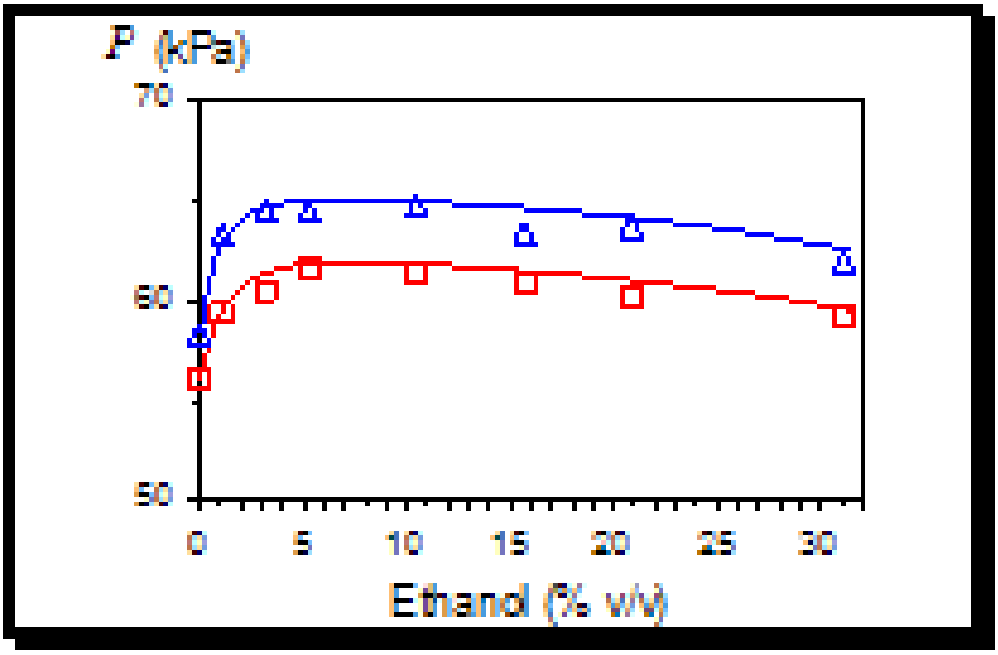
Project Title:

Ethanol/Petrol Blends: Volatility Characterisation in the Range 5-25 vol% Ethanol

Final Report

Project Acronym: **BEP525**



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[1] Shell Global Solutions (UK) is a division of Shell Research Ltd.

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1. BEP525 Project Final Report

The BEP525 Project Final Report contains the following information:

- Literature review on the impact of ethanol on the volatility of ethanol/petrol blends and on vehicle driveability (**Section 2** and **CONCAWE Report 8/09 [4]**)
- Specifications and rationale for the analytical characterisation of the fuel blends (**Section 3** and **Appendix 2**)
- Description and rationale for the fuel design matrix (**Section 3**)
- Description and rationale for the pre-study to investigate the potential impact of water content in ethanol on the volatility of the ethanol/petrol blend (**Section 3.2**)
- Description of the statistical methods used in the design of the fuel matrix (**Appendix 1**)
- Preparation and characterisation of the fuel blends (**Section 4**)
- Assessment of the precision of E70 and E100 measurements for ethanol/petrol blends (**Appendix 5**)
- Evaluation and modelling of the ethanol/petrol blends (**Section 5**)
- Analysis of the potential impact of ethanol on the environmental performance on ethanol/petrol blends based on published data (**Section 6** and **Appendix 6**)
- Distillation curves from the BEP525 Study (**Appendix 7** and **Appendix 8**)
- Four data workbooks that provide all of the validated data and plots from this study.

2. Impact of ethanol on petrol properties and performance

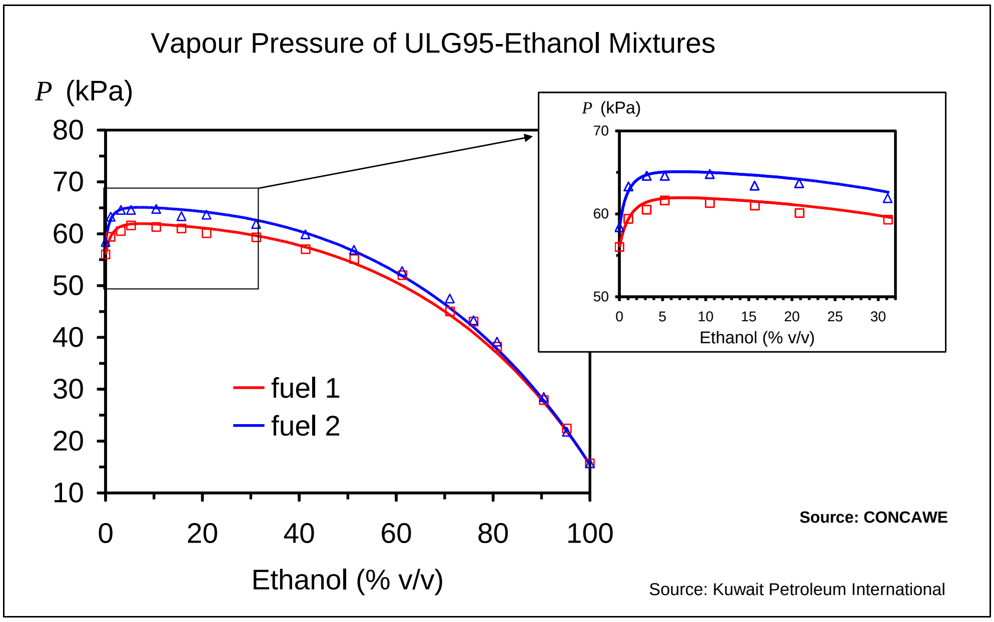
2.1. Impact of Ethanol on Petrol Vapour Pressure

Although ethanol has a lower molecular mass than most of the hydrocarbons used in petrol, pure ethanol is a liquid rather than a gas at ambient temperatures and pressures due to strong intermolecular hydrogen bonding interactions between ethanol molecules. These hydrogen bonding interactions are either very weak or are absent in pure hydrocarbon mixtures. As a consequence, pure ethanol has a much lower vapour pressure (15-20kPa) than petrol.

However, when ethanol is dissolved into a predominantly hydrocarbon mixture such as petrol, these same intermolecular interactions are observed to increase the volatility of the ethanol-hydrocarbon blend, most significantly at low concentrations of ethanol.

As shown in **Figure 1,** addition of only about 2% v/v of ethanol into unleaded petrol is observed to increase the vapour pressure of the blend by about 6-8 kPa potentially leading to non-compliance with the requirements of the EN228 quality standard for petrol [1] unless this increase is taken into account in the fuel blending process [2]. The vapour pressure increase with low concentrations of ethanol is also typically larger when the vapour pressure of the base petrol is lower.

Figure 1 Vapour Pressure of Mixtures of Ethanol and Unleaded Petrol 95 (ULG95)



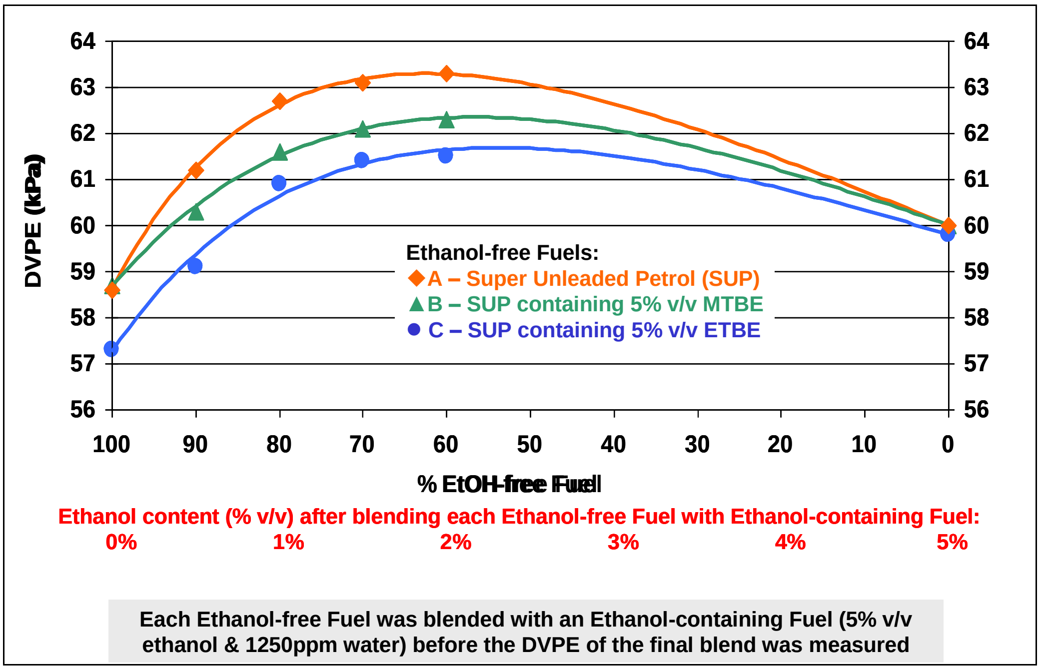
Source: CONCAWE

Source: Kuwait Petroleum International

This positive deviation from ideal mixture behaviour (Raoult's Law) occurs because the intermolecular interactions between ethanol and hydrocarbon molecules are weaker than they are in the two pure liquids making it easier for molecules to volatilize from the ethanol-hydrocarbon blend. Although this phenomenon is generally well known, the exact dependence of this behaviour on the concentration of the ethanol and on the composition of the petrol base fuel is not well understood.

As another example, **Figure 2** shows the change in Dry Vapour Pressure Equivalent (DVPE) of three different hydrocarbon-only petrols when mixed with a fourth petrol that already contains 5% v/v ethanol [3]. (This ethanol-containing petrol also contains 1250 ppm of water.) In this example, two of the three hydrocarbon-only petrols also contain other oxygenates, namely Methyl Tertiary-Butyl Ether (MTBE) and Ethyl Tertiary-Butyl Ether (ETBE). Although the deviations are subtle, the change in DVPE of the ethanol/petrol blend is affected by the composition of the blend, including the ether components.

Figure 2 Dry Vapour Pressure Equivalent (DVPE) of Blends of Ethanol-free and Ethanol-containing Petrols



2.2. Assessment of Volatility Changes from Published Literature[2]

CONCAWE has completed an assessment of the change in volatility parameters for petrol containing 5% v/v ethanol and higher levels. For this assessment, fuel composition and volatility data were collected on 108 base petrols and their corresponding ethanol splash blends. This assessment is based on published literature citing European, US, and Australian data [4].

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[2] This assessment and specific references can be found in CONCAWE Report 8/09 [4] titled "Volatility and vehicle driveability performance of ethanol/gasoline blends: a literature review".

Most of these published data were obtained on 5% and 10% v/v ethanol blends (72 and 76 fuel sets, respectively). Some data were available on higher ethanol blends at 15% and 20% v/v (13 and 23 fuel sets, respectively) although no reliable data have been found on ethanol blends above 20% v/v. Many of these published datasets (especially the US and Australian studies) did not report E70 and/or E100 values, making an interpolation to European volatility values necessary.

In order to estimate the increase in E70 and E100 values due to ethanol blending, CONCAWE reviewed published literature from at least 15 different studies for fuel analysis data on ethanol/petrol splash blends[3]. Published data were only analyzed where the study reported results for both the base petrol fuel and for the splash blends of ethanol in that same fuel.

Many of the fuel analysis datasets were incomplete. Few had full compositional information (olefins, aromatics, etc), some had nominal ethanol contents, and others reported measured values. Because only one of the base fuels contained ethers, specifically ETBE at 4% v/v, this fuel and its one 5% v/v ethanol blend have been excluded. The limited data that are available on petrols 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 the ΔE70[4] by 2-4%.

Most data from USA and Australian studies did not report E70 and E100 values which were essential for this analysis. This is because these countries typically report TxxE values, the temperature required to reach a given percent of sample evaporated, as required by prevailing specifications. In these countries, specifications typically require reporting of temperatures to achieve 10% of sample evaporated (T10E), 50% of sample evaporated (T50E), and 90% of sample 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 provided full distillation information (i.e., TxxE values), although only in 10% v/v or at best 5% v/v increments. Using the reported data, it was possible to interpolate the missing E70 and E100 values by use of a fitting function. This interpolation adds some uncertainty to the E70 and E100 values as do differences in the compositional measurement techniques used in the various studies. Such interpolations can never be as accurate as direct measurements of E70 and E100 but the data shown in [4] suggest that the data from all studies can be compared using this interpolation approach.

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

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[3] A splash blend is one in which the ethanol is added directly to the base petrol fuel without readjusting the volatility of the finished fuel.

[4] Where ΔE70 equals the E70 of the ethanol/petrol blend (E70(Blend)) minus the E70 of the base petrol (E70(Base)).

Table 1 Summary of Ethanol/Petrol Samples Evaluated from Published Literature

Nominal Ethanol Content (% v/v)	Range in Ethanol Content (% v/v)	Total Number of Samples
5	1 – 6% v/v	91
10	8 – 11% v/v	80
15	15 – 17% v/v	16
20	19 – 22% v/v	27
Total	**1 – 22% v/v**	**214**

Notes:

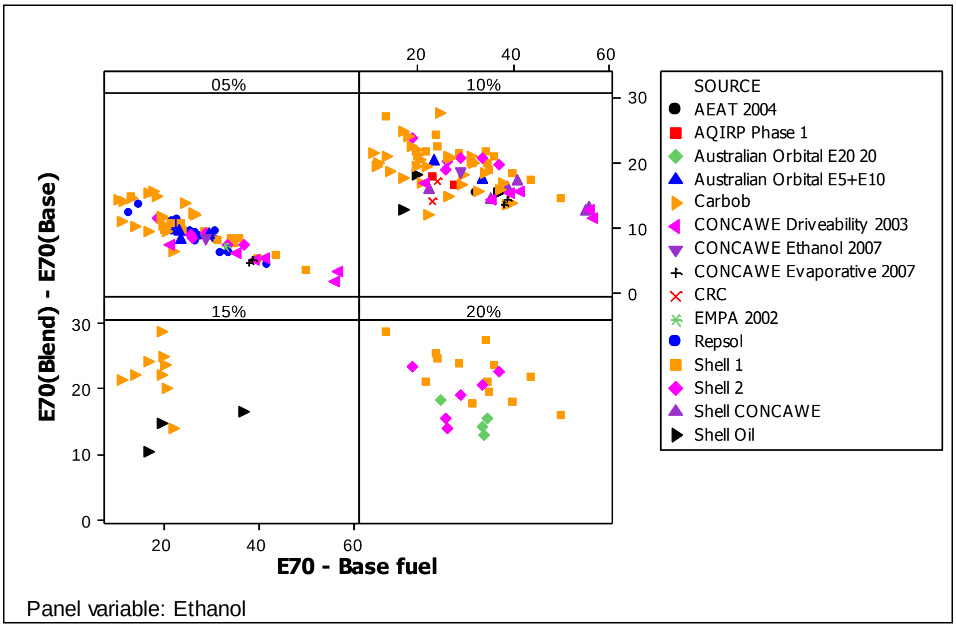
1. The ranges have been narrowed to 4-6%, 9-11%, 14-16% and 19-21% in **Figures 3-6**; blends that are outside of these limits are not shown.
2. Two of the 214 blends were not used in this analysis because there were insufficient distillation data to estimate the E70 and E100 of the base fuel. These two samples were blended from the same base fuel.

2.2.1. Effect of Ethanol on E70 Volatility

Using the data collected from these studies, **Figure 3** shows the change in ΔE70 compared to the E70 of the base petrol (E70(Base)) as a function of ethanol content at 5, 10, 15, and 20% v/v. For 5, 10, and 20% v/v ethanol blends, there is a clear trend: ΔE70 gets smaller as the E70 of the base petrol increases. At the same E70(Base), however, the ΔE70 is much higher at 10% v/v ethanol than at 5% v/v ethanol. For 15% v/v ethanol, there is no clear trend but the data are also very limited. For 10, 15, and 20% v/v ethanol blends, ΔE70 values up to 30% v/v can be seen at the lower E70(Base) levels (20–30% v/v).

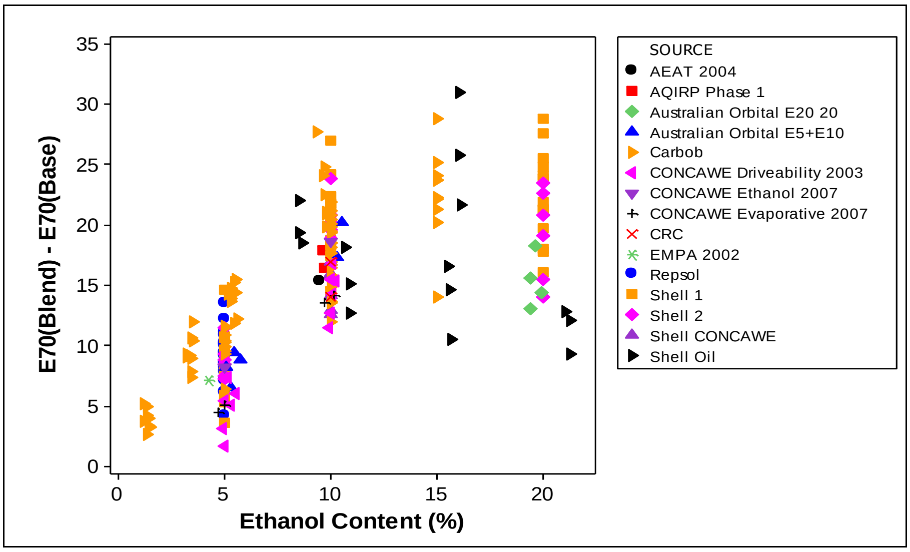
Figure 4 shows ΔE70 plotted against ethanol content. This figure shows that the ΔE70 increases rapidly up to 10% v/v ethanol, but then levels off at higher ethanol levels. The ΔE70 exhibits a wide range of values between 2-15% v/v at 5% v/v ethanol and 10-30% v/v at ethanol concentrations of 10% v/v or higher. This clearly shows that ethanol blending is not a simple linear-by-volume process and may also be sensitive to the properties of the base petrol.

Figure 3 ***Variation in ΔE70 with E70(Base) at four different ethanol concentrations***



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

Figure 4 ***Variation in ΔE70 with ethanol concentration***



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

2.2.2. Effect of Ethanol on E100 Volatility

Using the same approach, the ΔE100[5] data have been plotted in the same format as for ΔE70. **Figure 5** shows ΔE100 plotted against E100(Base). The ΔE100 values are considerably smaller than the ΔE70 values plotted in **Figure 3**, particularly at lower ethanol concentrations. Although there are less data available at 15 and 20% v/v ethanol levels, ΔE100 levels up to 20% v/v can be seen at these higher ethanol blend levels. Again, ΔE100 gets smaller as E100 of the base petrol increases.

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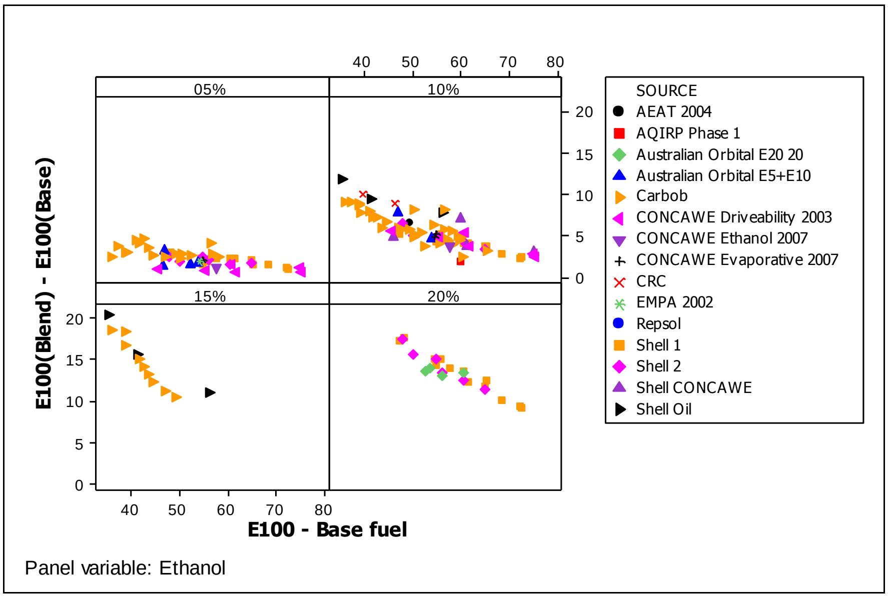
[5] Where ΔE100 equals the E100 of the ethanol/petrol blend (E100(Blend)) minus the E100 of the base petrol (E100(Base)).

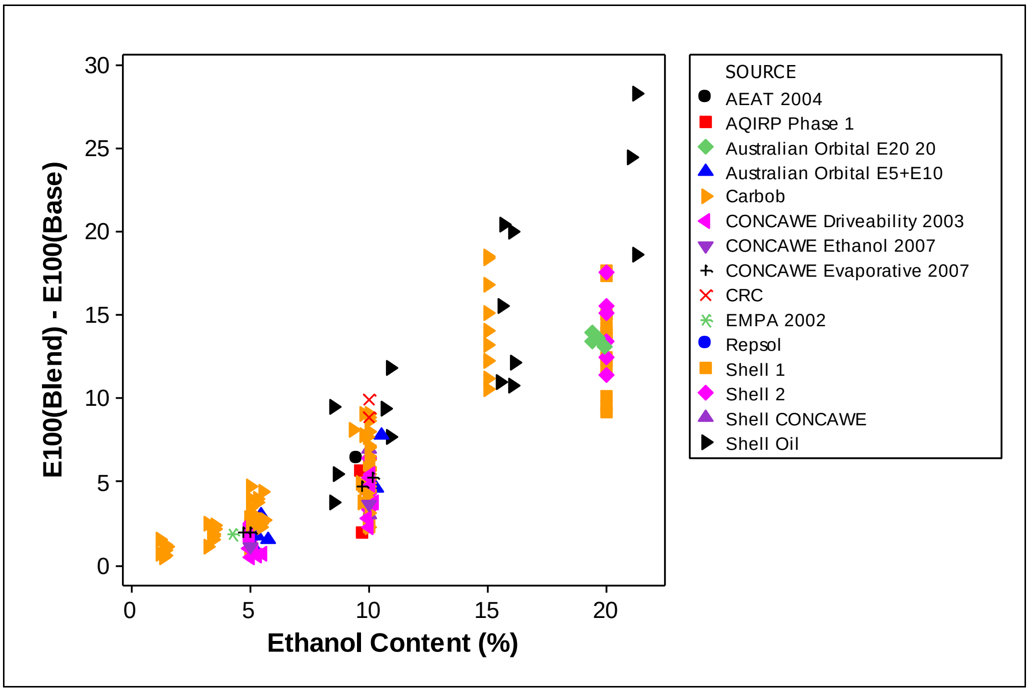
Figure 5 ***Variation in ΔE100 with E100(Base) at four different ethanol concentrations***



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

Figure 6 suggests that ΔE100 continues to increase with increasing ethanol content up to 15% v/v. It is not entirely clear whether ΔE100 levels off between 15% and 20% v/v because the data come from several different sources. The spread of ΔE100 values is generally less than that seen for ΔE70, 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/petrol blends is very flat at about 70°C, while the curve is much steeper at 100°C. For this reason, E70 values for ethanol/petrol blends will always be more variable than the higher distillation values, like E100 or E150 (see **Appendix 5**).

Figure 6 ***Variation in ΔE100 with ethanol concentration***



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

2.2.3. Conclusions regarding Ethanol and Petrol Volatility

From an analysis of these limited data, the following conclusions can be drawn (see [4] for references and a more complete explanation):

- Complete composition and volatility data as per EN228 specifications are limited for ethanol/petrol blends having 10% v/v or greater ethanol.
- There are limited data available from the already published studies on the impact of gasoline composition (aromatics, olefins, etc.) on E70 and E100 volatility even though some compositional effects are to be expected.
- None of the fuels shown in these plots contained MTBE, ETBE, or other oxygenates which were shown in **Figure 2** to have an impact on DVPE of ethanol/petrol blends. With future EN228 specifications likely to allow higher percentages of ethanol, ether, and other oxygenates, this represents a significant gap in technical data.

For this reason, a consistent, uniform, and detailed analytical blending study was needed in order to reveal the impact of ethanol content and petrol properties on critical volatility parameters for ethanol/petrol blends. This BEP525 Study provides a much more consistent database of fuel properties that can be used to assess the impact of ethanol on ethanol/petrol volatility as well as on environmental emissions (tail-pipe and evaporative emissions, fuel consumption) and vehicle performance (Hot and Cold Weather Driveability).

2.3. Effect of Petrol Volatility on Vehicle Hot Weather Driveability

The volatility specifications for petrol contained in the current EN228 specification were originally based on technical studies that showed that vehicle driveability performance depends on the following parameters:

- Vapour pressure[6]
- Evaporated fraction at 70°C (E70)
- Evaporated fraction at 100°C (E100)
- Evaporated fraction at 150°C (E150) and
- Final Boiling Point (FBP)

Based on extensive vehicle testing under controlled conditions, it was found that Hot Weather Driveability (HWD) performance (also called Hot Fuel Handling (HFH)) could be controlled by limiting the petrol's range of volatility. The relevant parameter, the Vapour Lock Index (VLI), depends on the RVP (or DVPE) and the petrol's E70 value:

- VLI = 10 x RVP(kPa) + 7 x E70 (% v/v) (Eqn 1)

Based on this dependence and the climatic and seasonal conditions in the European Member States, ten volatility classes are now included in the EN228 petrol specification with limits placed on DVPE, E70, E100, E150, and VLI. Member States specify the volatility classes that best cover their geographical region and weather conditions.

The EU Fuels Quality Directive (2009/30/EC) specifies that DVPE should be no higher than 60kPa max for the summer period, beginning no later than 1 May and ending no earlier than 30 September. For markets having arctic conditions, DVPE is limited to 70kPa max for a summer period beginning no later than 1 June and ending no earlier than 31 August (minimum 3 months).

If there is a mismatch between the maximum ambient temperature in which a vehicle is expected to operate and the volatility of fuel with which the vehicle has been fueled, HWD malfunctions can be experienced by trained drivers or by consumers if the malfunctions are severe enough. These problems, including hesitations, stumbles on acceleration, etc., are caused by overheating of the vehicle fuel system leading to vaporisation of the petrol within the vehicle's fueling system. This vaporisation can cause problems with fuel pumps and metering systems (including injectors or carburetors) that are designed to handle liquid fuel and cannot cope with vapour.

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[6] Vapour pressure was originally measured as RVP (Reid Vapour Pressure) but is now measured as DVPE (Dry Vapour Pressure Equivalent).

Modern multi-point electronic fuel injection (EFI) engines are much less prone to HWD problems than are carbureted engines. This is mainly because of the higher operating pressure of the fuel system that reduces fuel vaporisation and re-circulation systems that cool the injectors and dissipate heat energy into the fuel stored in the fuel tank. For these reasons, modern vehicles are more tolerant of hot weather conditions and higher volatility fuels and there are now very few cases of HFH problems reported in the marketplace. At the same time, consumers are generally more sensitive to vehicle malfunctions than they were in the past and are likely to report even small hesitations in vehicle performance to their car repair dealership.

The effect of fuel properties on HWD has been widely studied and the key parameters are as follows:

- **TV/L(X), the temperature required to give a Vapour/Liquid Ratio of (X**): where X can be between 10 and 40, and is typically 20. This parameter correlates well with HFH and is used in US ASTM specifications. It is hard to measure, however, and is generally determined from a diagram.

- **TV/L$_{1-500}$, the temperature required to give a Vapour/Liquid Ratio of 1 at 500kPa pressure**: This parameter was proposed by General Motors in order to simulate the conditions considered to be representative of modern fuel delivery systems. This parameter was evaluated by the US CRC and found to correlate well with HWD but it is not a standard parameter and is hard to measure. For this reason, it has not been pursued as a control parameter for HWD.

- **VLI (Vapour Lock Index) or FVI (Flexible Volatility Index):** This index was developed in the 1970s and correlates with TV/L(X). It is generally accepted as the best parameter to describe the fuel-related hot-weather performance of today's vehicles and is included in EN228.

- **ASVP (Air Saturated Vapour Pressure) at 100°C:** This has been proposed as an alternative to VLI, but studies have shown that it does not provide any better correlation to HFH problems than the VLI.

