - 400	842 - 930
Lower Heating Value (MJ/kg)	44.40	28.86
Stoichiometric Air/Fuel Ratio	14.5 - 14.7	8.9 - 9.0

Table A3-1: Typical Properties of Gasoline and Ethanol

Source: US Department of Energy, NIST Chemistry WebBook

Table A3-2: Properties of Ethanol-Hydrocarbon Azeotropes

Hydrocarbon Component	Boiling Point of the Hydrocarbon Component (°C)	Boiling Point of the Ethanol-Hydrocarbon Mixture (°C)	Weight %
Benzene	80.2	68.2	67.6
Cyclohexane	80.7	64.9	69.5
Toluene	110.8	76.7	32
n-Pentane	36.2	34.3	95
n-Hexane	68.9	58.7	79
n-Heptane	98.5	70.9	51
n-Octane	125.6	77.0	22

Source: Lange's Handbook of Chemistry, 10th Ed., pp 1496-1505.

CONCAWE Boulevard du Souverain 165 B-1160 Brussels Belgium

Tel: +32-2-566 91 60 Fax: +32-2-566 91 81 e-mail: info@concawe.org website: http://www.concawe.org