Since HFH problems are sensitive to the petrol's volatility, any change in volatility due to the addition of ethanol would be expected to impact the HWD performance. Fortunately, the impact of volatility changes on HWD is predictable, based on correlations with VLI (or TV/L(X)).

HWD performance of light-duty vehicles has been studied in a number of studies over the past two decades [4]:

1. CRC Studies (1999-2006)
2. CONCAWE/GFC Study (2003) ← European vehicles
3. Australian Orbital Study 1 (2003-4)
4. Australian Orbital Study 2 (2007)
5. Minnesota E20 Study (2007)
6. Neste Oil Review (2009) ← European vehicles

In the USA, the Coordinating Research Council (CRC) has evaluated HWD many times and recently completed several studies of HWD with gasoline/ethanol blends. The CRC work represents the most comprehensive set of published data on vehicle driveability performance. Two Australian studies and one from the US State of Minnesota were also reported within the past five years. Although the results are useful, they were not strictly conducted on vehicles considered to be representative of the European light-duty fleet.

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 not published but were used as the basis for one CONCAWE report. More recently, CONCAWE conducted a study with the French GFC on hot and cold weather driveability performance on ethanol/petrol blends and Neste Oil published a review on ETBE blends tested in early 1990’s European cars. A JEC study on evaporative emissions from gasoline vehicles was also carried out by the EU’s Joint Research Centre (JRC) in collaboration with EUCAR (the European Council for Automotive R&D) and CONCAWE.

In general, these studies demonstrate that it is important not to vaporise fuel in the vehicle’s fuel supply system in order to avoid HWD problems in older cars. This is a challenge, of course, since there is plenty of available engine heat under hot weather conditions and fuel temperatures can rise to 70-80^{o}C. Clearly, the lower temperature properties of the petrol fuel, especially DVPE and E70, are more important than the higher temperature properties, such as E100 or E150. Limited statistical analysis suggests that DVPE is more important than E70 for achieving acceptable HWD performance.

The published vehicle studies show that modern light-duty vehicles are much less susceptible to HWD problems than older vehicles. For example, port-fuel injected (PFI) are much less sensitive to HWD than are carburetted vehicles, as has been shown by many studies. The CONCAWE/GFC study did show problems on two early technology direct injection (DI) vehicles when operating at 40°C on 60kPa fuels having E70 values higher than 55%. Other studies showed minor HWD problems with hot starting and idle stability but nothing serious and with little quantitative data.

The impact of ethanol in petrol on HWD performance does not appear to be due to ethanol *per se*, but is instead due to the change in DVPE and E70 properties of the ethanol/petrol blend because ethanol has been added. In general, however, the published studies support the conclusion that ethanol/petrol blends will only impact HWD performance of some older model vehicles under extreme values in climate and fuel properties. For this reason, increasing the E70 volatility class limits when blending higher ethanol levels is not likely to impact the HWD performance of modern vehicles.

Of course, the volatility of the fuel can also impact the vehicle’s evaporative emissions and there are indications from the JEC study that the presence of ethanol in petrol can reduce the loading capacity of the vehicle’s carbon canister.

2.4. *Effect of Petrol Volatility on Vehicle Cold Weather Driveability*

Cold Weather Driveability (CWD) performance of light-duty vehicles has also been studied over the past two decades [4]:

1. Shell Study (1998) 🡐 European vehicles
2. Older CRC Studies (1990-2000)
3. Recent CRC Studies (2000-2008)
4. CONCAWE/GFC Study (2003) 🡐 European vehicles
5. Australian Orbital Study 1 (2003-4)
6. Australian Orbital Study 2 (2007)
7. Minnesota E20 Study (2007)
8. Lubrizol Study (2002)
9. Neste Oil Review (2009) 🡐 European vehicles

In addition to the extensive CRC studies described above, the Australian Government sponsored the Orbital Engine Company to carry out two major studies on the use of ethanol/petrol 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)”. A second test programme was reported by Orbital in 2007 on the CWD performance of vehicles operating on 5% and 10% v/v ethanol/petrol blends. This 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 blending ethanol into petrol were evaluated without correcting for the change in volatility upon ethanol addition.

In general, there are little CWD data available on ethanol/gasoline blends above 10% v/v. The first Australian study described above looked at 20% v/v blends as did a more recent study completed by the University of Minnesota. In the Australian study, a driveability evaluation was completed on a vehicle test fleet comprising 40 pairs of similar 2000–2006 vehicles exhibiting similar driving patterns. Vehicle drivers were asked to complete daily log sheets indicating any driveability problems that they experienced. 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 covering each climatic season (fall, winter, spring, and summer). Thus, the results covered both HWD and CWD vehicle performance.

One additional study, completed 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 instances where threshold pressure values were not reached. Since this study was conducted on a single bench engine and not on a vehicle, the results are interesting but extrapolating the conclusions to CWD performance in vehicles is difficult. Toyota has also published a fundamental review of the effect of ethanol on combustion, especially under cold temperature conditions.

The Inter-Company Working Group in Europe also tested CWD and the results were published as an SAE paper before the Group was disbanded. The CONCAWE/GFC programme investigated CWD as did the recently published Neste Oil review on ETBE blends tested in early 1990’s European cars. Shell has investigated CWD performance of European vehicles and reported a fundamental “Enthalpy Requirement” parameter for ethanol/gasoline blends.

From these studies, it has been shown that cold starting performance of vehicles is not significantly affected by DVPE but is affected by higher distillation points. Early fundamental work showed that the time required to start a cold engine depends on the air/fuel vapour ratio which can be calculated from distillation properties. For satisfactory cold engine operation, the objective is to vaporise enough fuel even though there is not much heat available to do so. The vaporisation process is limited by the available heat and by the rate of heat transfer to the fuel injected into the combustion chamber of the engine.

As such, higher volatility properties, such as E100 and higher values, are more important than lower volatility properties, (DVPE and E70). The addition of ethanol to petrol affects this process because of ethanol’s higher latent heat of vaporisation (that is, more heat is required to vaporise the injected fuel volume) and the change in the air/fuel ratio within the combustion chamber due to ethanol’s oxygen. The US CRC has developed various “Driveability Indexes” (DIs) based on a combination of distillation properties and one of these has been adopted in the US ASTM gasoline specification. In order to account for the impact of ethanol on CWD, an ethanol concentration dependent term (an ethanol offset) has also been applied.

This work showed that at -18°C, cold starting correlated best with E70 (or T10E), while at -7°C, the best correlation was with E100 or E120. More recent work on fuel injected vehicles has confirmed that for temperatures between 0 and 16ºC (more typical of spring and autumn transition periods) the fuel property which correlates best with cold starting performance is E100 (or T50), giving a significantly better correlation to performance than does E70. The cold starting performance of modern vehicles is very good, such that in this recent work, cold start times greater than 2 seconds were only seen for fuels that were well outside the volatility specification limits.

CWD does not depend on RVP but does correlate with mid-range volatility, that is, the E100 (or T50E) value. Where CWD performance has been correlated with other distillation properties (for example the US Driveability Index (DI) based on T10, T50 and T90), the front-end volatility (E70 (or T10)) had only a weak effect on CWD performance. Recent CRC work suggested that a DI based on E70 and E121 or E93 and including an ethanol offset term gave the best correlation to CWD. An analysis of European cars showed that a DI based on E100 and E150 with an MTBE or ethanol offset gave a good correlation with CWD performance. Thus, the CWD performance of European vehicles depends more strongly on mid-range volatility, such as E100, and is affected by the ethanol content.

Most importantly, there is also a correlation between exhaust emissions and driveability performance. This is because driveability malfunctions are a manifestation of engine misfires that increase HC emissions. This was shown in the EPEFE programme where increased emissions occurred with reported driveability problems although only on some vehicles tested on very low volatility fuels. Work by General Motors and the Inter-Company Volatility Group have both demonstrated a clear correlation between HC emissions and driveability performance.

From the published vehicle studies, CWD is only mildly affected by the specific use of ethanol even though ethanol increases the petrol's volatility. For this reason, increasing the E100 volatility class limits when blending higher ethanol levels is not likely to significantly impact the CWD performance of modern vehicles. The effects that can be attributed to ethanol are thought to be a combination of ethanol's higher latent heat of vaporisation and the leaning effect on the air/fuel ratio under cold engine (open-loop) conditions. Including an ethanol offset term can improve CWD performance predictability as has been found in the US CRC studies.

3. BEP525 Ethanol/Petrol Blending Study

3.1. Statistical Design

The BEP525 ethanol/petrol blending study was organised using the principles of statistical experimental design and full details can be found in **Appendix 1**.

Previous studies (**Section 2**) have shown that the volatility characteristics of ethanol/petrol blends depend upon the following parameters:

- Ethanol content,
- Water content,
- Composition of the base petrol blend, especially aromatics and olefins,
- Volatility parameters of the base petrol blend, especially Dry Vapour Pressure Equivalent (DVPE) and the evaporated fractions at 70 and at 100°C (E70, E100), and
- The presence of other oxygenates, such as MTBE or ETBE.

While the use of ETBE is expected to increase over time, MTBE is widely used in the European fuels market today so it was important to include MTBE in the design matrix for this study.

The original scope of this study specified that the distillation properties, DVPE, density, and molecular composition should be measured for a range of base fuels and for splash blends of ethanol in those base fuels at 5%, 10%, and 25% v/v concentrations. Because the distillation properties of ethanol/petrol blends depend in a non-linear way on ethanol content (see **Figures 1** and **2** in **Section 2**), it was recommended that data should be collected at two additional ethanol concentrations, namely at 15% and 20% v/v ethanol. The marginal cost to complete this additional work was relatively small and the extra measurements were expected to provide valuable information on the behaviour of ethanol between 10 and 25% v/v, leading to more robust blending models.

In order to simplify the analysis, the ethanol used in this study complies with the EN 15736 specification for fuel grade ethanol and contains one denaturant as permitted in the EN 228 specification. Although denaturants are not expected to alter volatility characteristics of the final ethanol/petrol blends, the ethanol must contain a low concentration of denaturant in order to ensure that the ethanol is suitable for fuel blending. The denaturant used in this study was petrol complying with EN 228 added into the ethanol at 2% v/v.

The objective of the test programme was to determine what happens to volatility, specifically E70 and E100 (and DVPE), when ethanol is splash-blended into a wide range of base petrol fuels.

The E70 of such a blend can be written as

- $\text{E70(blend)} = (1 - c) \times \text{E70(base fuel)} + c \times \text{BE70(EtOH)}$ (Eqn 2) where c is the final concentration of ethanol in the blend (0 < c < 1) and BE70(EtOH) is its *Blending E70*. It is postulated that the Blending E70 will depend on the concentration of ethanol in the blend and the base petrol volatility and composition. There may also be a dependence on water content.

For this reason, this study developed predictive models expressing BE70(EtOH) as a function of ethanol concentration and base fuel properties as detailed in **Appendix 1**. E100 was modeled in a similar way.

A preliminary design for this study suggested that a base fuel design matrix having about 60 base fuels would be appropriately sized. In order to properly span the range of values already included in the EN228 specification, it was decided that the range of base petrol fuel properties to be tested would be as follows:

1. Composition of the base petrol blend, especially aromatics and olefins
    - Aromatics: 20 to 45% v/v
    - Olefins: 5 to 20% v/v
    - Plus constraint:
        - Paraffins = 100 – (Aromatics + Olefins + MTBE + ETBE) where the name means the measured concentration of that component class in the base petrol blend

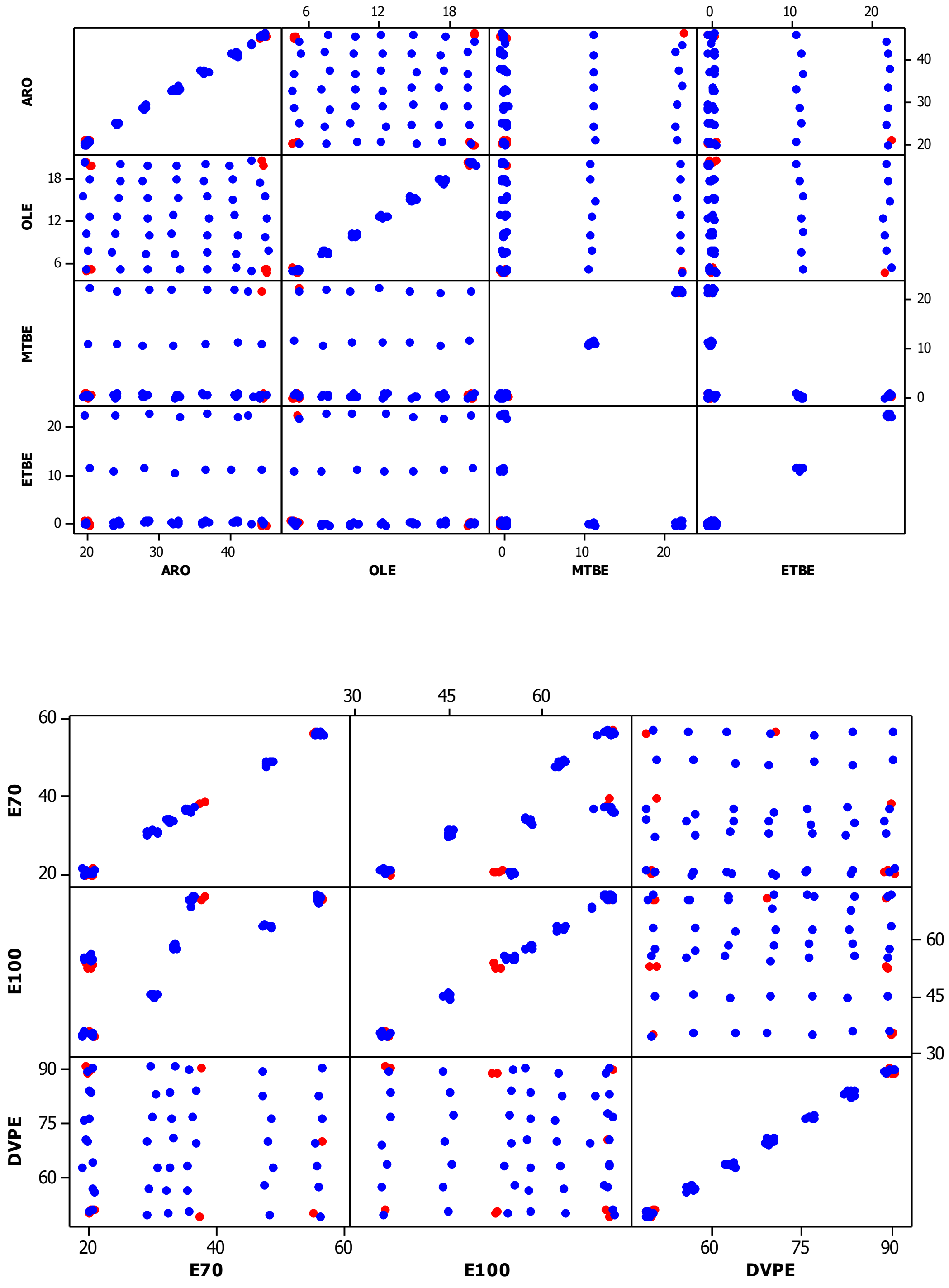
2. Volatility parameters of the base petrol blend, especially DVPE, E70 (evaporated fraction at 70°C), and E100 (evaporated fraction at 100°C)
    - DVPE: 50 to 90 kPa
    - E70: 20 to 56% v/v
    - E100: 35 to 71% v/v
    - Plus constraint:
        - Delta(E100 – E70) must be between 15 and 35% v/v

3. The presence of other oxygenates, such as MTBE and ETBE
    - MTBE: 0 to 22% v/v
    - ETBE: 0 to 22% v/v
    - Plus constraint:
        - Only one ether oxygenate included in any one base petrol blend

The base fuel matrix was constructed in two stages. First, a 49-fuel sub-matrix was constructed in order to fill the above region as evenly as possible. This was based on a fractional replicate of a 7×7×7×7×7 factorial generated using the KEYFINDER program [5,6]. The levels of the first three factors in this design determined the levels of aromatics, olefins and DVPE for each base fuel while the last two factors determined the combinations of levels of the constrained pairs of factors E70 & E100 and MTBE and ETBE respectively (see **Table A1-1** in **Appendix 1**). Eleven additional fuels were then added at the corners and edges of the region, using a D-optimality algorithm, in order to improve the model fitting capability.

Figure 7 shows scatter plots of the final 60-fuel design matrix. Full details can be found in **Appendix 1** including a summary of these 60 petrol base fuels in **Table A1-3**.

Figure 7 ***Scatter plots showing the values of pairs of design variables (Note that some points have been slightly displaced in order to reveal points that are superimposed when plotted in two dimensions)***



● Initial 49 base fuel compositions

● Additional 11 base fuel compositions added to fill in gaps

Measurements of E70 and E100 by EN ISO 3405 [7] are subject to measurement error with the repeatability (r) varying as fuel properties and the shape of the distillation curve change. Typical values for r are 2 to 3% for E70 and 1.5 to 2.5% for E100[7]. Therefore, it was decided that the distillation curves would be measured in triplicate for each base fuel and each ethanol/petrol blend. This resulted in a total of 1,080 distillation curves: 60 base fuels x 6 fuel blends x 3 distillation curves per blend.

The primary interest was in the differences between the E70 and E100 of the ethanol/petrol blends and the E70 and E100 of the base petrol. Therefore, the 18 base and blend measurements for each base fuel were carried out within a short time interval of one another on the same equipment at the same laboratory.

A typical test order for a particular base fuel was:

Block 1	E10 - Base - E25 - E15 - E20 - E5
Block 2	E20 - E10 - E5 - Base - E15 - E25
Block 3	E25 - E5 - E15 - E20 - Base - E10

Each randomized block was conducted by the same operator in a single day. The other measurements (DVPE and density) were performed once on each sample on the same day and in the same order as Block 1.

The base fuels themselves were processed in a randomized order, the final test order being listed in **Table A1-4** in **Appendix 1**[8]**.**

3.2. Effect of water content on petrol volatility

While analyzing the literature in preparation for this study, it was found that there is some evidence that the water content of ethanol/gasoline blends can affect the DVPE and perhaps the distillation properties of the final blend. If this evidence were to be correct, it would be very important in the current study to ensure that the water content was either (1) fixed at a single value, such as that allowed in EN 228, or (2) included as an independent fuel matrix design variable covering two or more water concentrations. Obviously, Option 2 would substantially increase the complexity of the design matrix and potentially the number of fuels that would need to be blended and tested in the study.

The EN 15376 specification for ethanol as a petrol blending component limits the water content of ethanol to a maximum of 0.3% m/m. However, higher water contents are allowed in anhydrous ethanol in the USA (1.0% m/m max) and in Brazil (0.5% m/m max). For this reason, a literature study and then a water pre-study were conducted in order to measure the impact of water content on ethanol/petrol volatility for several fuels that were already included in the design matrix. Based on the results, a decision could then be made on the potential impact of the water findings on the number of samples to be evaluated in the main blending study.

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[7] The repeatability of E70 measurements can be worse than these values for blends having higher ethanol contents. This is discussed in **Appendix 5**.

[8] The designed test order was as shown in **Table A1-4** of **Appendix 1** but there were some changes in this order due to laboratory difficulties and delays in blending some of the base fuels (see **Section 4.1**). The actual test order can be determined from the dates that are shown in the data workbooks (see **Section 4.3**).

3.2.1. Effect of Water in Ethanol on Petrol Volatility

Anecdotal information has suggested that increasing the water content of ethanol will increase the DVPE caused by ethanol in the ethanol/petrol blend. However, through a limited literature study, we found that there is very little evidence to support this. In fact, the only data immediately available was from DGMK Project 645 [3] published in 2005 and described here.

This DGMK project looked at the water absorption capacity of different fuel blends and the effect of different additives including water on DVPE increase. Unfortunately, the study did not evaluate the DVPE increase due to water in simple ethanol/gasoline blends, but only in blends containing other cosolvents, such as MTBE, ETBE, and TBA. All of these tests were completed with 1250 ppm water, which made some of the blends turbid. Although DVPE was evaluated, the volatility parameters, including E70 and E100, were not.

As shown in **Table 2** recalculated from the DGMK project, four base fuels varying in DVPE were selected for this study into which various cosolvents were systematically added to produce Blends A to H. The base fuels were all commercial blends with 35% m/m aromatics content, except for Fuel 2, that had 25% m/m aromatics content.

The DVPE increases due to ethanol and other cosolvents varied from 3.7 to 6.2kPa (values in blue) for the 60kPa base fuels (Fuels 1 and 2) and -0.6 to 2.0kPa for the higher DVPE base fuels (Fuels 3 and 4). For the lower DVPE fuels, the DVPE increase due to 1250ppm water varied from 0.9 to 2.5kPa (values in red), with one higher value at 3 kPa. For the higher DVPE fuels, the DVPE increase due to 1250ppm water was greater than that due to the addition of ethanol and cosolvents alone.

Table 2 DVPE and DVPE increases for 5% v/v ethanol/petrol blends due to cosolvents and water (table recalculated from [3])

	Cosolvent Concentrations					**DVPE***					**Change in DVPE with Cosolvent:**			
	EtOH	**TBA**	**ETBE**	**MTBE**	**Water**	**Fuel 1**	**Fuel 2**	**Fuel 3**	**Fuel 4**		**Fuel 1**	**Fuel 2**	**Fuel 3**	**Fuel 4**
	%v/v	**%v/v**	**%v/v**	**%v/v**	**ppmv**	**60kPa**	**60kPa**	**85kPa**	**90kPa**					
Base Fuel						59.5	59.9	86.6	91.4					
Blend A	5	1	4			63.2	64.8	86.8	90.8	Blend A minus Base	3.7	4.9	0.2	-0.6
Blend B	5	1	4		1250	64.9	66.6	89.3	93.8	Blend B minus Blend A	1.6	1.8	2.5	3.0
Blend C	5	1		3.5		64.0	65.1	88.0	92.7	Blend C minus Base	4.5	5.2	1.4	1.3
Blend D	5	1		3.5	1250	65.1	67.2	89.2	93.6	Blend D minus Blend C	1.1	2.1	1.3	0.9
Blend E	5	0.5	5			63.8	64.7	87.8	91.7	Blend E minus Base	4.3	4.8	1.2	0.3
Blend F	5	0.5	5		1250	65.0	66.9	89.4	93.3	Blend F minus Blend E	1.2	2.1	1.6	1.6
Blend G	5	0.5		4		64.0	66.1	88.0	93.4	Blend G minus Base	4.5	6.2	1.4	2.0
Blend H	5	0.5		4	1250	66.2	67.2	90.3	95.4	Blend H minus Blend G	2.2	1.1	2.3	2.0

* DVPE values in this table are the average of two measurements

Based on these data and anecdotal information from fuel blenders, it was decided that a water pre-study should be conducted in order to determine whether water content should be considered as an additional design variable in this study.

3.2.2. Design of the Water Pre-Study

The effect of water content on distillation properties was investigated using the PAC OptiDist™ Analyser in a pilot study on 5% and 25% v/v ethanol/petrol blends. Before preparing the blends, the water content of the bio-ethanol (see **Section 3.3**) was adjusted by water addition so that it contained 0.2% or 1% m/m water. The water contents were verified by means of Karl-Fischer titration measurements.

Seven base fuels were then selected that spanned the range of aromatics, DVPE, E70, E100, and ETBE that had already been determined for the main blending study (see **Section 3.1**). For this study, MTBE was not used and there was no specific target for olefins content since there is no clear evidence that the olefins content is an important factor. For this reason, olefins were held constant at 5% v/v in these base petrols. The target fuel properties for the water pre-study are shown in **Table 3**.

Table 3 Base petrol blending targets for the water pre-study

FUEL	AROMS	DVPE	E70	E100	ETBE
A	45.0	90.0	20.0	35.0	0.0
B	38.0	50.0	56.0	71.0	0.0
C	20.0	50.0	20.0	35.0	0.0
D	45.0	50.0	20.0	55.0	0.0
E	20.0	90.0	56.0	71.0	0.0
F	45.0	50.0	20.0	55.0	22.0
G	20.0	90.0	56.0	71.0	22.0

Each of the seven base fuels was then blended with ethanol containing either 0.23%v or 1.07%v water to produce final ethanol/petrol blends containing 5% or 25% v/v (hydrated) ethanol. The four ethanol/petrol blends and the base fuel without ethanol were tested in triplicate in three randomized blocks of 5 tests. The test order for evaluating these samples is shown in **Table 4**.

Table 4 Test order for the water pre-study*

TEST	FUEL	BLOCK	1	2	3	4	5
1	D	1	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH	BASE	0.2% H2O, 25% ETOH
		2	BASE	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH
		3	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH	BASE	1.0% H2O, 5% ETOH
2	B	1	0.2% H2O, 25% ETOH	BASE	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH
		2	BASE	1.0% H2O, 5% ETOH	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH
		3	0.2% H2O, 5% ETOH	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH	BASE	1.0% H2O, 5% ETOH
3	C	1	1.0% H2O, 5% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH	BASE	0.2% H2O, 25% ETOH
		2	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH	BASE	1.0% H2O, 5% ETOH	0.2% H2O, 25% ETOH
		3	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH	BASE	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH
4	E	1	BASE	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH	0.2% H2O, 25% ETOH	0.2% H2O, 5% ETOH
		2	BASE	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH	0.2% H2O, 25% ETOH
		3	1.0% H2O, 5% ETOH	1.0% H2O, 25% ETOH	BASE	0.2% H2O, 5% ETOH	0.2% H2O, 25% ETOH
5	F	1	0.2% H2O, 5% ETOH	BASE	1.0% H2O, 5% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 25% ETOH
		2	BASE	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH
		3	BASE	0.2% H2O, 25% ETOH	0.2% H2O, 5% ETOH	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH
6	G	1	1.0% H2O, 5% ETOH	0.2% H2O, 5% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 25% ETOH	BASE
		2	0.2% H2O, 25% ETOH	BASE	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH	1.0% H2O, 5% ETOH
		3	1.0% H2O, 25% ETOH	1.0% H2O, 5% ETOH	0.2% H2O, 25% ETOH	0.2% H2O, 5% ETOH	BASE
7	A	1	0.2% H2O, 5% ETOH	1.0% H2O, 25% ETOH	BASE	0.2% H2O, 25% ETOH	1.0% H2O, 5% ETOH
		2	BASE	1.0% H2O, 5% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH	0.2% H2O, 25% ETOH
		3	BASE	1.0% H2O, 5% ETOH	0.2% H2O, 25% ETOH	1.0% H2O, 25% ETOH	0.2% H2O, 5% ETOH

* Nominal water contents are shown in the table. The measured water contents were 0.23% and 1.07% v/v.

3.2.3. Results of the Water Pre-study

Because each distillation was repeated three times, there were a total of fifteen distillation curves obtained for each base fuel and its four different ethanol/water blends. Two examples of the resulting distillation curves are shown in **Figure 8** (Fuel A) and **Figure 9** (Fuel G). The distillation curve is highly expanded in order to highlight small differences in the 70^{o}C and 100^{o}C temperature regions. Clearly, the base fuel composition and the ethanol content impact the E70 and E100 values but the purpose of the study was to determine whether changes in the water content introduced an additional variable.

Figure 8 Fuel A: Distillation curves for different ethanol and water contents

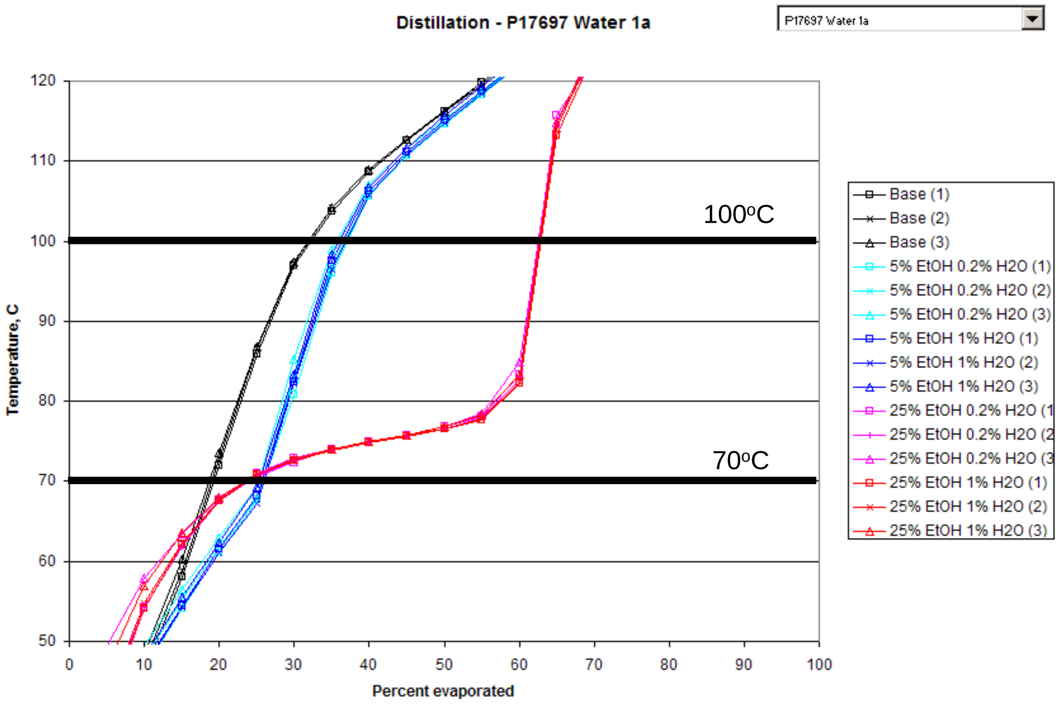
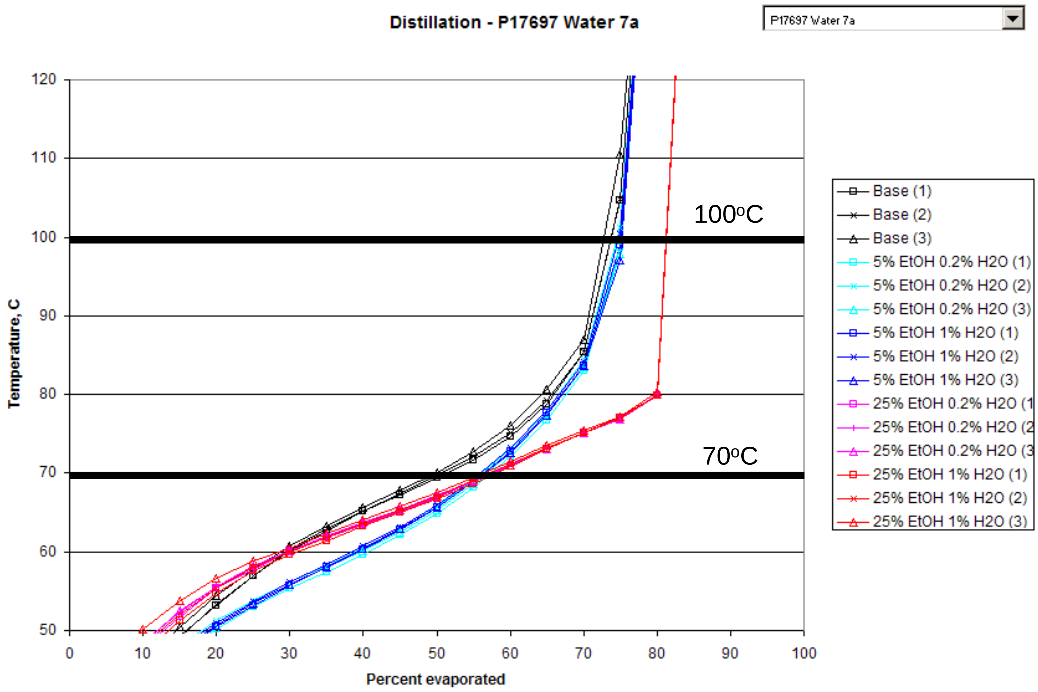


Figure 9 Fuel G: Distillation curves for different ethanol and water contents



The E70 and E100 values obtained from these distillation curves are summarized in **Table 5** along with the statistical analysis of the impact of water on E70 and E100 values. The mean E70 and E100 values are derived from triplicate measurements on each sample.

In **Table 5**, the right-hand columns show the impact of water on the volatility of ethanol/petrol blends in terms of the difference in E70 (or E100) between the two blends with different water contents. That is:

- Impact of water = $E70_{1.0\%\ H_2O} - E70_{0.2\%\ H_2O}$

This difference is also expressed as a percentage of the value at 0.2% water. Similar calculations are provided for the impact of water on E100.

Table 5 ***Statistical analysis of the impact of water on E70 and E100 values for fuels tested in the water pre-study***

E70 Results									Impact of Water on E70 Values			
Base Petrol Identifier	Base Petrol E70 (in % v/v)		Plus 5% EtOH with 0.2% H20	Plus 5% EtOH with 1% H20		Plus 25% EtOH with 0.2% H20	Plus 25% EtOH with 1% H20		At 5% EtOH		At 25% EtOH	
A	19.4		25.7	25.8		23.6	23.4		0.07	0.26%	-0.17	-0.71%
B	45.1		50.5	50.6		57.6	57.7		0.13	0.26%	0.10	0.17%
C	20.1		29.3	28.7		30.1	30.4		-0.57	-1.93%	0.33	1.11%
D	21.8		31.0	30.3		38.5	38.8		-0.67	-2.15%	0.30	0.78%
E	55.4		59.2	59.2		58.3	58.9		0.00	0.00%	0.60	1.03%
F	22.3		31.0	30.2		33.5	33.0		-0.80	-2.58%	-0.47	-1.39%
G	50.6		56.8	56.3		57.6	57.3		-0.47	-0.82%	-0.30	-0.52%
									🟨	SIGNIFICANT AT P < 5%		

E100 Results									Impact of Water on E100 Values			
Base Petrol Identifier	Base Petrol E100 (in % v/v)		Plus 5% EtOH with 0.2% H20	Plus 5% EtOH with 1% H20		Plus 25% EtOH with 0.2% H20	Plus 25% EtOH with 1% H20		At 5% EtOH		At 25% EtOH	
A	32.2		36.2	36.1		62.7	62.9		-0.07	-0.18%	0.17	0.27%
B	70.1		71.2	71.2		82.7	82.7		0.07	0.09%	0.00	0.00%
C	36.0		39.2	39.0		64.2	64.2		-0.20	-0.51%	0.03	0.05%
D	55.6		56.9	56.6		75.1	75.3		-0.37	-0.64%	0.13	0.18%
E	71.1		72.4	72.5		85.6	86.2		0.03	0.05%	0.53	0.62%
F	56.8		58.9	58.7		75.1	74.7		-0.20	-0.34%	-0.37	-0.49%
G	74.0		75.1	75.2		81.6	81.5		0.07	0.09%	-0.03	-0.04%
									🟨	SIGNIFICANT AT P < 5%		

From these results, it can be seen that the water content did not have a statistically significant impact on the E70 and E100 values in most cases. For the three occurrences where water did have an impact, no consistent trends could be identified in the results based on the petrol composition or ethanol content.

For this reason, it was concluded that the water content did not sufficiently impact the volatility parameters of the ethanol/petrol blends to be included as an independent design variable in the main fuel blending matrix. The water content of the ethanol was then fixed at 0.23% m/m for all subsequent tests which is in compliance with the current EN 228 specification.

3.3. Detailed characterisation of the bioethanol

The ethanol used in this study complied with the EN 15376 specification for fuel-grade ethanol and was confirmed to be of biological origin based on measurement of the ^{14}C isotope. The ethanol contained 2% v/v petrol conforming to EN 228 as the denaturant (**Section 3.1**). The molecular composition of the ethanol before addition of denaturant was determined by gas chromatography and is summarized in **Table 6**.

Table 6 Composition of the bioethanol used in this study

Compound	Weight %	Volume %
Ethanol	99.79	99.77
3-Methylbutan-1-ol	0.07	0.08
ETBE	0.06	0.06
2,2-Dimethylhexane	0.04	0.05
Propan-1-ol	0.03	0.03
Unknown	0.01	0.02

4. BEP525 Project Results

The following tasks were identified at the start of the BEP525 Project (see also **Appendix 4**).

Work Package: Task Number	Description	Status
WP10: Task 1	Literature review of volatility and vehicle driveability performance	Sections 2.3 and 2.4 and CONCAWE Report 8/09
WP20: Task 1	Results of problem analysis	Sections 2 and 3
WP30: Task 1	Base petrol blends based on statistical design	Section 3.1 and 4
WP30: Task 2	Ethanol/petrol blends based on statistical design	Section 3.1 and 4
WP30: Task 3	Analytical characterization of base petrol and ethanol/petrol blends	Section 4
WP40: Task 1	Preliminary analysis of results and environmental performance	Section 6 and Appendix 5
WP40: Task 2	Final analysis of results and environmental performance	Section 6
WP50: Task 1	Properties of designed fuel matrix for action in WP30	Section 3.1
WP50: Task 2	Detailed description of statistical methodology	Section 3 and Appendix 1
WP50: Task 3	Detailed statistical analysis of fuel blending and characterization of results	Section 5

4.1. Fuel Blending

4.1.1. Base Fuel Blending: Strategy and Components

A range of refinery blending components, narrow distillation refinery-type streams, and commercial chemicals were available for this project and used to prepare the base fuel blends. The properties of these streams are included in **Tables 7** and **8**. The actual streams used for blending included:

- Paraffinic blending components: isomerate, alkylate, butane, iso-pentane, iso-hexane, and other narrow distillation streams that covered the required boiling range, especially for fuel components boiling between 70 and 100°C.
- Olefinic blending components: light catalytically cracked gasoline (LCCG), light mixed olefins, and mixed C8-olefins.
- Aromatic blending components: toluene, a C8 aromatics stream, a C9–C11 aromatics stream, and a heavy reformate.

- Ethers: MTBE and ETBE were purchased from commercial sources and their compositions are shown in **Table 7**. The composition of the ethers was determined using an in-house GC method specially calibrated for samples containing high concentrations of oxygenates. The MTBE was found to be 99.1 vol% pure with small amounts of olefins and paraffins as impurities. The ETBE was found to be 93.2 vol% pure, with small amounts of ethanol, t-butyl alcohol, paraffins, olefins, and naphthenes as impurities.

- Ethanol: The ethanol used in this study was bio-derived and complied with the EN 15376 specification for fuel grade ethanol (see **Section 3.3**). Two vol% of commercial unleaded gasoline was added as denaturant. The water content for the main blending programme was fixed at 0.23 vol% (see **Section 3.2.3**). A separate ethanol sample was treated with more water in order to raise the water content to 1.07 vol%; this ethanol was used exclusively for the water pre-study (see **Section 3.2**). The composition of the denatured ethanol is shown in **Table 7**.

Each blending component was sourced in sufficient volume in order to complete the entire blending study. Relevant properties for each blending component were measured and are shown in the following tables.

Table 7 Properties of the aromatic and oxygenate blending components

		Aromatic Blending Components				Oxygenate Blending Components			
Property	Units	Toluene	C8 Aromatics	C9 - C11 Aromatics	Heavy Reformate	MTBE	ETBE	Denatured Ethanol + 0.2%v Water	Denatured Ethanol + 1.0%v Water
Density @ 15°C	kg/m3	871.4	871.2	875.0	850.8	746.3	742.1	793.4	796.3
DVPE	kPa	8.2	3.7	2.0	6.2	55.4	37.5		
Distillation									
E70	%v	0.0	0.0	0.0	0.0	100.0	30.4	0.0	0.0
E100	%v	0.0	0.0	0.0	0.0	100.0	100.0	100.0	100.0
E120	%v	100.0	0.0	0.0	14.9	100.0	100.0	100.0	100.0
E150	%v	100.0	100.0	0.0	75.0	100.0	100.0	100.0	100.0
E180	%v	100.0	100.0	100.0	96.7	100.0	100.0	100.0	100.0
Water Content	%v							0.23	1.067
Composition									
By GC	MTBE					99.05	0.00	0.00	
	ETBE					0.00	93.15	0.09	
	Ethanol					0.00	1.13	98.32	
	Other Alcohols					0.00	1.32	0.21	
By PONA	Paraffins, %v	0.08	0.48	0.00	14.58	0.10	2.68	0.58	
	Olefins, %v	0.00	0.00	0.00	0.89	0.85	1.64	0.15	
	Naphthenes, %v	0.00	0.01	0.00	0.59	0.00	0.08	0.03	
	Aromatics, %v	99.99	99.30	99.00	86.23	0.00	0.00	0.62	

Table 8 Properties of the paraffinic and olefinic blending components

		Paraffinic Blending Components								Olefinic Blending Components		
Property	**Units**	**Butane**	**Iso-pentane**	**Iso-hexane**	**C6 - C8 paraffins**	**C8 - C9 paraffins**	**C10+ Paraffins**	**Isomerate**	**Alkylate**	**LCCG**	**Light Olefins**	**C8 Olefins**
Density @ 15°C	**kg/M3**	**583.0**	**624.5**	**664.8**	**718.5**	**722.1**	**752.0**	**661.8**	**700.3**	**696.7**	**665.6**	**720.4**
DVPE	**kPa**	**370.0**	**140.0**	**50.1**	**20.2**	**7.4**	**1.1**	**94.6**	**42.6**	**73.8**	**102.2**	**13.9**
Distillation												
E70	**%v**	**100.0**	**100.0**	**100.0**	**0.0**	**0.0**	**0.0**	**96.4**	**10.7**	**70.5**	**100.0**	**0.0**
E100	**%v**	**100.0**	**100.0**	**100.0**	**100.0**	**0.0**	**0.0**	**100.0**	**50.2**	**86.6**	**100.0**	**0.0**
E120	**%v**	**100.0**	**100.0**	**100.0**	**100.0**	**74.4**	**0.0**	**100.0**	**82.9**	**89.9**	**100.0**	**100.0**
E150	**%v**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**0.0**	**100.0**	**91.9**	**95.8**	**100.0**	**100.0**
E180	**%v**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**50.0**	**100.0**	**96.9**	**100.0**	**100.0**	**100.0**
Water Content	**%v**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**	**Nil**
Composition												
By PONA	**Paraffins, %v**	**98.0**	**100.0**	**94.8**	**64.1**	**98.3**	**99.2**	**81.7**	**78.8**	**45.3**	**0.0**	**0.9**
	Olefins, %v	**2.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.3**	**1.8**	**33.6**	**99.9**	**97.8**
	Naphthenes, %v	**0.0**	**0.0**	**5.2**	**36.0**	**1.0**	**0.6**	**15.4**	**1.1**	**8.2**	**0.0**	**1.2**
	Aromatics, %v	**0.0**	**0.0**	**0.0**	**0.0**	**0.3**	**0.3**	**0.9**	**2.9**	**14.4**	**0.0**	**0.0**

4.1.2. Base Fuel Blending Procedure

Using the properties of these components and a proprietary blending model that predicts non-linear blending effects, an initial recipe was developed for each base fuel in order to meet the design values (see **Section 3.1**). Eight litres of each base fuel was then blended according to this initial recipe and a representative sample was taken for analysis.

The base fuel blend was accepted if the properties fell within the following limits compared to the design values.

- Aromatics, olefins, and ether: +/- 2 vol%
- DVPE: +/- 3kPa
- Distillation: +/- 3.5 vol%

If a fuel did not meet the above criteria, a modified recipe was calculated, the composition of the initial fuel blend was adjusted accordingly and a new sample of the adjusted fuel blend was analysed versus the design limits shown above. This process was repeated if the fuels were still found to be outside the design limits. Usually, no more than two adjustments were required in order to meet the design values within the indicated blending criteria. It was not possible to reblend a small number of fuels to the design targets, generally those that were at the edges of the design matrix. These blends were accepted when they were as close as possible to the design targets.

4.1.3. Preparation of the Ethanol/Petrol Blends

When the base fuel blend was as close as possible to the design specification, ethanol was splash-blended at five different concentrations. Before blending the ethanol into the base fuel, both the ethanol and base fuel were stored at 5°C to minimize evaporative losses during the blending process.

To prepare the ethanol/base fuel blends, the base fuel was transferred into six separate cans as shown in the table below. Ethanol was then added to five of the cans at the prescribed levels. The cans were mixed by shaking and small samples were withdrawn for DVPE and Reformulyzer® composition measurements. This approach ensured that all six cans received identical treatment. All fuels were then submitted for distillation, DVPE, and density analyses as indicated below. In this way, the base fuel blend was measured a second time and the results were compared to those for the five fuels that contained ethanol.

Blend	Base	E5	E10	E15	E20	E25
Base Fuel, ml	1000	950	900	850	800	750
Ethanol, ml	0	50	100	150	200	250

4.2. Characterization of the Ethanol/Petrol Blends

4.2.1. Handling of Fuel Blends

Samples for detailed characterization were received from the blending team in sets of 6 (the base fuel blend plus 5 blends containing between 5 and 25% v/v ethanol). At any one time, the number of sample sets received in the laboratory ranged from one to four (that is, from 6 to 24 fuel blends). The fuel blends were refrigerated after receipt in the analytical laboratory (immediately up to 12 hours) and until they could be analyzed, in order to minimize evaporative losses.

Each fuel blend was received in two separate sealed cans: a 1x125ml can and 1x500ml can. The smaller can contained 70-80% by volume of sample and was used for the DVPE analysis. The larger can contained sufficient sample to carry out a minimum of 4 distillation measurements (i.e. over 420ml), if any problems were encountered during the distillation analysis.

4.2.2. Analysis of the Fuel Blends: Distillation, Density, and DVPE

Each fuel set was then analyzed by three different analysts for the following properties:

- Analyst 1: Distillation, density, and DVPE
- Analyst 2: Distillation
- Analyst 3: Distillation

Thus, each analyst was specified and responsible for carrying out the analysis in a prescribed time frame (i.e. over a given day or night shift). In each case, the fuel blends were analysed in a specific order, as defined in a document provided to the analytical laboratory by the project's statistician. The test order for distillation measurements was different for all three analysts.

All density and DVPE analyses were carried out on the same pieces of equipment for the whole study. For the distillation measurements, two different but identical models of the PAC OptiDist™ Analyzer were used throughout the programme, called OptiDist 1 and OptiDist 2. Only one of these two analyzers was used for a given set of six fuel blends in order to reduce measurement differences.

4.2.3. Analysis of Fuel Blends: Molecular Composition

The base fuels and ethanol-containing blends were analyzed using the Reformulyzer® instrument according to the EN 14517 method. See **Appendix 2** for details.

4.2.4. Reporting Results

Each analyst completed a spreadsheet given to them, with the results achieved during the analysis. For the distillation measurements, results were initially reported on these spreadsheets. During the course of the project, however, an automatic download facility was developed which enabled the distillation results to be transferred electronically from the OptiDist™ Analyzer into a spreadsheet format which helped to minimize potential data transcription errors. As soon as this capability was in place, all distillation results that had previously been transcribed by hand were replaced with automatically downloaded results, thus removing 'human error' factors from this aspect of the data collection.

4.2.5. Equipment Validation

Density: The equipment was checked on a weekly basis against both air and water. Correlation scheme samples were also run each month (a minimum of 3 different sets of samples per month) which were entered into a multi-laboratory correlation scheme. This correlation scheme is used to assess the competence of laboratories to perform standardized tests.

DVPE: The equipment was checked each day against a known secondary standard (ethanol) to ensure that it was performing within the allowed tolerance. The results of these checks were also included in the correlation scheme described above.

Distillation: Both OptiDist™ analyzers were rigorously checked before putting them into service by completing comparative testing on standard samples that had been analyzed previously. These samples included ones that had been tested as part of the correlation scheme described above. The results compared very favourably with the mean values of the correlation scheme results. Certified Reference Materials (CRMs) were also used to validate the equipment.

4.3. Results and Analysis

4.3.1. Guide to the Data Files

All of the results from this test programme have been collated into four Workbooks that can be found on the CD accompanying this report.

The first workbook (‘*BEP525 Distillation Plots FINAL.xls’*), called the **Distillation Plots Workbook**, contains a table and graphing capability for viewing the three measured distillation curves for each base fuel and its ethanol/petrol blends. The base fuel series to be plotted can be selected using a simple drop-down menu. Reference lines are shown at 70°C, 100°C, and 150°C corresponding to E70, E100 and E150. A table of measured base fuel properties is also included in this workbook.

This Workbook’s spreadsheets are described below:

- ReadMe:
    - Instructions on how to use this workbook and notes on data quality

- Distillation:
    - Chart displaying the three distillation curves for a selected base fuel and each of its five ethanol blends on a single plot. The base fuel can be selected using the drop-down menu.

- Distillation (no drop):
    - Similar plot to the above but without the drop down box. The base fuel can be selected using the shortcut keys (see ReadMe for details).

- Table:
    - Tabulation of the three measured distillation curves for each base fuel and blend, with the derived E70, E100, E120, and E150 values and the recovery, residue and loss (ml). Also included are the measured density and DVPE values for each base fuel and blend (single determinations) and the blending targets (E70, E100, DVPE, aromatics, olefins, MTBE, and ETBE) for each base fuel.

- Base fuel properties:
    - Measured properties (E70, E100, E120, E150, DVPE, density, aromatics, olefins, MTBE, ETBE, ethanol) of the 60 base fuels. Except where noted in the workbook, the E70, E100, E120, E150 values are all averages of the values derived from the three individual distillation curves. All other values are single determinations.

The second Workbook (‘*BEP525 Summary Plots FINAL.xls’*), called the **Summary Plots Workbook**, contains a table of the measured fuel properties (E70, E100, E120, E150, density, DVPE, aromatics, olefins, MTBE, ETBE, EtOH) for each base fuel and its five ethanol blends. The E70, E100, E120, and E150 values are averages over the three repeat distillations.

The target and measured values (E70, E100, DVPE, aromatics, olefins, MTBE, ETBE) for the corresponding base fuel are also included. The differences in distillation and volatility values (E70, E100, E120, E150 and DVPE) between the various blends and the corresponding base fuel have also been tabulated. These are expressed both as simple differences (Delta.E70, Delta.E100, etc.) and as blending numbers (B.E70, B.E100, etc.) (see **Section 3.1** and **Appendix 1** for details).

This Workbook includes five dynamic chart sheets that allow users to visualize the data in a number of interesting ways. The variables and/or base fuel series to be plotted can again be selected using simple drop-down menus. The spreadsheets in this Workbook are described below:

- ReadMe:
    - Instructions on how to use this workbook and notes on data quality

- Table:
    - Table of the measured fuel properties (E70, E100, E120, E150, density, DVPE, aromatics, olefins, MTBE, ETBE, EtOH) for each base fuel and ethanol blend. The target values (E70, E100, DVPE, aromatics, olefins, MTBE, ETBE) for the corresponding base fuel are also included. The differences in distillation and volatility values (E70, E100, E120, E150, DVPE) between the various blends and the corresponding base fuel are also tabulated, expressed both as simple differences (Delta.E70, Delta.E100, etc.) and as blending numbers (B.E70, B.E100, etc.). Except where noted in the workbook, the E70, E100, E120, E150 values, as well as the blending numbers and delta values, are all averages of the three measurements derived from the three individual distillation curves. All other values are single determinations.

- Base fuel props – Act vs des:
    - Chart for comparing measured base fuel properties with their blending targets. Properties are selected using the drop down menu.

- y vs EtOH (by fuel):
    - Chart for plotting any of the measured values in the ‘Table’ tab (see above) against the nominal ethanol content (5%, 10%, etc.) for a particular base fuel and ethanol blend series. The measured value of interest and the base fuel can be selected using the two drop-down menus. The properties of the base fuel are shown at the top of the graph. Shortcut keys can also be used to cycle forwards and backwards through the results for each of the 60 base fuels and their ethanol blends.

- y vs EtOH (all fuels):
    - Chart for showing one of the measured values in the ‘Table’ above plotted against nominal ethanol content (5%, 10%, etc.) for all base fuels and ethanol blends. The measured value of interest can be changed using the drop-down menu. The symbols denote the 60 different base fuels.

- y vs Base fuel props:

  - Chart showing one of the measured values in the 'Table' above plotted against a particular base fuel property (either target or measured values). The values on each axis can be changed using the drop-down menus. The symbols denote the different ethanol concentrations (5%, 10%, etc.).

- y vs Base fuel props (by conc):
  - Similar plot to the above with the five different ethanol concentrations (5%, 10%, …, 25%) shown on different panels. Drop-down menus are provided to select the parameters of interest. Three different scaling buttons for the y-axis are also provided. This sheet may need to be resized to fit the screen or page.

The third Workbook ('*BEP525 Reformulyzer® Indexed FINAL.xls*'), called the **Reformulyzer® Workbook**, contains compositional measurements for each of the 60 base fuels and their 5 to 25% v/v ethanol blends. The spreadsheets in this Workbook are described below:

- ReadMe:
  - Description of the main data table and notes on data quality.

- Table:
  - Tabulation of the composition of each base fuel and its five ethanol blends, as measured by the Reformulyzer®. The target base fuel compositions (aromatics, olefins, MTBE, and ETBE) and volatility parameters (DVPE, E70, and E100) are also shown.

The fourth Workbook ('*BEP525 Models FINAL.xls*'), called the **Models Workbook**, contains tables and plots showing the measured values of Delta.E70, Delta.E100, B.E70 and B.E100 for each base fuel and ethanol blend, and the fitted values from the statistical models developed in **Section 5.3**. Tables and plots can also be constructed for future base fuel and ethanol blends provided that the base fuel properties used in the models are known.

- ReadMe:
  - Instructions on how to use this workbook.

- Fitted models:
  - Tabular summary of the models for Delta.E70, Delta.E100, B.E70 and B.E100 fitted on an ethanol concentration-by-concentration basis. Models are also tabulated that can be used at any ethanol concentration between 5% and 25%.

- Table:
  - Fitted values of Delta.E70, Delta.E100, B.E70 and B.E100 for each base fuel and ethanol blend derived from statistical models fitted on an ethanol concentration-by-concentration basis. The fitted values appear to the right of a table of fuel properties taken from the Summary Plots Workbook described earlier in this section.

- y vs EtOH (by fuel):

  - Chart for plotting the measured and fitted values of Delta.E70, Delta.E100, B.E70, and B.E100 against the nominal ethanol content (5%, 10%, etc.) for a particular base fuel and ethanol blend series. Fitted values are shown for both the concentration-by-concentration (red squares) and cross-concentration models (red line). The measured value of interest and the base fuel can be selected using the first two drop-down menus. Shortcut keys can also be used to cycle forwards and backwards through the results for each of the 60 base fuels and their ethanol blends. The third drop down can be used to estimate Delta.E70 or Delta.E100 at ethanol concentrations between 0% and 5% using linear or quadratic interpolation, as described in **Section 5.3.3**.

- New fuel table:
  - This sheet may be used to create tables and plots of measured and fitted Delta.E70, Delta.E100, B.E70, and B.100 values for a new base fuel and its 5%, 10%, 15%, 20%, and 25% ethanol blends. The properties of the base fuel and (if known) its 5%, 10%, 15%, 20%, and 25% ethanol blends should be entered in the yellow cells. Next the measured value of interest and the interpolation rule should be chosen using the two drop down menus. The fitted values will then appear in the green cells. The plot may be found on the next chart sheet. A warning appears if the properties of the new base fuel are outside the ranges listed in **Section 3.1** or if they violate other constraints.

- y vs EtOH (new fuel):
  - Chart similar to y vs EtOH for the new base fuel series specified on the previous sheet.

More Information on Using the Workbooks:

In the charts that display the results from a particular base fuel/ethanol blend series, shortcut keys[9] have been provided to allow the user to quickly cycle forwards and backwards through the 60 base fuels. To use these shortcuts or the scaling buttons in the Summary Plots Workbook, it is necessary to ‘Enable macros’ when first opening the workbook. Details can be found in the ‘ReadMe’ sheets included in these Workbooks.

It is recommended that the Workbooks are opened as ‘Read only’ files in order to avoid accidental corruption. If you would like to analyze data outside of the Workbooks, it is recommended that you copy and paste the data from the tables to another spreadsheet.

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[9] The shortcut keys differ from Workbook to Workbook in order to avoid potential conflicts when two or more Workbooks are open at the same time. If an Excel error occurs, close the other workbooks.

4.3.2. Missing Values and Outliers

The study protocol (see **Table A1-4**) required the distillation curves to be measured in triplicate for the 60 base fuels and 300 ethanol/petrol blends. One block of results (single measurements of base fuel #15 and its five ethanol blends) was not completed due to operational problems. One of the three distillation curves for the E10 blend of Base Fuel #34 was also missing. Because there was not enough blended sample remaining to repeat these measurements, it was decided to rely upon the results from the two satisfactory distillation curves.

The distillation data (both the curves and the derived E70 and E100 values) were investigated for outliers using both statistical and graphical techniques. Each distillation curve was plotted and compared with the other two distillations on the same sample. The distillations were also compared with those of the base fuel and its ethanol blends at all concentrations; see **Appendix 8** where the complete set of distillation curves will be found.

It was noted that a small number of distillation curves had some short sections where the measured temperature vs. the percent evaporated curve went downwards instead of upwards (see, for example, the distillation curves for the E20 and E25 blends for Base Fuel #16). It is believed that this occurs because the heater in the distillation instrument is not able to compensate quickly enough for the heat loss due to evaporation of the ethanol/fuel blend. This problem was generally more evident at higher ethanol concentrations.

On six other occasions, the distillation curves crossed the 70^{o}C line several times leading to some ambiguity in the value of E70. This problem was due to the same phenomenon described above but occurred exactly in the area of measurement interest. When this occurred, it was decided that the measured E70 would be based on the first crossing point.

Two distillations showed multiple crossings of the 100^{o}C line and there were some issues estimating E150 for several fuel blends that had final boiling points below 150^{o}C.

As a second check on data quality, we calculated the standard deviation for E70 and E100 from each set of triplicate measurements and then investigated those sets where the Standard Deviation (SD) was abnormally high.

Combining the visual and statistical evidence and applying good engineering judgment, the following five distillation curves (out of a total of 1,080 measured curves) were deemed to be outliers:

Table 9 Distillation curves that were excluded from analysis

Base Fuel	Block Number	Fuel Blend
9	2	Base Fuel
9	2	E5
12	1	E25
28	3	E10
49	3	E5

The values of E70 and E100 from these five curves were excluded when calculating the average values for these particular fuels but the curves themselves have been retained in the Distillation Plots Workbook and in **Appendix 8**.

The compositional data were also checked for errors or inconsistencies. The expected composition of each blend was calculated taking into account (a) the target and/or measured base fuel properties, (b) the ethanol concentration, (c) the impurities in the ethanol and ETBE blending components (discussed in **Section 4.1.1**) and (d) the addition of denaturant. From this check, it was found that one base fuel blend (Base Fuel 15) had mistakenly been blended with 11% v/v MTBE instead of 11% v/v ETBE as intended from the design matrix. The measured values for Base Fuel 15 were retained and are shown in the Summary Plots Workbook.

Particular emphasis was placed on verifying the base fuel composition and the ethanol content of the various base fuel and ethanol blends. These are the key parameters which were used in the subsequent modeling of E70 and E100 (see **Section 5.3**).

Because the GC composition measurements were all single point determinations, it was not possible to detect outliers by simply looking at variations between sets of repeat results. For this reason, each set of GC measurements was plotted against the target ethanol content (0 to 25%) for each base fuel in turn and the most serious discrepancies from linearity were noted. Reformulyzer® measurements were repeated on fifteen fuel blends due to unexpected results and these are highlighted in blue in the Summary Plots and Reformulyzer® Workbooks. In each case, the second set of Reformulyzer® results was retained.

While some departures from linearity were noted for aromatics and olefins contents (e.g. in Base Fuel series 16, 30, 35, and 39), these were generally small compared to the overall range of values in the base fuel design matrix. The effects of these differences on the modeling of E70 and E100 were not expected to be important.

The measured ethanol values were generally in line with expectation. The only major departure from linearity was the low measured value of 23.1% for E25 in Base Fuel 46. It is believed that this is due to overlap of the ethanol with other components in the GC trace that must be manually deconvoluted.

It is worth noting that the scope of the ASTM D 6839-02 method used here does not cover fuels containing oxygenates (ethanol and ethers) at concentrations higher than 15% v/v. Because there is no more suitable method, and for consistency in the overall study, the same method was used for all base fuel and ethanol blends. A change in scope for this test method will be needed if it will be used in the future for ethanol/petrol blends containing more than 15% v/v ethanol.

4.3.3. Final Data for Interpretation

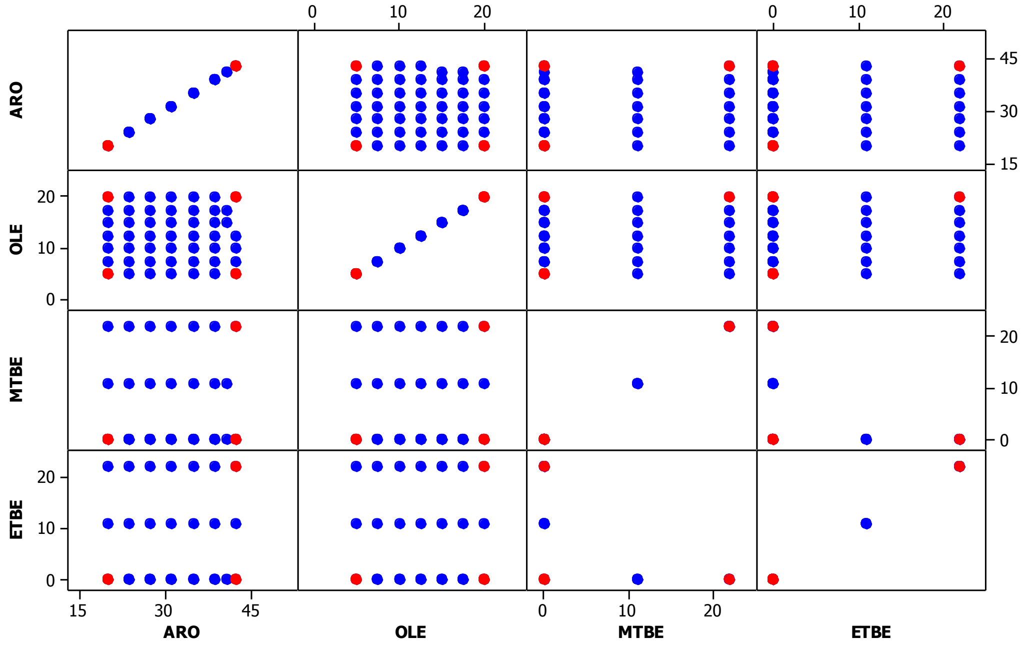
As described in **Section 3.1** and **Appendix 1**, an initial base fuel design matrix was developed that consisted of 49 different formulations. An additional 11 formulations were added to this design matrix in order to fill in apparent gaps in the design properties. The design matrix was set up to span the broadest range of properties allowed in the EN228 specification. The detailed data showing the design and actual values are included in the Workbooks.

One way to visualize the entire base fuel matrix is to compare the various parameters of interest in this study in the design matrix with the values that were actually measured. The two sets of values are shown in **Figure 10** for the composition variables, **Figure 11** for the distillation variables and DVPE, and **Figure 12** for the composition versus distillation variables. In these figures, the data point ‘jitter’ that was added to the points in **Figure 7** (**Section 3)** has been removed so that less than 60 formulations may be evident in these plots. Finally, the “Base fuel props – Act vs des” chart in the Summary Plots Workbook allows measured values to be plotted directly against the corresponding blending targets for each variable.

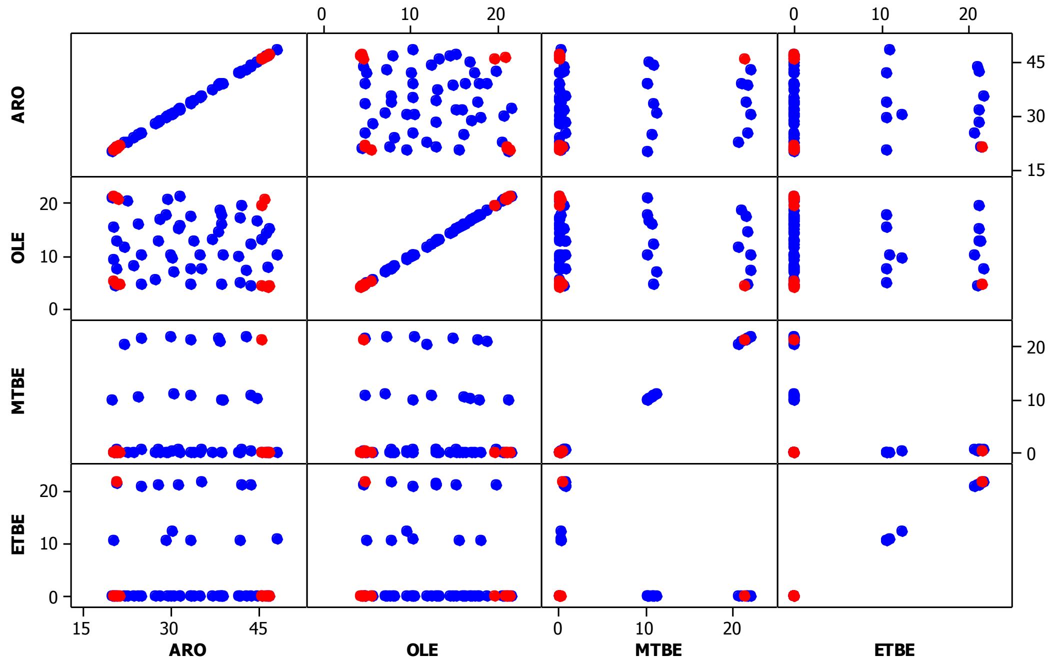
It can be seen from the various plots and charts that the blended fuels are generally close to target and that the measured fuel properties have a similar correlation structure to the target values in the design matrix.

Figure 10: Design vs. Measured Values: Composition Variables

Design Matrix[10]**:**



Measured Values:



● Initial 49 base fuel compositions
● Additional 11 base fuel compositions added to fill in gaps

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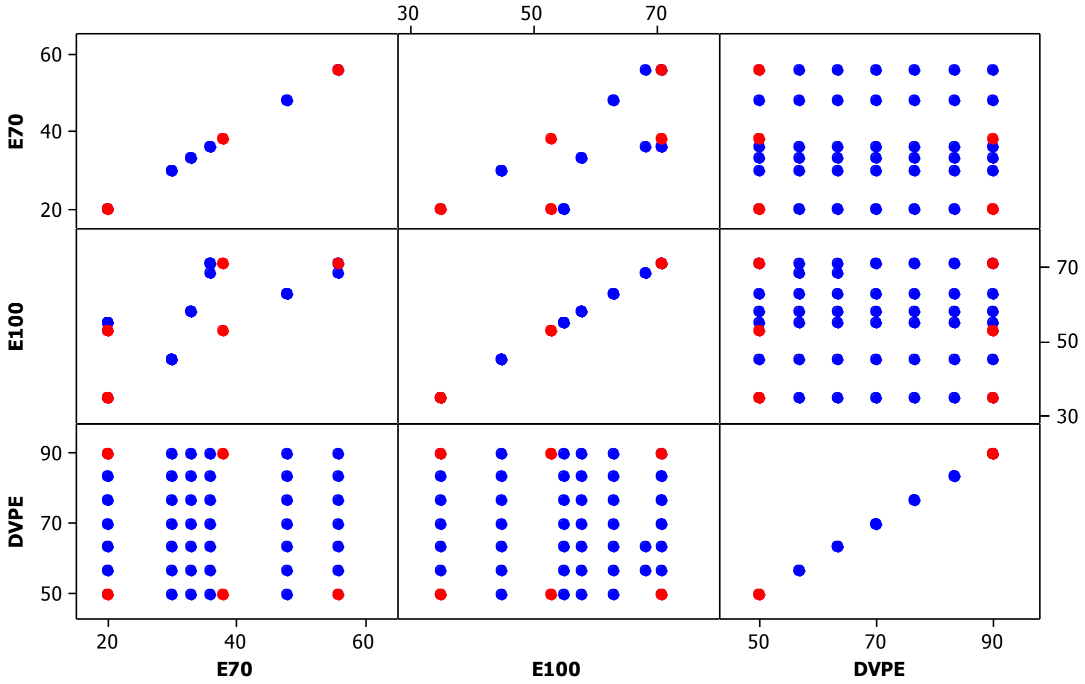
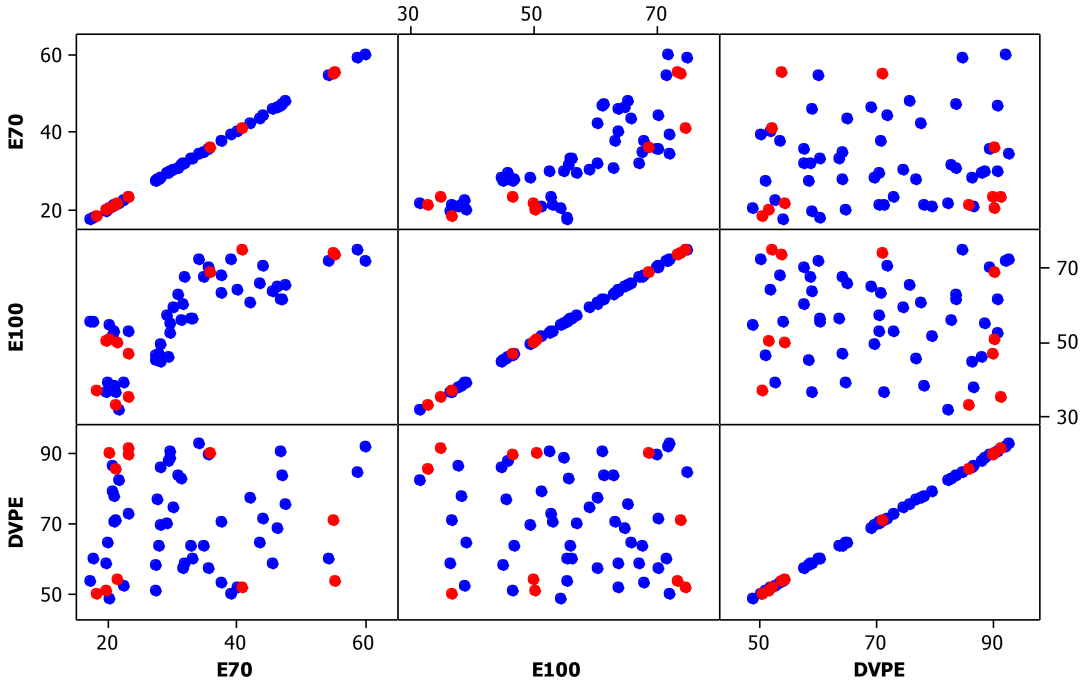
[10] Note that 'jitter' has been removed from the three design matrix charts in this section (see **Section 3.1** for an explanation of 'jitter').

Figure 11: Design vs. Measured Values: Distillation Variables and DVPE

Design Matrix:



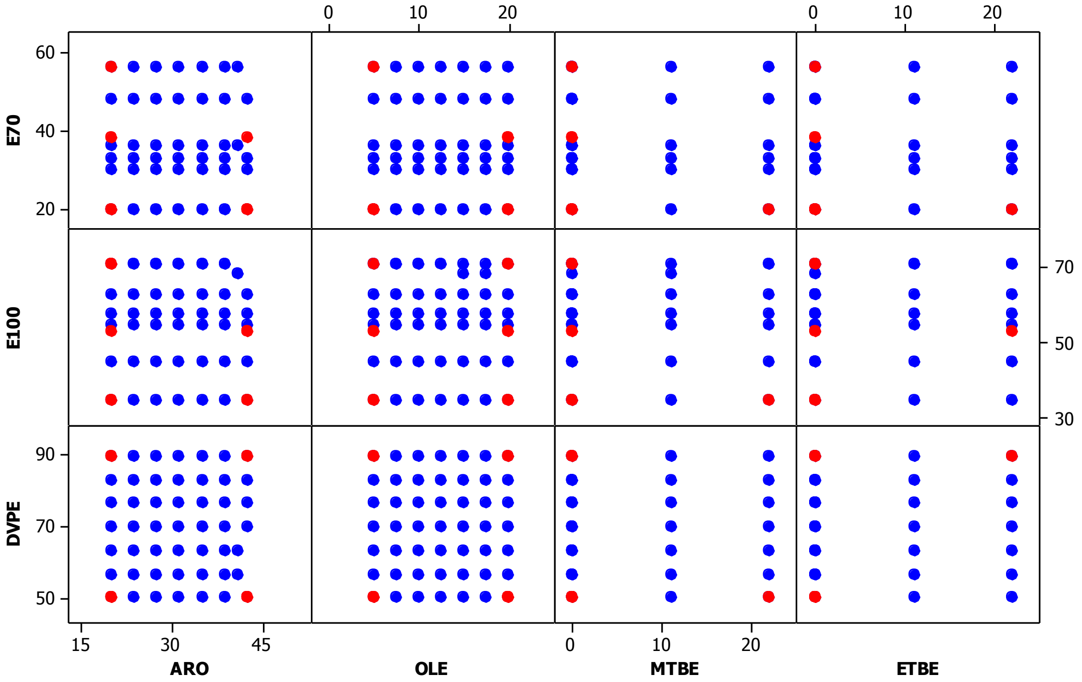
Measured Values:



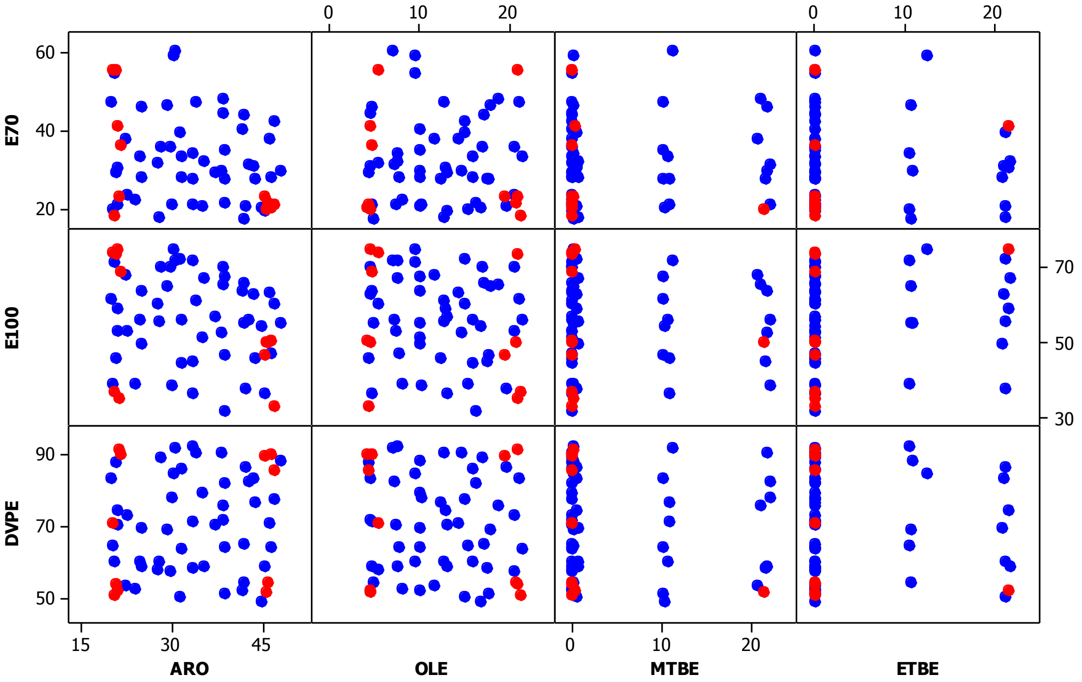
● Initial 49 base fuel compositions
● Additional 11 base fuel compositions added to fill in gaps

Figure 12: Design vs. Measured Values: Composition and Distillation Variables

Design Matrix:



Measured Values:



● Initial 49 base fuel compositions
● Additional 11 base fuel compositions added to fill in gaps

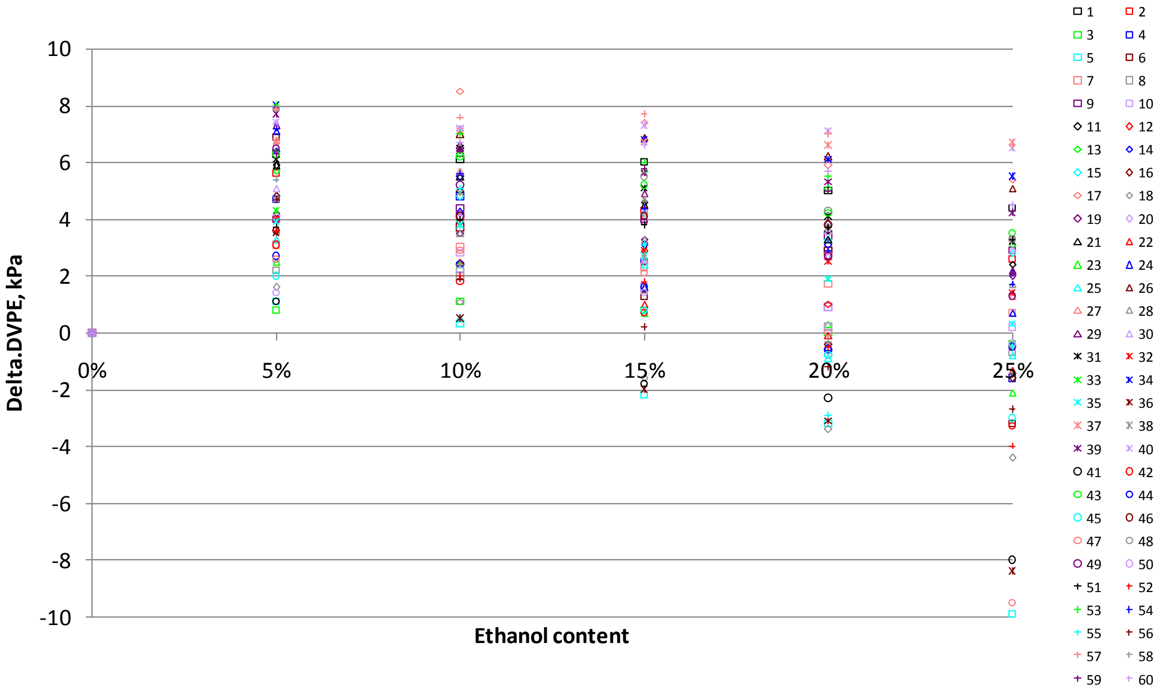
5. Interpretation of BEP525 Results

5.1. Overall Observations

The menu-driven graphing facilities in the Summary Plots Workbook provide many options for assessing the change in a measured value due to a change in a particular design variable. Some interesting relationships of this sort will be highlighted in this section using charts obtained from this workbook.

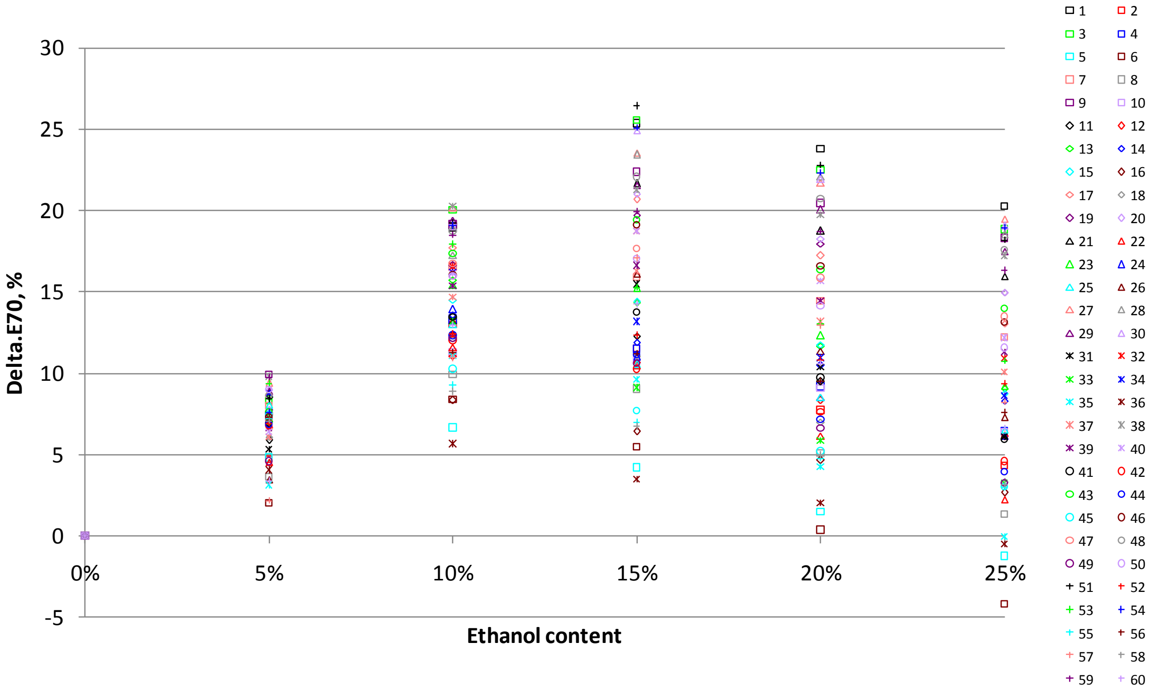
Figure 13 shows the variation in Delta.DVPE (= DVPE(blend) – DVPE(base)) as a function of the designed ethanol content for all 300 base fuel/ethanol blends with the symbols representing the 60 base fuels. This chart shows that the DVPE increase after addition of ethanol depends on the base fuel properties and can range from about 1 to 8kPa at 5% v/v ethanol to -10 to 7kPa at 25% v/v ethanol. The overall range in Delta.DVPE increases as the ethanol concentration increases.

Figure 13: Measured Delta.DVPE for each blend versus the designed ethanol concentration



Similarly **Figure 14** shows the variation in Delta.E70 (= E70(blend) – E70(base)) as a function of ethanol content for the 300 blends. This chart demonstrates that the maximum E70 increase after addition of ethanol varies from base fuel to base fuel, initially increasing up to 10% v/v or 15% v/v ethanol and then decreasing again up to 25% v/v ethanol. For a small number of base fuel compositions, the Delta.E70 is negative at 25% v/v ethanol. Wide variations in Delta.E70 are observed at each ethanol concentration confirming that there must be additional dependencies on base fuel properties. These complex dependencies will be explored statistically in **Section 5.3.**

Figure 14: Measured Delta.E70 for each blend versus the designed ethanol concentration



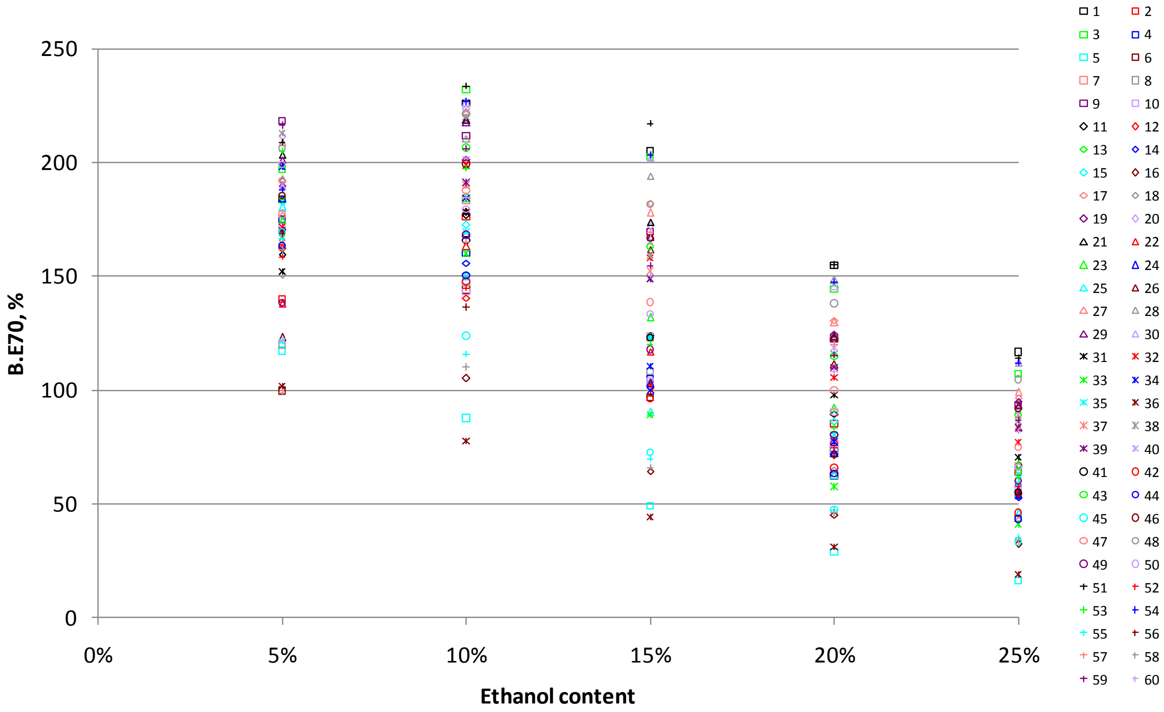
Of greater concern from a fuel blender's perspective is the increase in the E70 values and the overall range of Delta.E70 values for different base fuel compositions. The ranges of Delta.E70 and Delta.E100 values measured in this study are shown in **Table 10** as a function of the ethanol content. The practical impact of this variation is that the E70 of the base fuel must be carefully adjusted with a particular ethanol concentration in mind so that the E70 of the final ethanol/petrol blend will remain within the prevailing specification. With Delta.E70 values as variable as shown in the table, this is a very difficult task unless a fundamental understanding or a good predictive model is available to guide the blender. Since most ethanol blending occurs at terminal locations, the options are quite limited to correct a blend that is found to be off-specification with respect to volatility. Although this task has been manageable at 5% v/v ethanol, the increase in E70 and the increasing variation in Delta.E70 mean that ethanol blending will become increasingly challenging as the ethanol concentration increases to 10% v/v and beyond.

Table 10: Ranges of measured Delta.DVPE, Delta.E70, and Delta.E100 values at each ethanol concentration for the 60-fuel series

Ethanol Concentration	Delta.DVPE	Delta.E70	Delta.E100
5% v/v	+1 to +8kPa	+2 to +10%	0 to +5%
10% v/v	0 to +9 kPa	+6 to +20%	+2 to +11%
15% v/v	-2 to +8kPa	+3 to +26%	+3 to +17%
20% v/v	-3 to +7kPa	0 to +24%	+6 to +22%
25% v/v	-10 to +7kPa	-4 to +20%	+9 to +28%

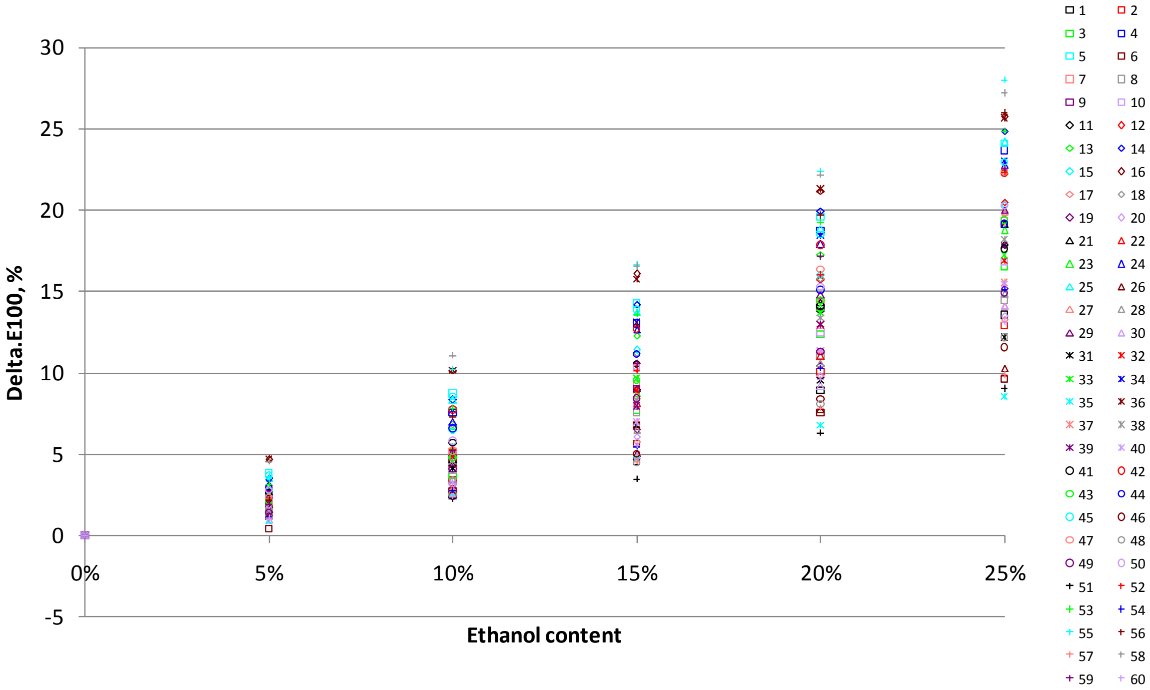
Figure 15 shows that the relationship between the Blending(E70) (B.E70) and ethanol concentration is just as complex as the relationship between Delta.E70 and ethanol concentration. B.E70 is generally highest at either 5% or 10% ethanol and then decreases. Large variations in B.E70 values are also found at each ethanol concentration.

Figure 15: Measured B.E70 for each blend versus the designed ethanol concentration



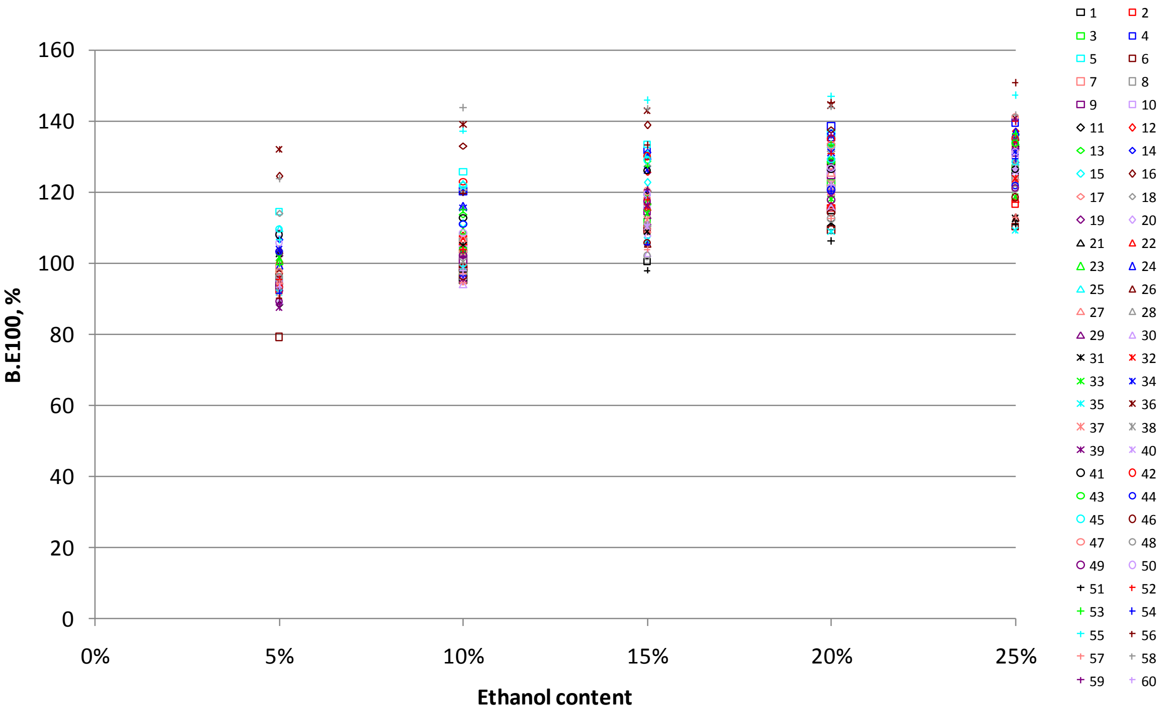
As shown in **Figure 16**, Delta.E100 (= E100(blend) – E100(base)) is better behaved than Delta.E70, increasing monotonically with the ethanol concentration. Nevertheless, large variations in Delta.E100 values are still observed at each ethanol concentration (see also **Table 10**), confirming again that there must be additional dependencies on base fuel properties.

Figure 16: Measured Delta.E100 for each blend versus the designed ethanol concentration



Finally, the B.E100 values are shown in **Figure 17** as a function of the ethanol concentration. The B.E100 values generally increase with increasing ethanol concentration but, in some cases, these values show slight decreases at higher concentrations. B.E100 values vary over a much smaller range than observed for B.E70 at any particular ethanol concentration.

Figure 17: Measured B.E100 for each blend versus the designed ethanol concentration



These figures represent only a small subset of the very interesting and complex dependencies that can be observed from these data.

5.2. Impact of Ethanol on Volatility

All of the distillation curves for the 60 base fuels and their five ethanol blends are plotted in **Appendix 8**. These distillations can be grouped into a number of distinctive patterns, based purely on a visual comparison. One attempt to do this is shown in **Appendix 7** in which the shape of the base fuel distillation curve and the response of the curve to ethanol addition has been visually evaluated. General comments regarding the range of base fuel E70 and E100 values for each group are also included in this appendix. This comparison begins to provide some clues on the properties of the base fuel that drive volatility behavior for ethanol/petrol blends.

In all cases, the addition of ethanol leads to a flattening of the distillation curve in the 70-80^{o}C region due to the formation of ethanol-hydrocarbon azeotropes [2]. The flat portions of the distillation curves end quite abruptly at higher ethanol concentrations and a large increase in temperature is required before more components of the blend are distilled.

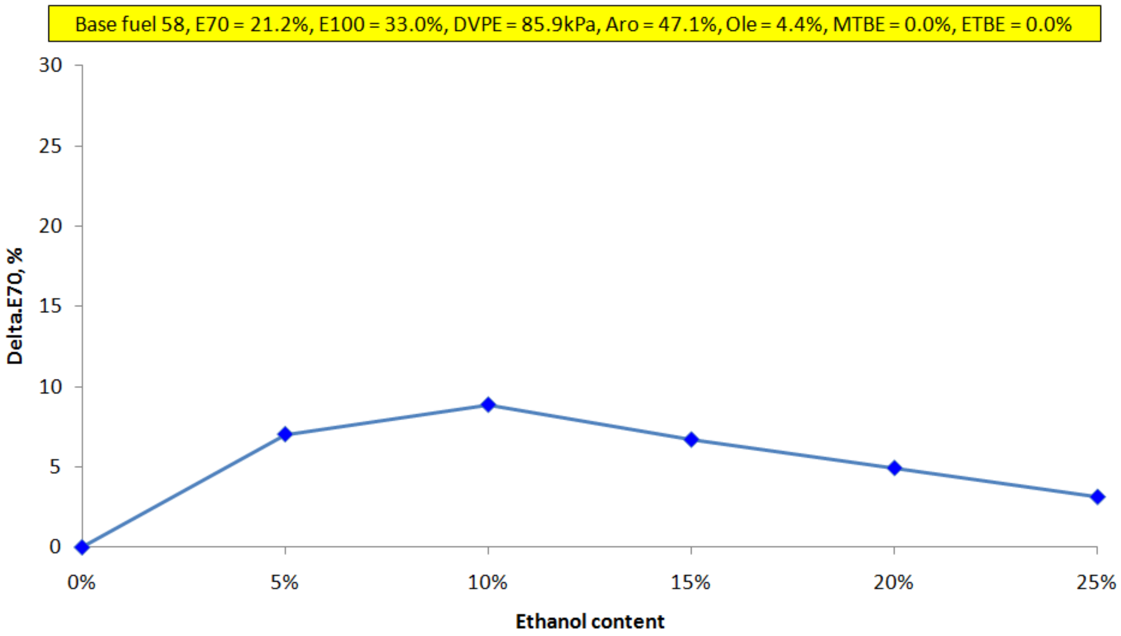
E70 is not a well defined parameter when the distillation curve is essentially flat at 70^{o}C. Minor shifts of the distillation curve either upwards or downwards will have a disproportionate effect on the measured E70 value. The precision of E70 measurements is discussed in more detail in **Appendix 5** where it is concluded that the repeatability and reproducibility can be as poor as 5% and 12% v/v, respectively, for E25 blends. This issue should be considered when specifying the volatility requirements for petrol containing higher levels of ethanol.

The complex relationships between Delta.E70, Delta.E100, the ethanol concentration, and the base fuel properties were explored further using the dynamic plots in the Summary Plots Workbook.

When Delta.E70 (that is, E70(blend) – E70(base)) is plotted against the designed ethanol concentration (0%, 5%, 10%, etc.) for different base fuels, all of the responses are observed to be nonlinear. The Delta.E70 is largest at either 10 or 15% v/v ethanol concentration.

Figure 18 shows two examples for Base Fuels 58 (top) and 1 (bottom). The greater the maximum value of Delta.E70, the higher the ethanol concentration at which the maximum value occurs. This can be seen more clearly in **Figure 19** where the 60 sets of Delta.E70 vs. ethanol plots are superimposed, with the smaller responses to the front and the larger responses to the back.

Figure 18: Delta.E70 versus the designed ethanol concentration for Base Fuels 58 (top) and 1 (bottom)



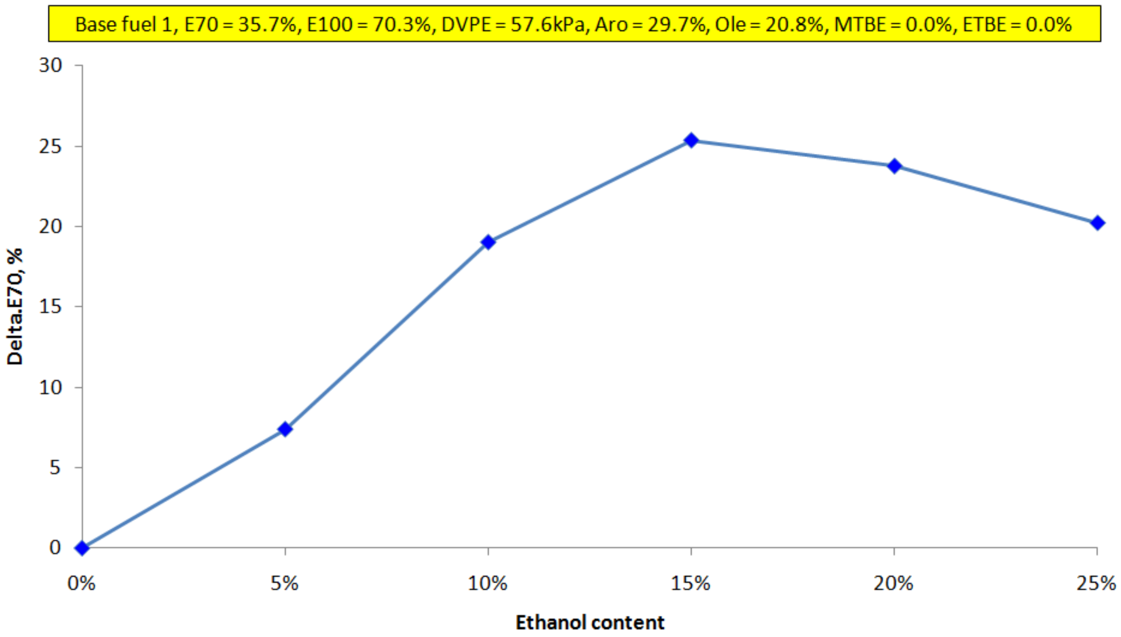


Figure 19: Delta.E70 versus the ethanol concentration between 0 and 25% v/v for all 60 base fuels. Smaller responses are plotted to the front and larger responses to the back.

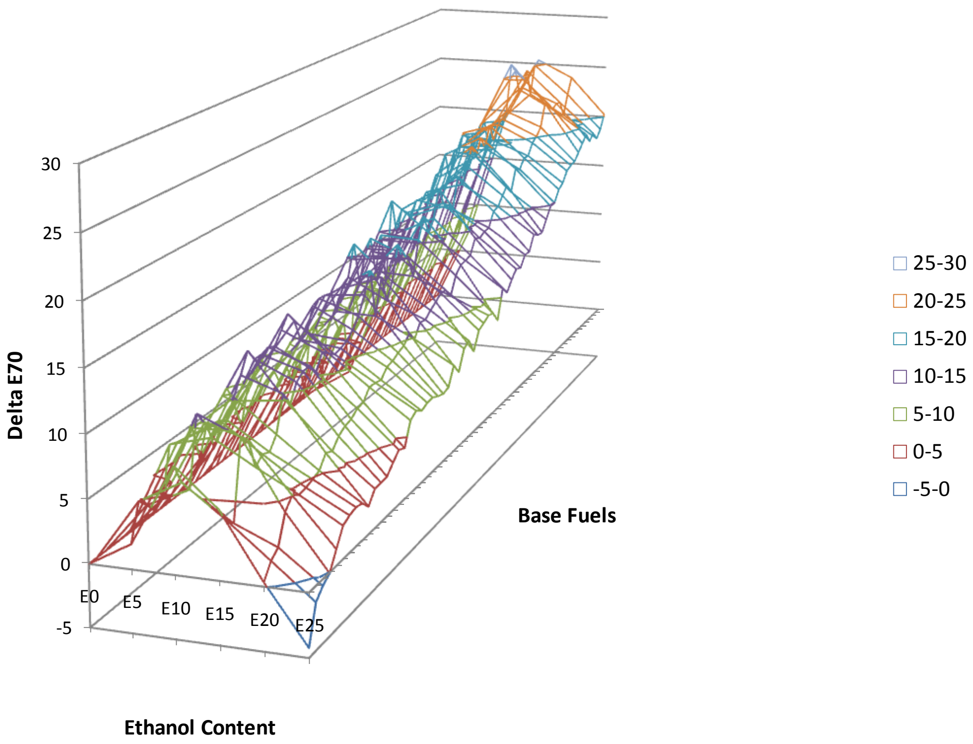
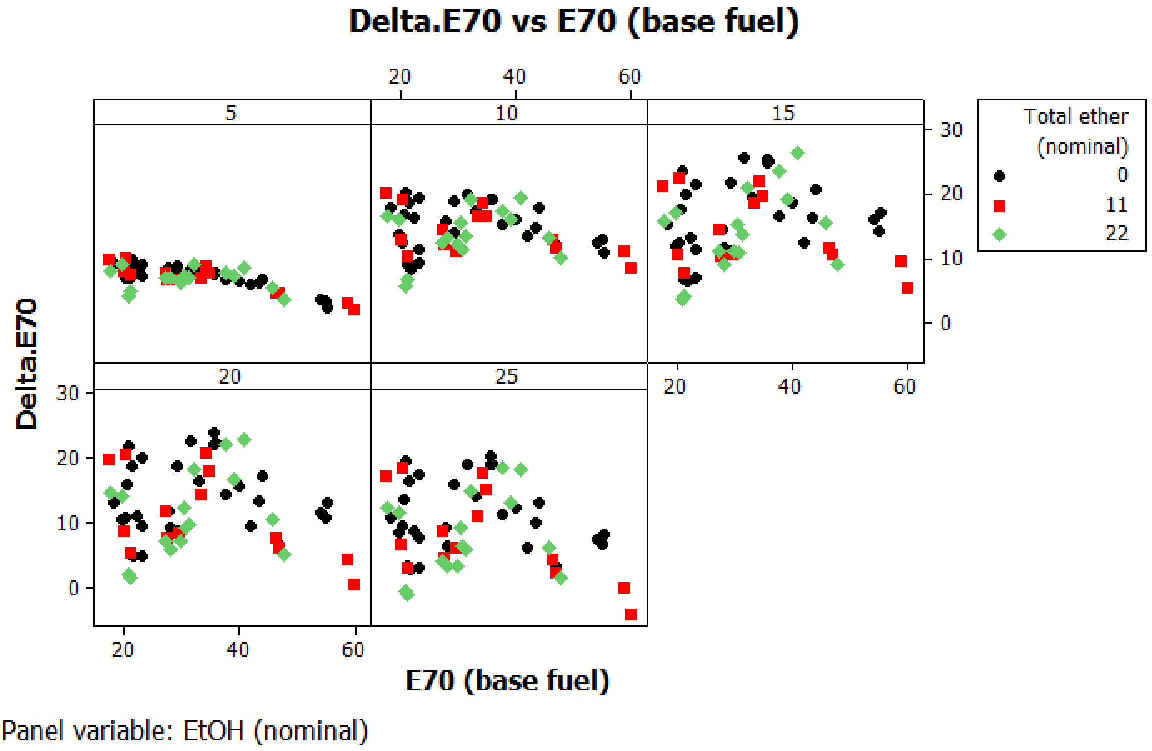


Figure 20 shows the Delta.E70 plotted against the E70 of the base fuel as a function of the ethanol concentration with the different coloured symbols indicating the three possible concentrations of ether (MTBE or ETBE).

Figure 20: Delta.E70 versus the E70 of the base fuel as a function of ethanol concentration. The effect of the total ether concentration is shown by the differently coloured points.



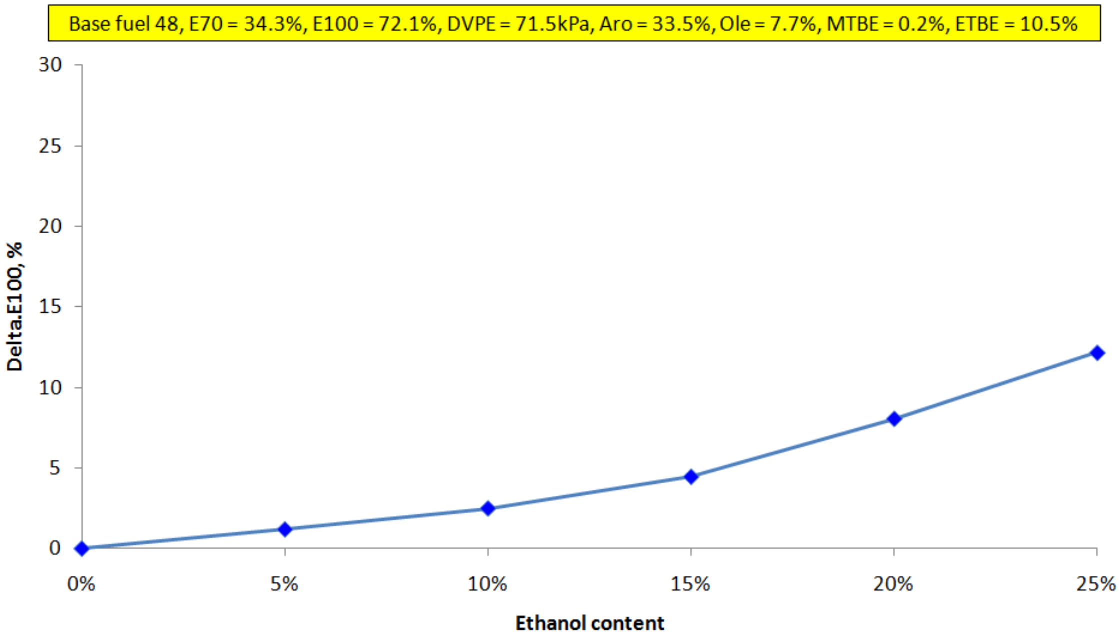
The patterns are unclear and any similarities to those found in the analysis of fuel compositions from the published literature (**Figure 3**) disappear at higher ethanol concentrations. There are also no obvious trends with changes in the designed ether concentration.

These dissimilarities are not too surprising because the base fuels in this study cover a much wider range of volatility and composition properties than those examined in the published literature, many of which were marketplace fuels.

The direct relationships between Delta.E70 and base fuel E70 in **Figure 20** are weak and generally nonlinear. In the next section, statistical models will be used to explain the variability in Delta.E70 at each ethanol concentration, i.e. in each of the five panels shown in **Figure 20**.

The Delta.E100 values behave very differently compared to Delta.E70 and increase monotonically with increasing ethanol concentration. This observation is in line with expectation because the boiling point of ethanol is less than 100°C. **Figure 21** shows two examples for Base Fuel 48 (top) and 58 (bottom).

Figure 21: Delta.E100 versus the designed ethanol concentration for Base Fuels 48 (top) and 58 (bottom)



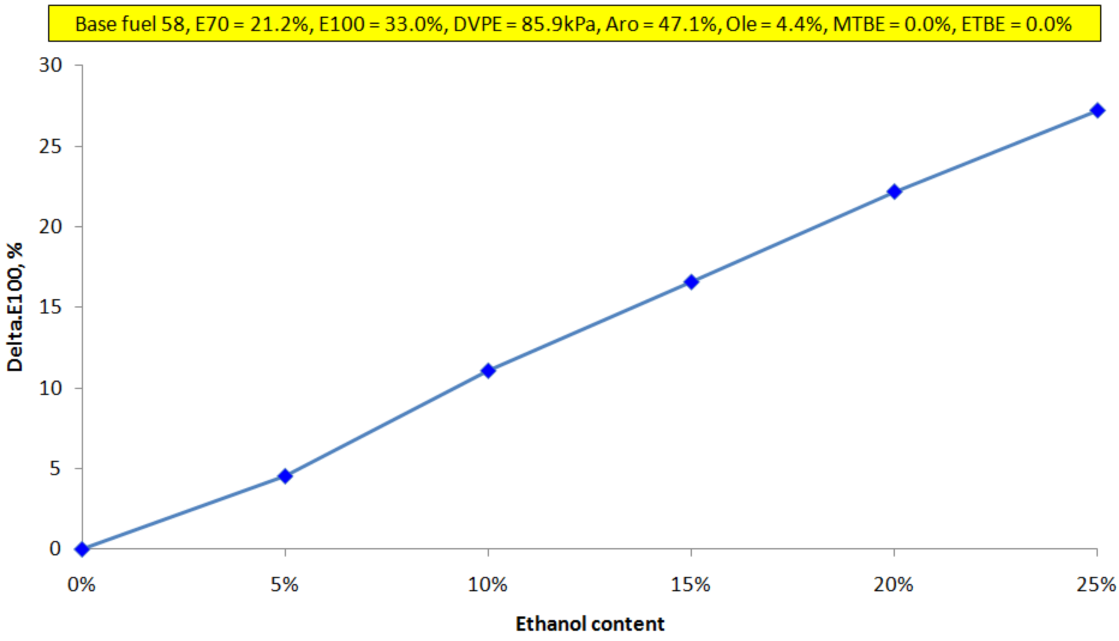


Figure 22 shows the Delta.E100 plotted against the designed ethanol concentration for all 60 base fuels. Again, smaller responses are plotted at the front and larger responses to the rear. Most of the responses show some nonlinearity, with a slight increase in slope at higher concentrations.

Figure 22: Delta.E100 versus the designed ethanol concentration for all 60 base fuels. Smaller responses are plotted at the front and larger responses at the rear.

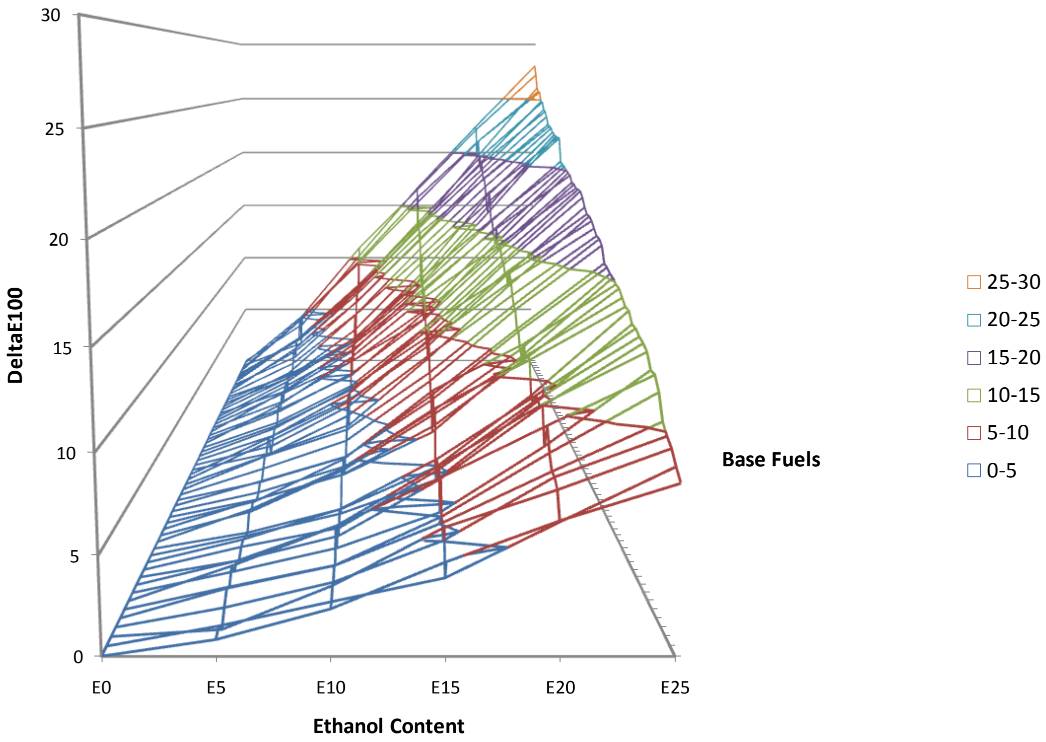
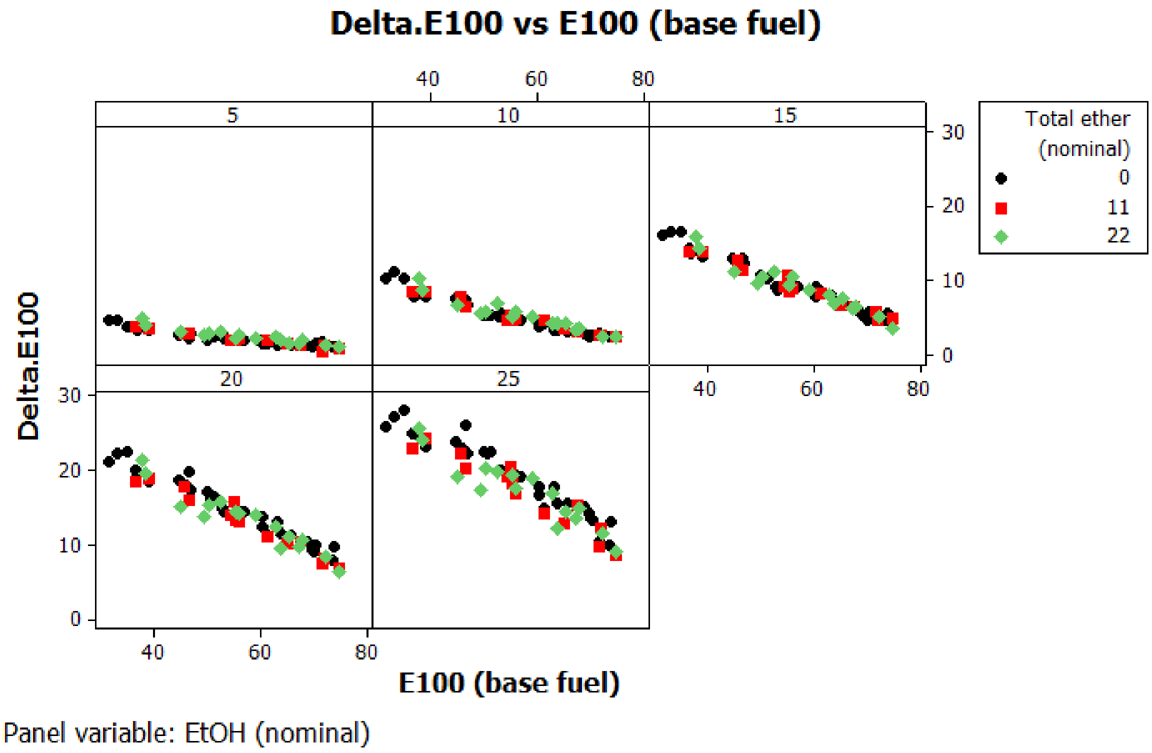


Figure 23 shows the Delta.E100 plotted against the base fuel E100 as a function of the ethanol concentration with the differently coloured symbols indicating the three possible concentrations of ether (MTBE or ETBE). The relationships are essentially linear, except perhaps at low ethanol concentrations and low E100(base) values. The Delta.E100 is highest at higher ethanol concentrations, again in line with expectation. The patterns are similar to those seen in the published literature and plotted in **Figure 5**.

Figure 23: ***Delta.E100 versus the E100 of the base fuel as a function of the ethanol concentration. The effect of the total ether concentration is shown by the differently coloured points.***



5.3. *Statistical Models: Preliminary Analysis*

5.3.1. Modelling Expectations

The results of this study are summarized in the four Workbooks described in **Section 4.3.1** that accompany this report. These Workbooks provide an extensive database that is expected to improve our understanding of the distillation characteristics of ethanol/petrol blends in the region of interest for future blending. This could in turn lead to the development of mechanistic models based on physical and chemical interactions between ethanol and the base fuel constituents. Mechanistic models are beyond the scope of the present study, however. In reality, mechanistic models may require more detailed speciation than just the percentages of aromatics, olefins and paraffins and may, as a consequence, be more difficult to use in practice.

Statistical models, on the other hand, provide empirical approximations to physical processes which can be useful to:

(a) understand the relationships between independent variables (base fuel properties and ethanol concentration in this study) and responses (distillation parameters of ethanol/petrol blends in this study) and
(b) predict the performance of future combinations (new ethanol/petrol blends).

5.3.2. Models for a single ethanol concentration

The first step in the statistical modeling process was to use multiple regression techniques to model Delta.E70 (and Delta.E100) at each nominal ethanol concentration (5%, 10%, etc.). Each model would thus be fitted to 60 data points, one for each base fuel, as plotted, for example, in each panel of **Figures 20** and **23**.

A large number of possible models of the generic form:

$$\text{Delta.E70} = a_1 + a_2 \times \text{E70(base)} + a_3 \times \text{E70(base)}^2 + a_4 \times \text{E100(base)} + \ldots + a_n \times \text{DVPE(base)} + a_{n+1} \times \text{Ether(base)} + a_{n+2} \times \text{Aromatics(base)} + \cdots \qquad \text{(Eqn. 3)}$$

or some subset thereof, were fitted to the 60 measured values of Delta.E70 where E70(base), E100(base), DVPE(base), Ether(base), Aromatics(base), … are the measured base fuel properties. In these models, Ether(base) is the total ether concentration (that is, Ether(base) = MTBE(base) + ETBE(base)).

The best of these regression models with 1, 2, 3, … fitted parameters a_k were then investigated further. From these candidates, models were selected that:

- fitted the observed data well (i.e. had low residual mean square errors and high adjusted R^2)
- avoided overfitting (models based on a limited number of terms provide more robust predictors for future blends)
- included similar sets of terms to models fitted to adjacent concentrations
- had fitted parameters (a_2, a_3, etc.) that were all significant at $P < 0.1\%$ (there was no such requirement on the intercept value a_1).

All the selected multiple regression models for Delta.E70 consist of subsets of terms from the following equation:

$$\text{Delta.E70} = A + C \times [\text{E70(base)}]^2 + D \times \text{E70(base)} \times \text{E100(base)} + E \times \text{E100(base)} + G \times \text{E120(base)} + J \times \text{DVPE(base)} + K \times \text{Ether(base)} \qquad \text{(Eqn. 4)}$$

and are listed in **Table 11**. The model for E5 blends is thus:

$$\text{Delta.E70} = 8.12 - 0.00264 \times [\text{E70(base)}]^2 + 0.0804 \times \text{E100(base)} - 0.0313 \times \text{DVPE(base)} - 0.0447 \times \text{Ether(base)}$$

Table 11 Parameters and coefficients for the fitted multiple regression model for Delta.E70 (Eqn.4)

Delta.E70 Model		$[E70(base)]^2$	E70(base) x E100(base)	E100(base)	E120(base)	DVPE(base)	Ether(base)
Coefficient	A	C	D	E	G	J	K
For E5	+8.12	-0.00264	===	+0.0804	===	-0.0313	-0.0447
For E10	+1.88	===	-0.00712	+0.792	-0.164	-0.0688	-0.198
For E15	-0.98	-0.00864	===	+0.911	-0.212	-0.104	-0.290
For E20	-3.21	-0.00946	===	+0.872	-0.167	-0.111	-0.308
For E25	-4.74	-0.00980	===	+0.815	-0.139	-0.108	-0.318

The selected models for Delta.E100 consist of terms from:

$$\text{Delta.E100} = A + B \times \text{E70(base)} + E \times \text{E100(base)} + F \times [\text{E100(base)}]^2 + H \times \text{E150(base)} + J \times \text{DVPE(base)} + K \times \text{Ether(base)} \qquad \text{(Eqn. 5)}$$

and are listed in **Table 12**.

Table 12 Parameters and coefficients for the fitted multiple regression model for Delta.E100 (Eqn. 5)

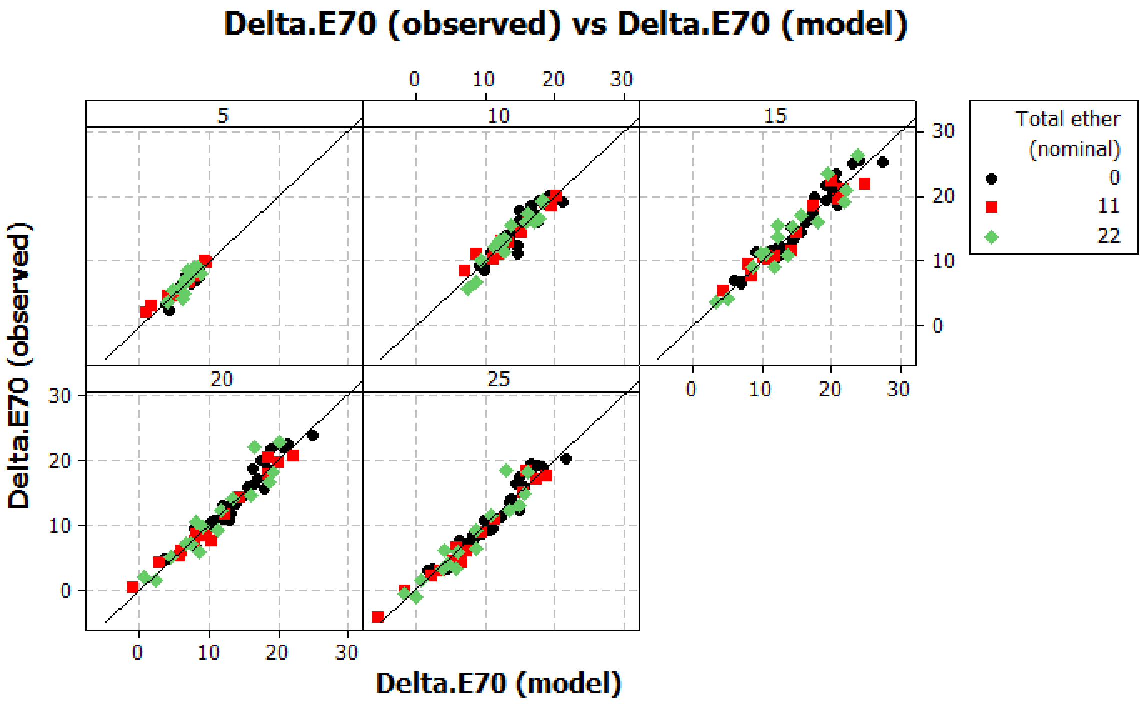
Delta.E100 Model		E70(base)	E100(base)	$[E100(base)]^2$	E150(base)	DVPE(base)	Ether(base)
Coefficient	A	B	E	F	H	J	K
For E5	+9.25	===	-0.192	+0.00107	===	===	+0.0196
For E10	+19.89	===	-0.421	+0.00219	===	+0.0208	+0.0246
For E15	+20.08	+0.0836	-0.371	===	+0.0660	+0.0207	+0.0252
For E20	+24.92	===	-0.385	===	+0.0979	+0.0310	===
For E25	+27.54	===	-0.480	===	+0.1767	+0.0342	===

It should be noted, however, that statistical models are only approximations and, in most cases, there will be no single “correct” model. Indeed, in many cases, there were many possible models that gave a similar quality of fit. It is prudent, therefore, to remember the words of the famous statistician George E.P. Box: “*All models are wrong, some models are useful.*”

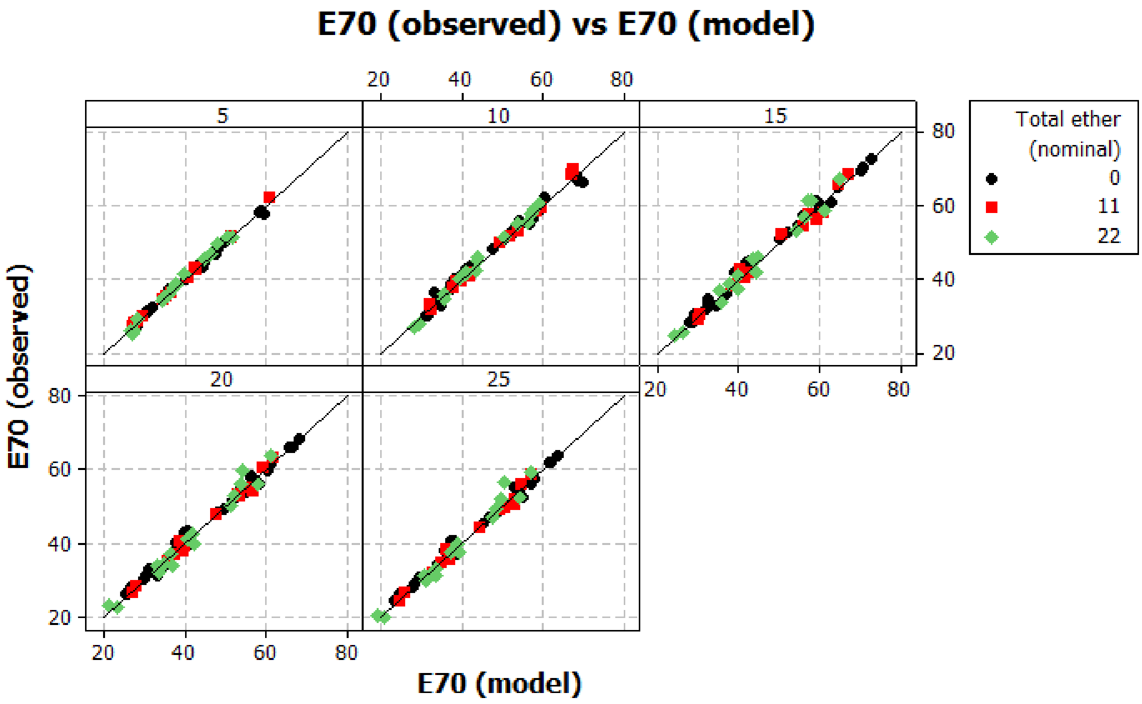
Figures 24 and **25** show the observed values of Delta.E70 and Delta.E100 plotted against those obtained from the models in **Tables 11** and **12**. Also shown are the corresponding observed and modeled values of E70 and E100 themselves. In each case, the fit is excellent.

The chart sheet “y vs EtOH (by fuel)” in the Models Workbook may be used to generate plots of observed and fitted values of Delta.E70 or Delta.E100 against nominal ethanol content. The figures in **Section 5.3.3** provide some examples.

Figure 24 Observed values of Delta.E70 and E70 plotted against the fitted values from the model in Table 11

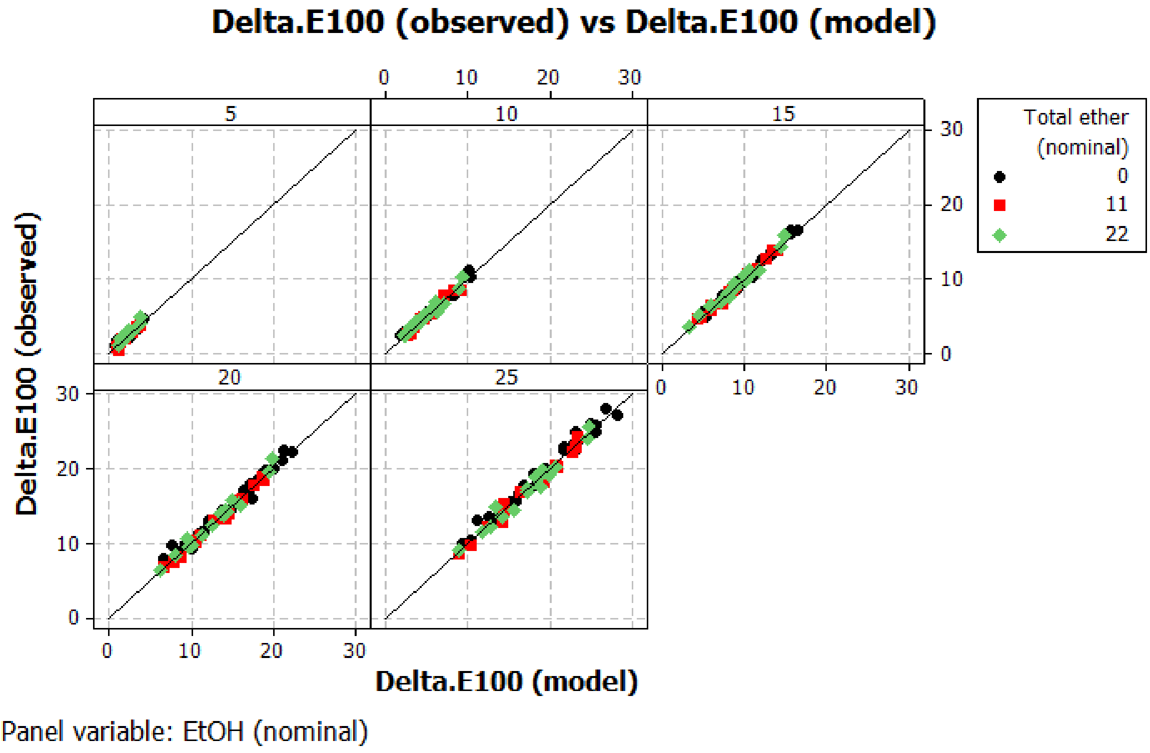

Delta.E70 (observed) vs Delta.E70 (model)

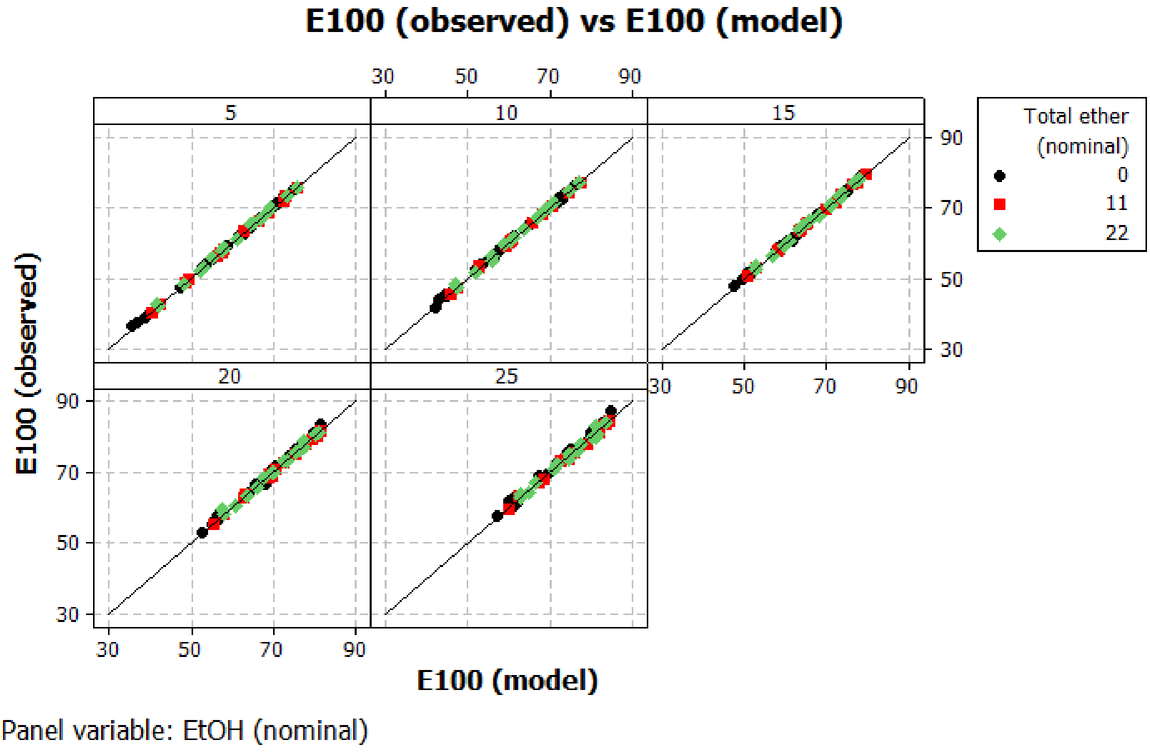
Panel variable: EtOH (nominal)


E70 (observed) vs E70 (model)

Panel variable: EtOH (nominal)

Figure 25 Observed values of Delta.E100 and E100 plotted against the fitted values from the model in Table 12





These models suggest that the relationships between Delta.E70 and Delta.E100 and base fuel distillation properties are quite complex. Each model contains up to three terms in Exxx numbers including terms in E120(base) and E150(base), which were not anticipated at the design stage. Non-linear terms such as $[E70(base)]^2$ and E70(base) x E100(base) also appear.

Such models do involve sets of correlated terms and so need to be properly validated to minimize the risk of overfitting. Thus the residuals (observed minus predicted values) were plotted against both the predicted values and base fuel properties to check that there were no clear patterns indicative of model inadequacy. Each model was also refitted repeatedly, leaving each point in turn out of the training set, to check how well the refitted models predicted the omitted values. The root mean square errors were inflated by no more than 14% indicating that there was not too much deterioration in predictive ability when the models were applied to new blends.

Facilities for fitting the models to new base fuels and blends are provided in the Models Workbook (see **Section 4.3.1** for details).These may not perform as well when extrapolated to base fuels and blends which are markedly different in distillation or composition to those used in this study. Unfortunately, it was not possible to validate satisfactorily against the literature study data [4] because there were too many gaps in the measured model parameters, there were no base fuels containing ether, and there were no ethanol blends containing 25% v/v ethanol.

When applying the models in **Tables 11** and **12**, it should be noted that E5, E10, etc. refer to the splash blending into base gasoline of a particular ethanol stream, including the impurities listed in **Table 6,** at 5:95, 10:90, etc. Adjustments may be needed if the composition of the ethanol stream differs in future gasoline/ethanol blends.

It should also be noted that none of the models in **Tables 11** and **12** have terms in aromatics, olefins, MTBE, or ETBE. These compositional parameters were expected to be important at the design stage. While aromatics, olefins, and separate MTBE and ETBE terms, did occasionally appear in the better models, they were not major factors and there was little consistency between different ethanol concentrations. It may thus be concluded that the distillation of a blend is primarily determined by the distillation properties of the base petrol fuel, the DVPE, and the total ether concentration (if ether is present).

The emergence of this particular set of predictive parameters does have a practical benefit. The absence of aromatics and olefins terms means that the models in **Tables 11** and **12** can be used by fuel blenders without the need to acquire detailed compositional data on the base petrol.

In the literature study [4], blending models were also sought for the Blending E70 and E100 values (B.E70 and B.E100), in addition to the Delta.E70 and Delta.E100 values. **Figures 26** and **27** show B.E70 and B.E100 plotted against E70(base) and E100(base) at each ethanol concentration.

Figure 26 Blending E70 values (B.E70) plotted against base fuel E70 at each ethanol concentration

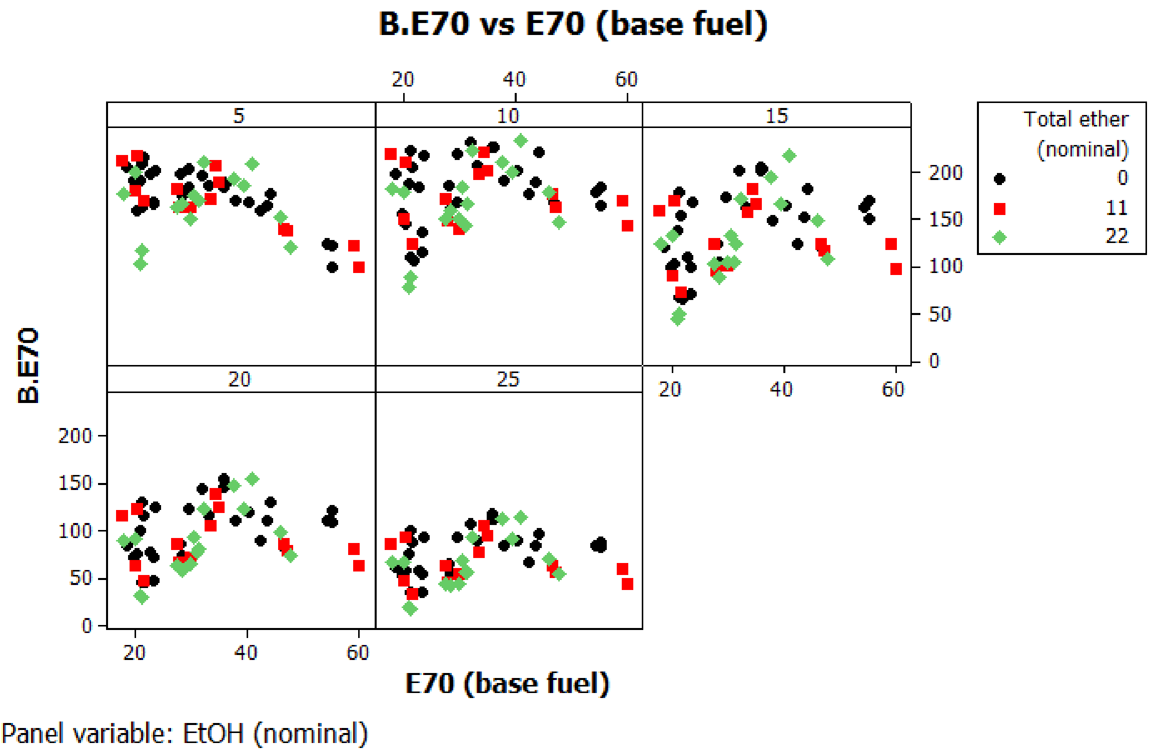
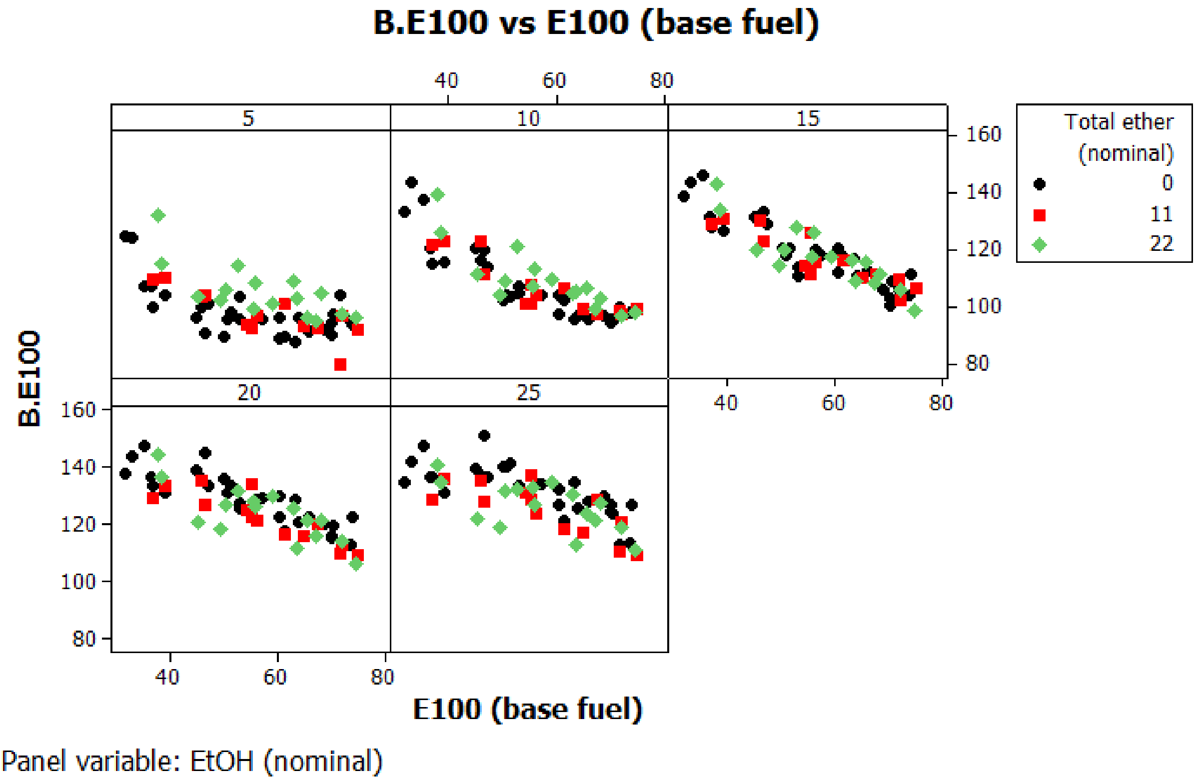


Figure 27 Blending E100 (B.E100) values plotted against base fuel E100 at each ethanol concentration



These figures show broadly similar patterns to those seen previously in **Figures 20 and 23**, which is not too surprising because:

B.E70 = E70(base) + Delta.E70 / [EtOH] (Eqn. 6)

where the ethanol fraction [EtOH] (0.05, 0.10, etc.) is a constant when considered at a single ethanol concentration. If ethanol blending were a simple linear-by-volume process, then one would expect B.E70 to be 0% and B.E100 to be 100%, which is clearly not the case.

To examine this more closely, **Table 13** shows the models in **Table 11** reformulated as models for B.E70 by substituting Eqn. 4 in Eqn. 6 above. Similarly **Table 14** shows the models in **Table 12** rewritten as models for B.E100. The chart sheet “y vs EtOH (by fuel)” in the Models Workbook may be used to generate plots of observed and fitted values of B.E70 or B.E100 against nominal ethanol content.

Table 13 Multiple regression model in Table 11 reformulated as a model for B.E70

B.E70 Model		E70(base)	[E70(base)]^2	E70(base) x E100(base)	E100(base)	E120(base)	DVPE(base)	Ether(base)
Coefficient	A	B	C	D	E	G	J	K
For E5	+162.4	+1.0	-0.0528	===	+1.61	===	-0.626	-0.89
For E10	+18.8	+1.0	===	-0.0712	+7.92	-1.64	-0.688	-1.98
For E15	-6.5	+1.0	-0.0576	===	+6.07	-1.42	-0.695	-1.93
For E20	-16.1	+1.0	-0.0473	===	+4.36	-0.84	-0.554	-1.54
For E25	-19.0	+1.0	-0.0392	===	+3.26	-0.55	-0.431	-1.27

Table 14 Multiple regression model in Table 12 reformulated as a model for B.E100

B.E100 Model		E70(base)	E100(base)	[E100(base)]^2	E150(base)	DVPE(base)	Ether(base)
Coefficient	A	B	E	F	H	J	K
For E5	+184.9	===	-2.84	+0.0213	===	===	+0.392
For E10	+198.9	===	-3.21	+0.0219	===	+0.208	+0.246
For E15	+133.9	+0.56	-1.47	===	+0.44	+0.138	+0.168
For E20	+124.6	===	-0.93	===	+0.49	+0.155	===
For E25	+110.2	===	-0.92	===	+0.71	+0.137	===

In the literature study [4], the following models were derived for B.E70 and B.E100:

B.E70 = 289 – 754 x [EtOH] – 0.384 x E70(base) (Eqn.7)

B.E100 = 142 + 247 x [EtOH] – 1.066 x E100(base) (Eqn.8)

where [EtOH] is the ethanol content expressed as a fraction between 0 and 1. These models were derived from measurements on a number of blends with ethanol concentrations between 1% and 22% v/v (0.01 and 0.22) and could be applied to blends at any concentration in this range.

Figures 28 and **29** show how well these models fit the data generated in the current blending study.

Figure 28 Observed values of E70 plotted against predicted values using Eqn.7 as described in the literature study [4].

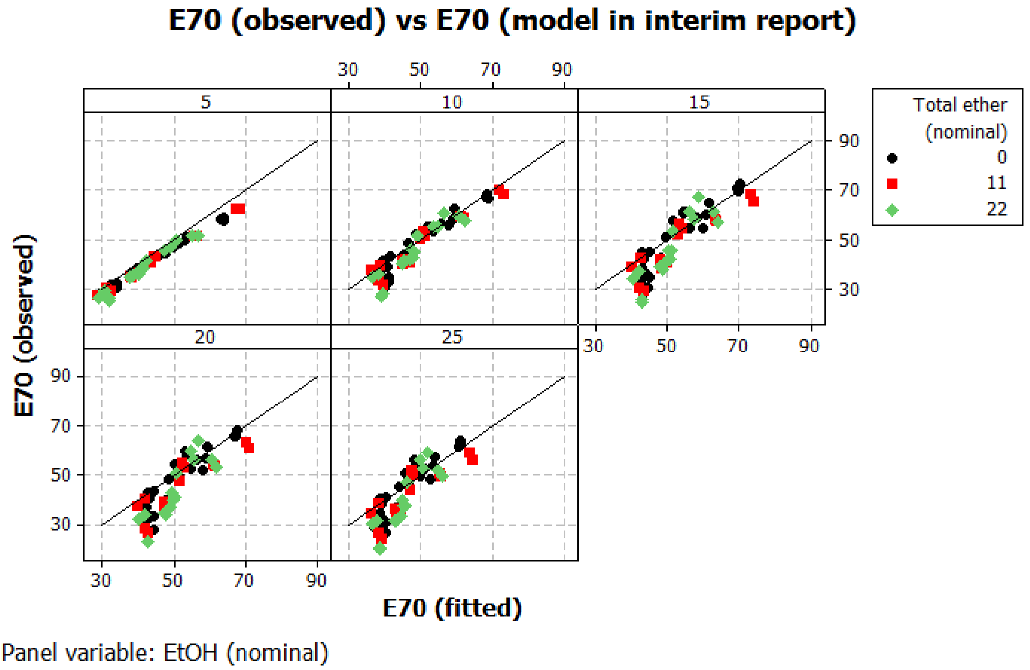
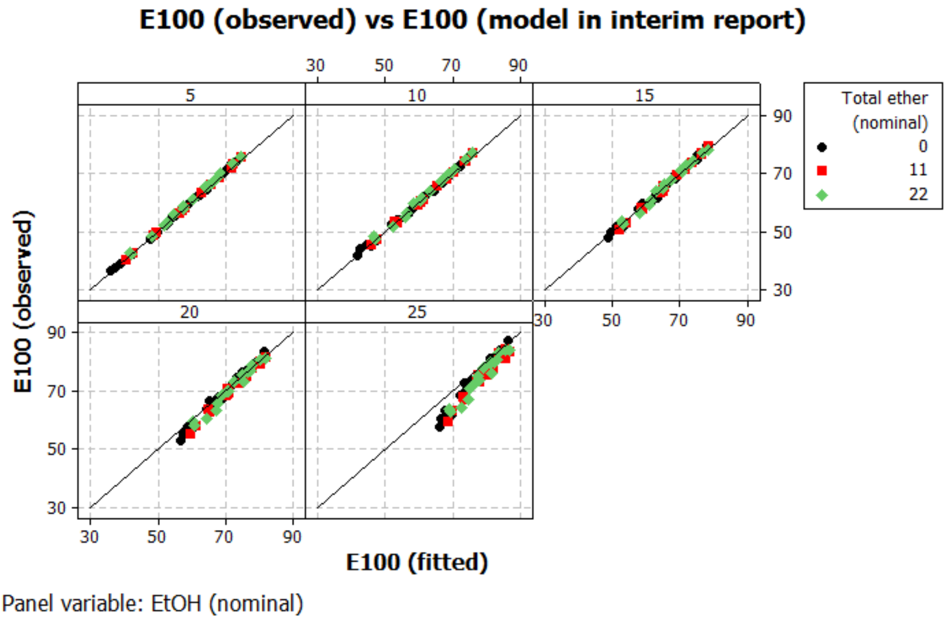


Figure 29 Observed values of E100 plotted against predicted values using Eqn.8 as described in the literature study [4].



The earlier B.E70 model (Eqn.7) does not fit the new blending data especially well. Refitting this model to the new data leads to the following equation:

$$B.E70 = 204 - 649 \times [EtOH] + 0.844 \times E70(base) \qquad \text{(Eqn.9)}$$

which represents a series of equally spaced parallel lines, as shown in **Figure 30**. This produces a most unsatisfactory fit failing to capture the nonlinearity. The sign of the E70(base) term is also reversed compared to the same term in Eqn.7. In fact, the fit of the earlier model to the literature study data was far from perfect and it was clear from **Figure 13a** in [4] that B.E70 would not be accurately modeled by a series of equally spaced parallel lines.

Figure 30 B.E70 versus the base fuel E70 at each ethanol concentration. The black lines show the fits based on Eqn.9.

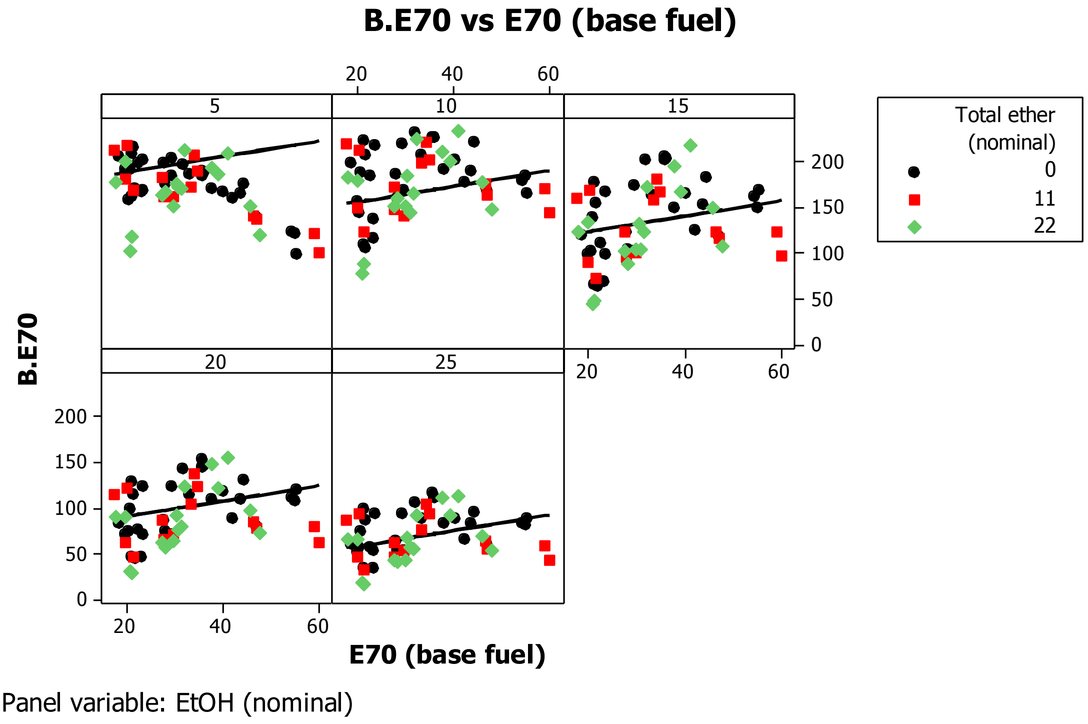


Figure 31 B.E100 versus the base fuel E100 at each ethanol concentration. The black lines show the fits based on Eqn.10.

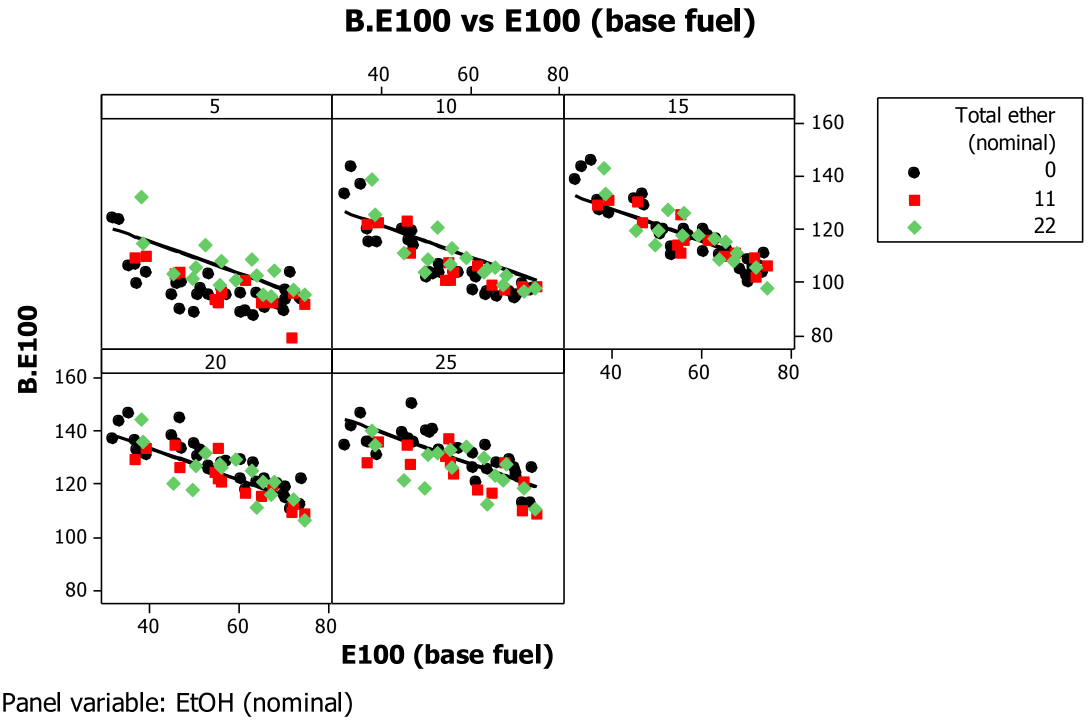


Figure 29 shows that while the earlier B.E100 model (Eqn.8) does fit the new E5, E10 and E15 data quite well, it over-estimates E100(blend) at 25% v/v ethanol and to a lesser extent at 20% v/v ethanol. This could be because there were few E20 blends and no E25's in the literature data used as the training set used for the earlier model. Using the nominal [EtOH] values of 0.20 and 0.25 when evaluating the model may also lead to bias because many of the values in the literature data set were measured concentrations of undiluted ethanol.

Refitting Eqn.8 to the new blending data leads to the following equation:

$$\text{B.E100} = 133 + 122 \times [\text{EtOH}] - 0.594 \times \text{E70(base)} \qquad \text{(Eqn.10)}$$

as shown in **Figure 31**. While this produces a better fit than Eqn.9 did for B.E70, it still fails to capture the nonlinearity. There is also some bias at E5 and E10 with the values of B.E100 being over-predicted in most cases.

5.3.3. Models for any ethanol concentration

Cross-concentration models are needed in order to estimate E70 and E100 at ethanol concentrations in between the designed values of 0%, 5%, 10%, etc. Simple linear interpolation between fitted values of Delta.E70 or B.E70 at different ethanol concentrations is not recommended due to the nonlinear responses observed in **Figures 20** and **26**. The nonlinearity in these figures is not as severe for Delta.E100 and B.E100 but could still cause bias, particularly at lower ethanol concentrations where the patterns tend to be more concave (**Figures 23** and **27**).

In view of the inadequacies of the models in the literature study [4], better models were sought for Delta.E70 and Delta.E100 (or for B.E70 and B.E100) that would be applicable at any ethanol concentration. In the first instance, models of the generic form:

$$\text{Delta.E70 (or B.E70)} = b_1 + b_2 \times [\text{EtOH}] + b_3 \times \text{E70(base)} + b_4 \times \text{E70(base)}^2 + b_5 \times \text{E100(base)} + \ldots + b_n \times \text{DVPE(base)} + b_{n+1} \times \text{Ether(base)} + \ldots + b_{n+2} \times [\text{EtOH}] + b_{n+3} \times [\text{EtOH}] \times \text{E70(base)} + b_{n+4} \times [\text{EtOH}] \times \text{E70(base)}^2 + b_{n+5} \times [\text{EtOH}] \times \text{E100(base)} + \ldots \qquad \text{(Eqn.11)}$$

or some subset thereof, were fitted where [EtOH] is the designed ethanol fraction (i.e., 0.05, 0.10, etc.) ignoring denaturants and other impurities and where E70(base), E100(base), DVPE(base), Aromatics(base), Ether(base), etc. are the measured base fuel properties. The use of designed rather than measured ethanol concentrations aids both the analysis and eases the application of these equations by the end user.

Such models must be fitted using a "generalized least squares" approach [8]. A large number of possible models of the above form were fitted to the 300 measured values of Delta.E70 (and Delta.E100) but none were found to be entirely satisfactory.

It is difficult to formulate simple equations which encapsulate the full complexity of the modeling problem and allow deltas or blending numbers to be estimated for blends at intermediate ethanol concentrations. To obtain reasonable fits at all concentrations, more convoluted model forms must be considered.

The following model for Delta.E70 is just one of the many possible empirical equations one might derive:

$$\text{Delta.E70} = 1.38 + 26.0 \times \text{Fcn1}([\text{EtOH}]) + 0.601 \times \text{E100(base)} - 1.44 \times \text{Fcn1}([\text{EtOH}]) \times \text{E100(base)} - 0.612 \times \text{Fcn2}([\text{EtOH}]) \times \text{DVPE(base)} - 1.069 \times \text{Fcn2}([\text{EtOH}]) \times \text{Ether(base)} - 0.0282 \times \text{Fcn2}([\text{EtOH}]) \times \text{E70(base)}^2 \qquad \text{(Eqn.12)}$$

where:

- $\text{Fcn1}([\text{EtOH}]) = \exp(-18.73 \times [\text{EtOH}])$
- $\text{Fcn2}([\text{EtOH}]) = \sqrt{(0.0762 + [\text{EtOH}])} - \sqrt{(0.0762)}$

Note that the ethanol concentration [EtOH] is expressed as a number between 0 and 1 in Eqns. 12 to 15 while the Ether(base) term is the measured concentration of pure ethers (MTBE + ETBE) in the base fuel, expressed in units of % v/v, and thus is a number between 0 and 22.

While Delta.E100 is more predictable than Delta.E70, a complex equation is still needed to obtain a reasonable fit to the experimental data:

$$\text{Delta.E100} = 0.414 - 0.0129 \times \text{Fcn3}([\text{EtOH}]) + 1273 \times \text{Fcn4}([\text{EtOH}]) - 2.00 \times [\text{EtOH}] \times \text{E100(base)} + 0.157 \times [\text{EtOH}] \times \text{DVPE(base)} + 3.00 \times [\text{EtOH}]^2 \times \text{E150(base)} \qquad \text{(Eqn.13)}$$

where:

- $\text{Fcn3}([\text{EtOH}]) = \exp(22.8 \times [\text{EtOH}])$
- $\text{Fcn4}([\text{EtOH}]) = 1 - \exp(-0.098 \times [\text{EtOH}])$

Eqns. 12 and 13 suffer from the imperfection that they do not pass through the origin, that is to say they do not predict a zero delta when no ethanol is added. We were unable to find equations meeting this constraint which fitted the observed Delta.E70 and Delta.E100 data sufficiently well. For this reason, Eqns. 12 and 13 should not be used for ethanol concentrations outside of the 5% to 25% v/v ethanol concentration range (0.05 to 0.25 for [EtOH]).

Because Delta.E70 must be zero at an ethanol concentration of zero, the linear interpolation formula:

$$\text{Delta.E70}([\text{EtOH}]=c) = c \times \text{Delta.E70}([\text{EtOH}]=0.05) / 0.05 \qquad \text{(Eqn.14)}$$

can be used to obtain estimates of Delta.E70 at ethanol concentrations between c = 0 and c = 0.05 (0 to 5% ethanol) where Delta.E70([EtOH]=0.05) is the estimated value of Delta.E70 at 0.05 (5%) ethanol from Eqn.12 above. However, because most of the observed Delta.E70 vs [EtOH] responses were nonlinear, the quadratic interpolation formula:

$$\text{Delta.E70}([\text{EtOH}]=c) = c \times (0.1 - c) \times \text{Delta.E70}([\text{EtOH}]=0.05) / 0.0025 + c \times (c - 0.05) \times \text{Delta.E70}([\text{EtOH}]=0.10) / 0.005 \qquad \text{(Eqn.15)}$$

will probably give better predictions. This takes into account additionally the estimated value at 10% v/v ethanol. Similar formulae can be used for Delta.E100.

Figures 32 and **33** show the measured values of Delta.E70 and Delta.E100 plotted against those obtained from Eqns. 12 and 13 above. Also shown are the corresponding observed and modeled values for E70 and E100 themselves. In each case, the fit is rather less good than that seen for the models in **Tables 11** and **12** in **Figures 23** and **24**. Eqns. 12 and 13 are coarser than those fitted at individual concentrations and are lacking in less important terms such as E120(base) for Delta.E70 and Ether(base) for Delta.E100. However, there is little evidence of any serious tendency to over- or under-predict except perhaps at higher Delta.E70 values at higher ethanol concentrations.

Eqns. 12 and 13 can be rewritten as blending models (B.E70 and B.E100) as follows:

$$\text{B.E70} = \text{E70(base)} + 1.38 / [\text{EtOH}] + 26.0 * \text{Fcn1}([\text{EtOH}]) / [\text{EtOH}] + 0.601 \times \text{E100(base)} / [\text{EtOH}] - 1.44 \times \text{Fcn1}([\text{EtOH}]) \times \text{E100(base)} / [\text{EtOH}] - 0.612 \times \text{Fcn2}([\text{EtOH}]) \times \text{DVPE(base)} / [\text{EtOH}] - 1.069 \times \text{Fcn2}([\text{EtOH}]) \times \text{Ether(base)} / [\text{EtOH}] - 0.0282 \times \text{Fcn2}([\text{EtOH}]) \times \text{E70(base)}^2 / [\text{EtOH}] \qquad \text{(Eqn.16)}$$

$$\text{B.E100} = -1.00 \times \text{E100(base)} + 0.414 / [\text{EtOH}] - 0.0129 \times \text{Fcn3}([\text{EtOH}]) / [\text{EtOH}] + 1273 \times \text{Fcn4}([\text{EtOH}]) / [\text{EtOH}] + 0.157 \times \text{DVPE(base)} + 3.00 \times [\text{EtOH}] \times \text{E150(base)} \qquad \text{(Eqn.17)}$$

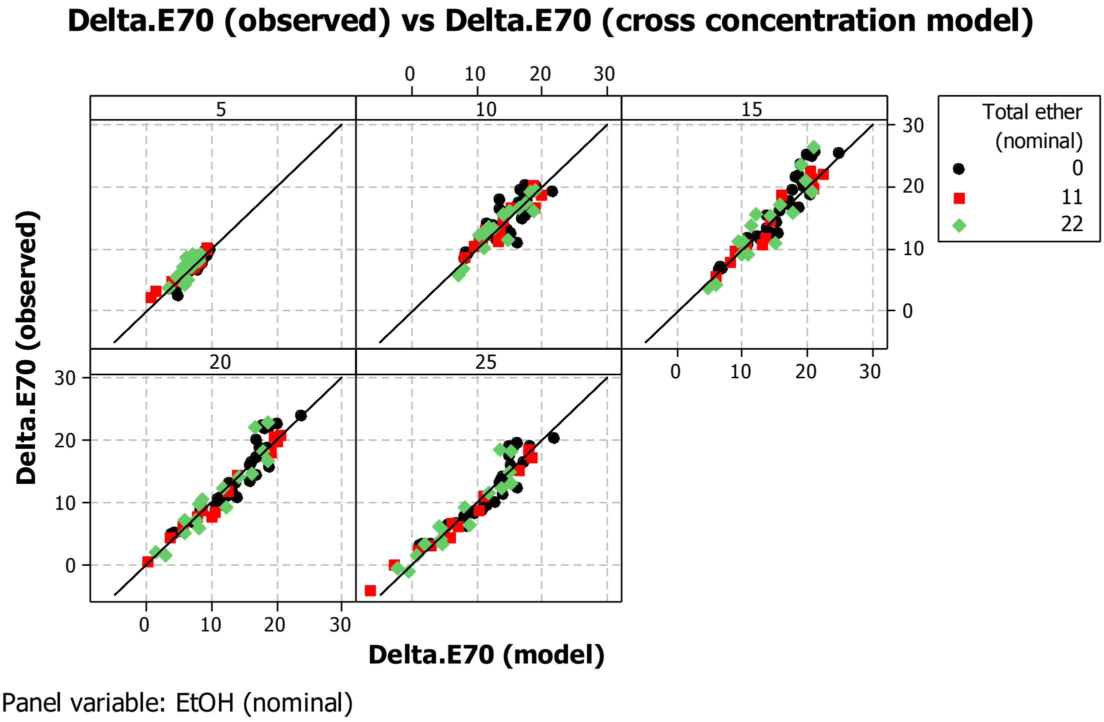
Again, Eqns.16 and 17 must not be used for ethanol concentrations outside of the 5% to 25% v/v ethanol range (0.05 to 0.25 for [EtOH]). Unlike Delta.E70 and Delta.E100, the blending numbers B.E70 and B.E100 are not well defined at ethanol concentrations lower than 5% because Eqn.6 requires a division by very small values of [EtOH]. Therefore, B.E70 and B.E100 values should not be inferred from this study for ethanol fractions less than 5% v/v ethanol (0.05 [EtOH]).

The chart sheet “y vs EtOH (by fuel)” in the Models Workbook may be used to generate plots of observed and fitted values of Delta.E70, Delta.E100, B.E70 or B.E100 against nominal ethanol content using the cross-concentration models (Eqns 12-13, 16-17, red lines) and the models fitted at the five fixed concentrations (Tables 11-14, red squares). Examples are shown in **Figures 34 and 35**. In most cases, the cross concentration models fit not quite as well as those fitted at fixed concentrations.

The user can choose whether to use linear or quadratic interpolation between 0% and 5%. Quadratic interpolation seems to perform better in most cases except perhaps for Delta.E70 and Base Fuel 6 where it causes negative values to appear.

In Eqns.12-13 and 16-17, [EtOH] represents the nominal volumetric fraction of an impure ethanol stream blended into the base fuel. Adjustments may need to be made if the models are to be used for blends of petrol when using ethanol streams of different purity levels. The Ether(base) term in Eqns.12 and 16 on the other hand, (also in the models in **Tables 11** to **14)**, is the sum of the measured ETBE and MTBE concentrations in the base fuel. These differ from the nominal 0, 11 and 22% v/v values and can be complicated further if the two ether components have different purity levels (see **Table 7**). Therefore, estimates of the total concentration of pure ethers in the base fuel should be used when applying these equations to new blends.

Figure 32: Observed values of Delta.E70 and E70 plotted against the modeled values from Eqn.12 at each ethanol concentration



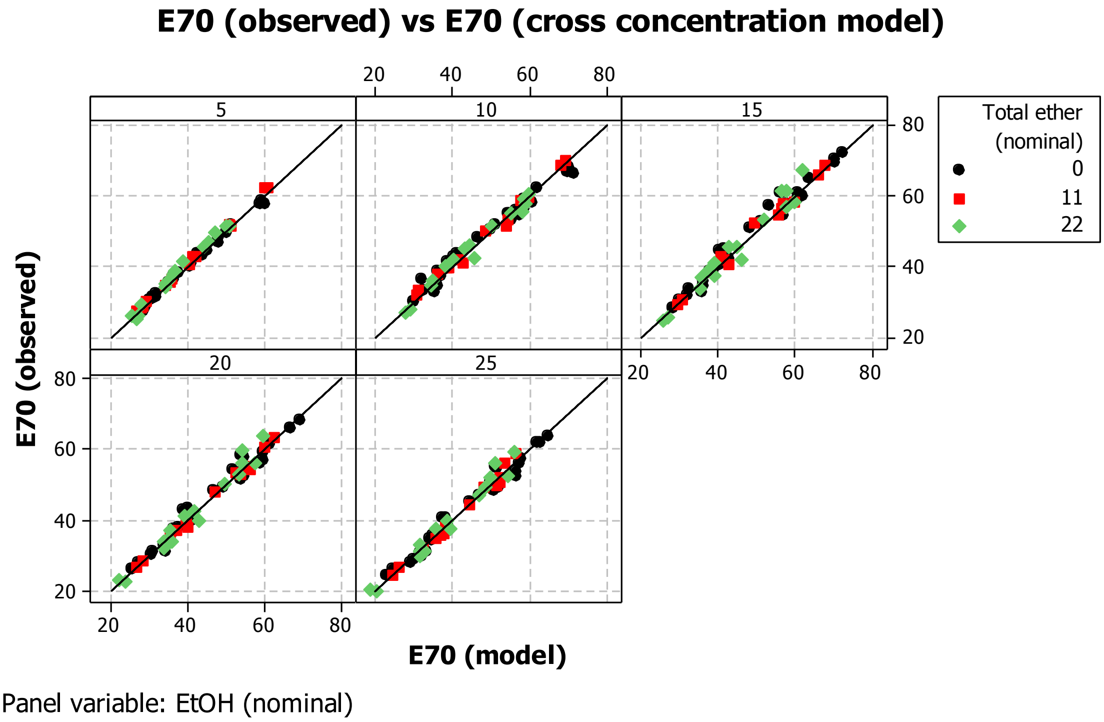
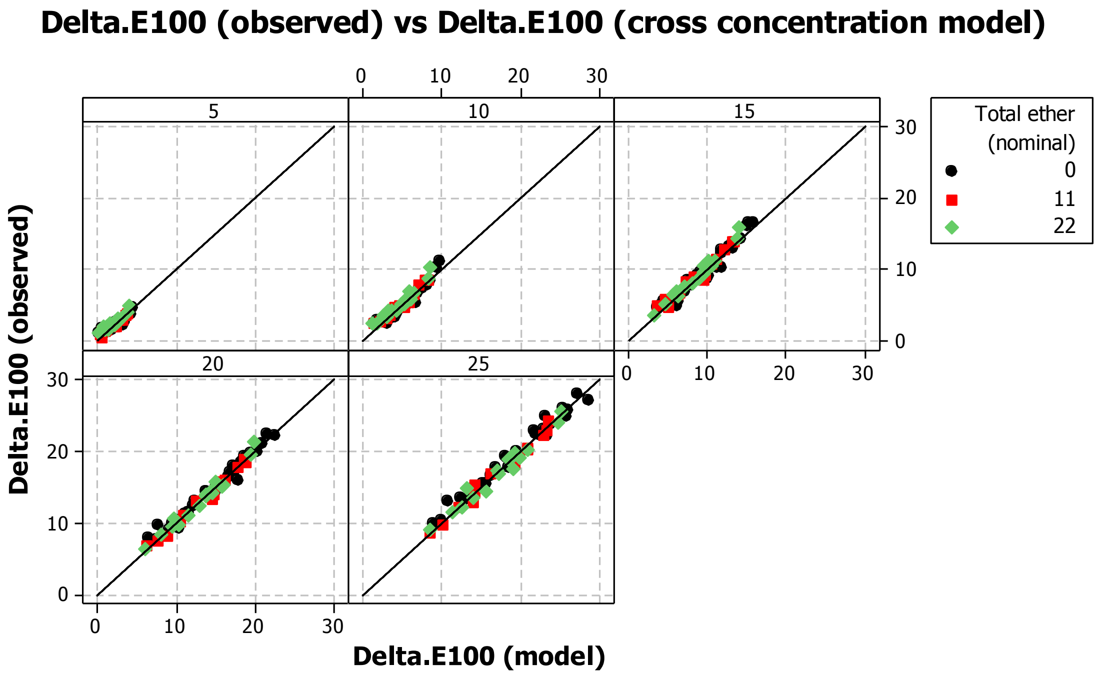
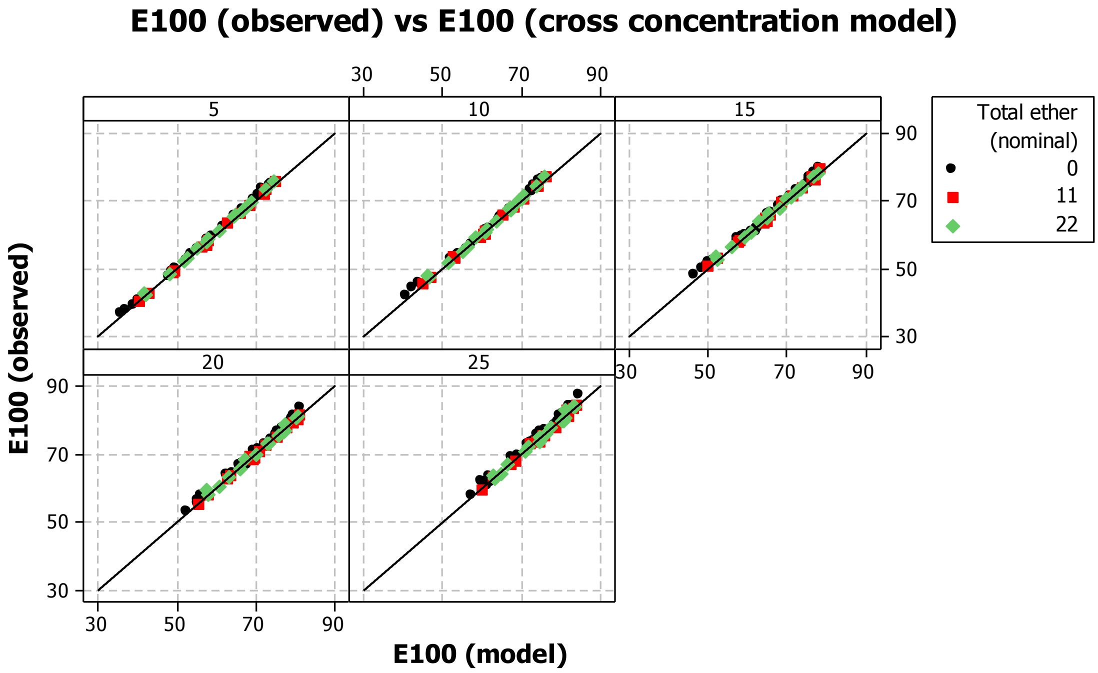


Figure 33: Observed values of Delta.E100 and E100 plotted against the modeled values from Eqn.13 at each ethanol concentration

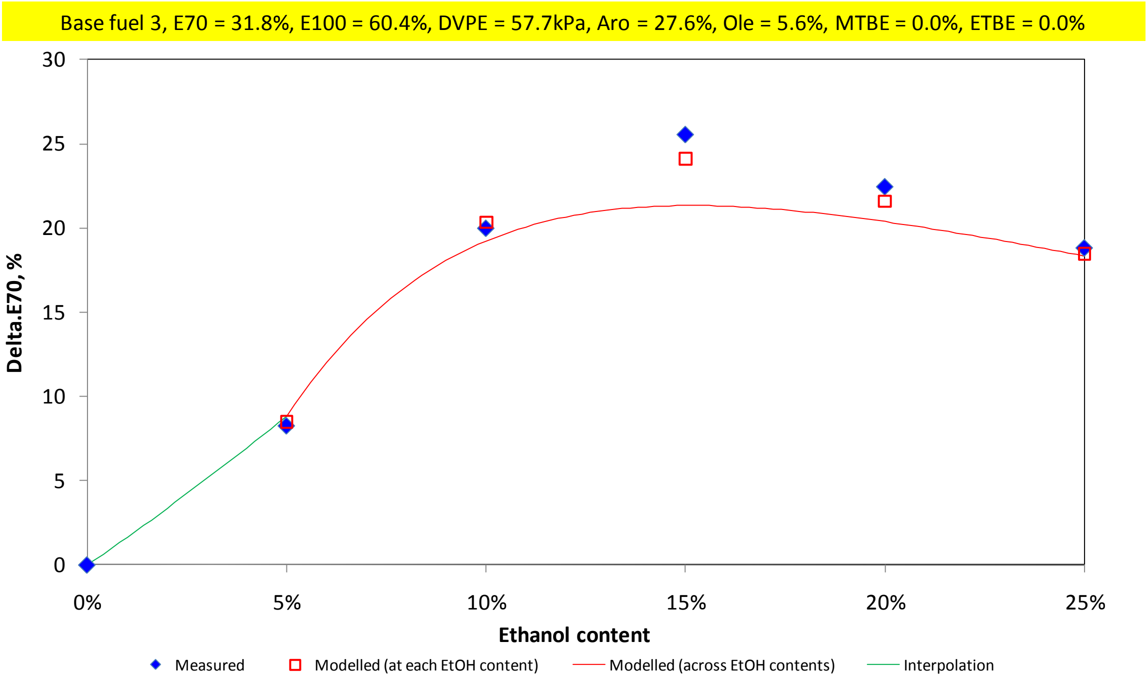

Delta.E100 (observed) vs Delta.E100 (cross concentration model)

Panel variable: EtOH (nominal)


E100 (observed) vs E100 (cross concentration model)

Panel variable: EtOH (nominal)

Figure 34: Measured and fitted values of Delta.E70 from Table 11 (red squares) and Eqn 12 (red line) versus the designed ethanol concentration for Base Fuels 3 (top) and 8 (bottom)



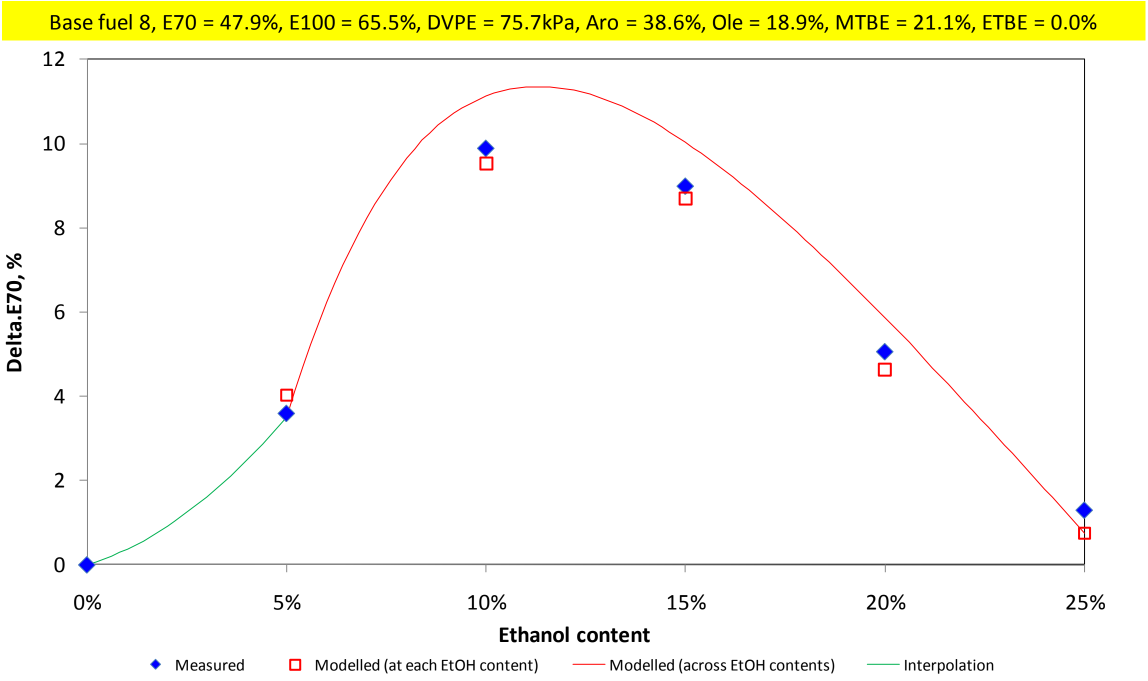
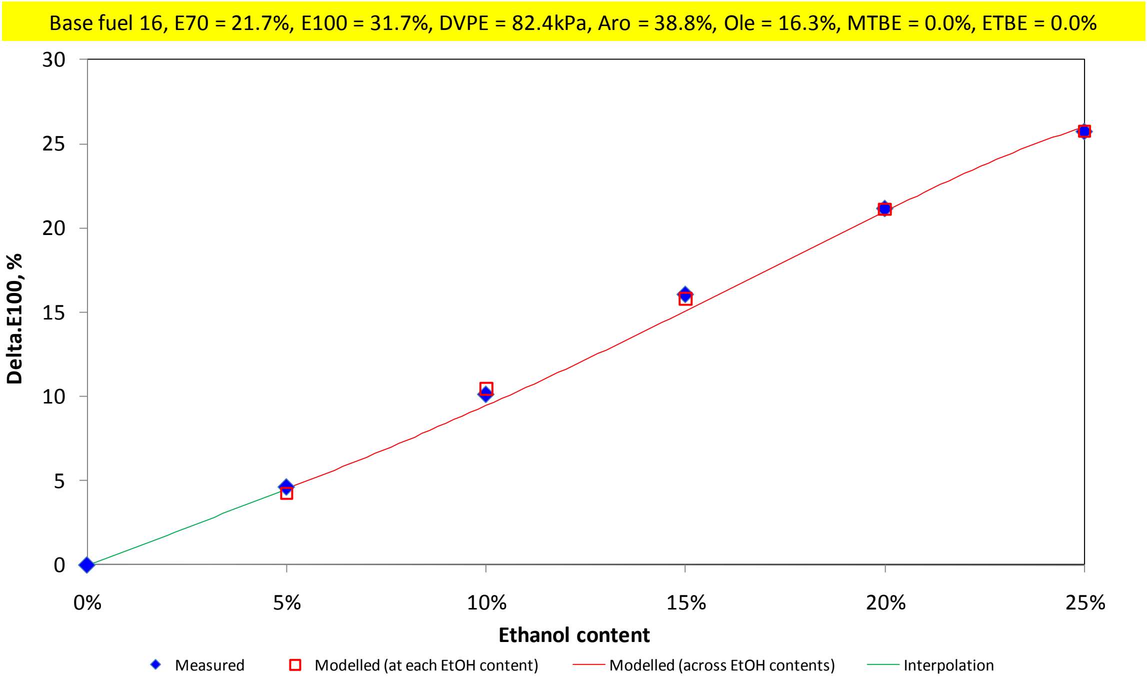
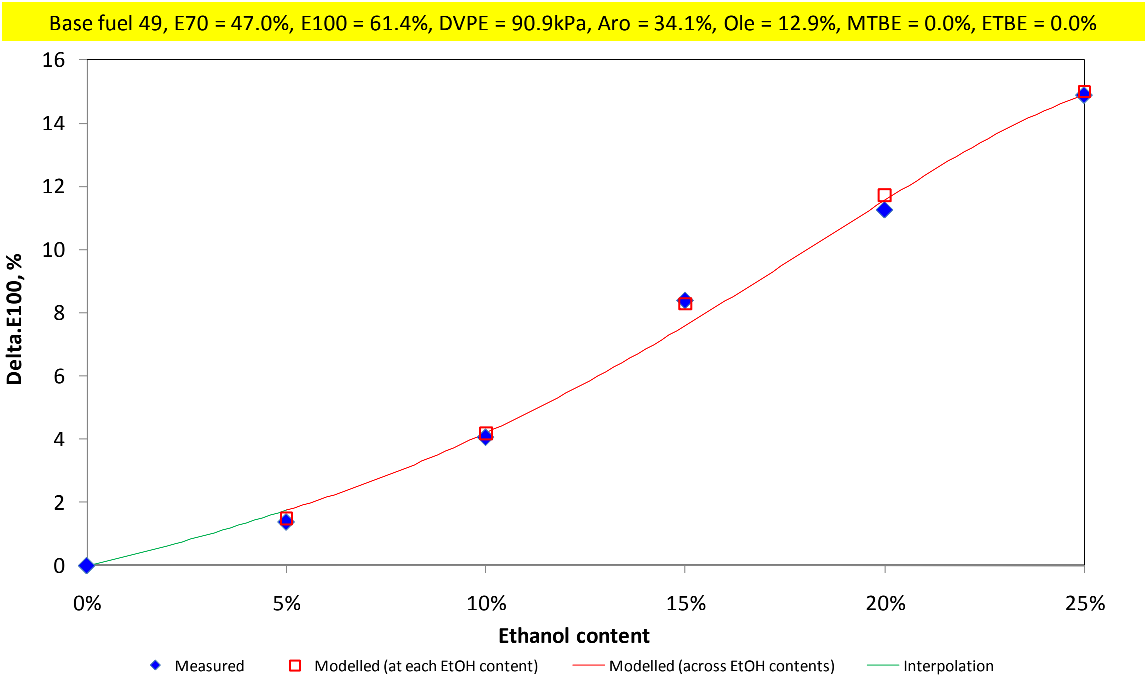


Figure 35: Measured and fitted values of Delta.E100 from Table 12 (red square) and Eqn 13 (red line) versus the designed ethanol concentration for Base Fuels 16 (top) and 49 (bottom)





5.4. BEP525 Study Results: Overall Conclusions

In this study, 60 base petrols were blended from refinery and chemical streams using a statistically designed fuel matrix. Ethanol was splash-blended into each of these base fuels at five concentrations between 5 and 25% v/v and two types of ether (MTBE and ETBE) at three different concentrations (0, 11, and 22% v/v) were used. The samples were consistently handled and analyzed using good analytical and statistical practices in order to ensure against experimental variability and bias.

The subsequent fuel blends were characterized by changes in distillation properties (DVPE and volatility parameters) and by changes in composition associated with ethanol blending. The results of these tests were modeled in order to derive preliminary predictive models for volatility parameters of interest, such as Delta.E70, B.E70, Delta .E100, and B.E100.

Compared to the results obtained on ethanol/petrol blends reported in the published literature [4], the variation in Delta.E70 in this blending study was larger and spanned a wider range. Furthermore, predictive models for these parameters were more complicated than those fitted to the literature study results and their applicability was restricted to the designed range of ethanol concentrations (although Delta.E70 and Delta.E100 could be estimated at ethanol concentrations between 0% and 5% by linear or quadratic interpolation). There was very little evidence that the molecular composition *per se* of the base fuel (such as the concentrations of aromatics, olefins, ethers, etc.) had a major impact on the volatility results.

It should be stressed, however, that the predictive models included in this report represent a starting point for modeling these results, and not an ending point. It is our expectation that additional work can be done using these data to unravel interesting dependencies and more fundamentally-based explanations for the behavior of ethanol/petrol volatility with ethanol concentration and base fuel properties.

6. Effect of Ethanol on Environmental Performance[11]

The addition of ethanol into petrol has the potential to impact environmental performance in several ways, including:

- Changes to vehicle exhaust and evaporative emissions to the atmosphere and their corresponding impact on air quality;
- The contamination of soil or groundwater from spills of ethanol or of petrol containing ethanol;
- The energy efficiency of vehicles fuelled with petrol containing different concentrations of ethanol;
- Overall greenhouse gas emissions from ethanol production and use.

Since these areas are quite broad, this assessment has focused primarily on recent published studies (1990 onwards) that highlight the effect of ethanol on vehicle exhaust and evaporative emissions and atmospheric reactivity. As such, the analyzed information should be considered to be a preliminary, and not comprehensive, assessment of all published literature.

The evaluated studies are not comprehensive but cover sufficient studies to infer directional trends due to the impact of ethanol. A 'weight of evidence' approach was used to draw conclusions on this literature based on the relative change in performance between hydrocarbon-only petrol and ethanol/petrol blends containing less than about 20% v/v ethanol. That is, general trends have been inferred from the relative changes in emissions from published studies even though the absolute emissions levels and details regarding the vehicles, fuels, and driving cycles may be different from one study to another. A more detailed assessment is presented in **Appendix 6** and a summary is provided next in **Section 6.1**.

6.1. Summary

The detailed assessment included in **Appendix 6** focuses primarily on the effect of ethanol in petrol on vehicle emissions and on the atmospheric environment. The results of published studies have been evaluated related to the following topics:

- Regulated exhaust emissions, including carbon monoxide, hydrocarbons, oxides of nitrogen (NOx), particulate matter (PM), and particle number (PN)[12];
- Unregulated exhaust emissions, including benzene, various aldehydes, and 1,3-butadiene;
- Evaporative emissions of ethanol and volatile organic compounds (VOCs) from the vehicle's fuel system;
- Atmospheric reactions and ozone-forming potential; and
- Tank-to-Wheels (TTW) CO_2 emissions.

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[11] The references to all the studies mentioned in **Section 6** can be found in **Section 15.7** of **Appendix 6**.

[12] PN emissions are considered to be a regulated exhaust emission even though they will not be included in European emissions regulations until 2012 for light-duty diesel vehicles.

A more detailed assessment would be required to capture the conclusions from all literature studies on the impact of ethanol on environmental performance.

6.1.1. Regulated Exhaust Emissions

The quantitative measurement of hydrocarbons from vehicles is a complicated and specialized task because there are a wide range of hydrocarbons emitted. European legislation requires these to be measured as Total Hydrocarbons (THC) while, in the USA, they are regulated as Non-Methane Organic Gases (NMOG). The NMOG measurement does not include methane which can be a substantial part of total HC exhaust emissions. Hence, European and US emissions standards are not directly comparable.

The main effect of ethanol on engine operation is to make the air/fuel ratio (AFR) of the mixture leaner. This is because the oxygen in the ethanol (or other oxygenate) molecule increases the oxygen concentration in the air/fuel mixture. A 10% v/v ethanol/petrol blend contains about 3.7% m/m oxygen which can change the AFR. The effect, however, depends on the sophistication of the engine technology which has been defined below in four different categories[13] and shown in **Figure 36**:

Category 1: Older engines without exhaust aftertreatment catalysts that operated with fixed calibration carburettors or simple fuel injection systems. These engines run significantly leaner at all conditions on ethanol/petrol blends.

Category 2: First-generation '3-way catalyst' systems equipped with an oxygen sensor and a rudimentary engine management system (EMS). The AFR was typically controlled to stoichiometric during normal running conditions. (Stoichiometric control is necessary in order for the 3-way catalyst to simultaneously control the emissions of CO, HC, and NOx.) Because the EMS exactly controls the AFR, the presence of ethanol in the petrol is not expected to have a leaning effect on the AFR.

Under cold-starting conditions, however, the EMS does not operate and the engine intentionally runs rich (more fuel than normally required) to ensure good driveability performance until the engine and catalyst are fully warmed up. Thus, the leaning effect of ethanol on the AFR does occur during cold-starting and warm-up conditions. This is beneficial since the highest exhaust emissions will occur before the 3-way catalyst becomes fully warmed-up and operational.

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[13] These categories do not represent industry-accepted terms but are used in this section to clarify the impact of ethanol/petrol blends on different vintages of engine/vehicle technology.

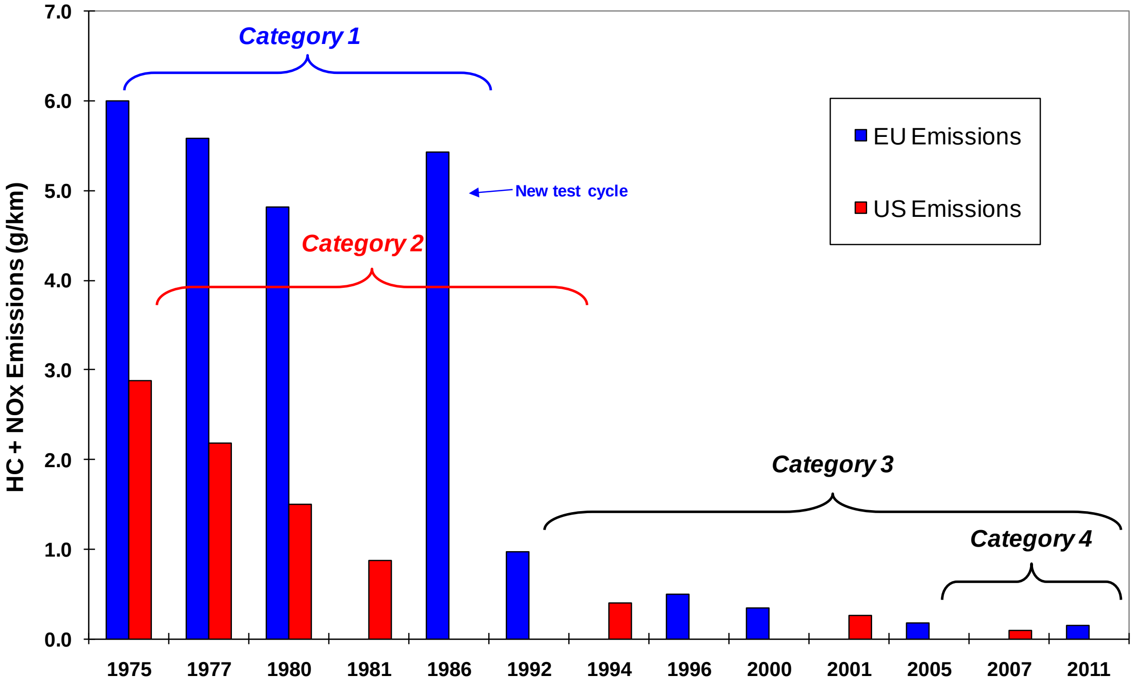
Category 3: Modern engines having a Multi Point Fuel Injection (MPFI) system, complex EMS, and more sophisticated exhaust aftertreatment systems. In this category, the EMS includes “adaptive learning” where the control system slowly “learns” the stoichiometric AFR of the fuel in the tank and corrects for changes during subsequent operation, including cold starts. The primary input to the EMS is the oxygen sensor in the exhaust system that informs the EMS of the actual engine-out combustion mixture. Thus, these modern systems are not expected to be sensitive to the presence of ethanol in the petrol but this is not always the case.

Category 4: The latest engine technology is Gasoline Direct Injection (GDI, also Direct Injection Spark Ignition (DISI)) where fuel is injected directly into the cylinder rather than into the inlet manifold. This approach provides less time for vaporisation of the injected fuel mixture and very sophisticated EMS with adaptive learning are used. Of course, the exhaust aftertreatment system is also quite sophisticated and fully optimized to the engine and vehicle design in order to achieve the desired emissions level.

There are usually considered to be two generations of GDI engines that depend on how the injected air/fuel mixture is guided toward the spark plug for ignition. In the first generation approaches, the air/fuel mixture is typically guided to the spark plug by means of a specially designed piston bowl (so-called ‘wall-guided’) or by a combination of the piston bowl design and intake port (so-called ‘air-guided’). Second generation approaches (so-called ‘stratified charge’) inject the air-fuel mixture into the top of the combustion chamber and directed toward the spark plug. In this approach, the air/fuel mixture is richer near the spark plug and leaner near the combustion wall. Most GDI engines today use first generation approaches although the more complicated second generation approaches are starting to appear on some higher-end vehicles. Because of their design features, first generation approaches are not expected to be very sensitive to ethanol while there is not yet enough data available on second generation GDI engines.

The effect of ethanol in petrol on the **regulated exhaust emissions** from vehicles strongly depends on the sophistication of engine and aftertreatment (catalyst) technologies (see also **Appendix 6**). For example, for non-catalyst vehicles (Category 1), ethanol substantially reduces the CO emissions with smaller reductions in HC emissions. At the same time, ethanol substantially increases the NOx emissions in these vehicles compared to a similar hydrocarbon-only petrol.

Figure 36: Comparison of EU and US regulated emission limits for light-duty petrol vehicles from 1975 to 2005



For early catalyst vehicles (Category 2) tested on ethanol/petrol blends, similar percentage changes in emissions have been reported. In general, CO emissions are reduced by about 10-20% while HC and Non-Methane Organic Gases (NMOG) are reduced by about 5-10%. The NOx emissions generally increase but with a wider variation, usually between 5 and 30%. One study, however, showed greater effects of ethanol on regulated emissions after the vehicle had acquired 80,000km of test mileage. The study concluded that this was due to higher catalyst operating temperatures on ethanol blends which increased the deterioration of the aftertreatment catalyst over time. This is a potentially important finding and similar work is in progress in the US to reproduce this finding on fuels containing up to 20% v/v ethanol in petrol.

For advanced catalyst vehicles (Category 3), the effects of ethanol are generally (but not always) smaller and more variable while the trends are usually in the same direction as in the earlier category vehicles. The absolute emissions levels in these modern vehicles are very low compared to earlier vehicles but it is somewhat surprising that these sophisticated vehicles with advanced Engine Management Systems (EMS) should be sensitive at all to ethanol.

So far, there are little data available in the published literature on very new Gasoline Direct Injection (GDI) vehicles (Category 4) except for one study on one vehicle. This study gives broadly similar results to Category 3 vehicles.

In recent years, **particulate emissions** from vehicles have become an increasing concern for human health. Particulate mass (PM) emissions from gasoline engines are usually very low although GDI engines can produce measureable quantities of PM emissions. Ultrafine particles, that is, those having an aerodynamic diameter of greater than 23 nm, can also be measured from gasoline engines and the particle number (PN) concentration is generally higher for GDI engine technology compared to Multi-Point Fuel Injection (MPFI) engine technology. Limited studies, however, have shown that both PM and PN emissions are usually lower for vehicles running on ethanol/petrol blends compared to hydrocarbon-only petrol.

6.1.2. Unregulated Exhaust Emissions

Among the **unregulated exhaust emissions**, **benzene** is normally reduced because ethanol/petrol blends contain lower levels of aromatic compounds. **1-3 butadiene** emissions are generally unaffected or reduced, although two studies did show increased levels.

Formaldehyde emissions are usually unaffected, but **acetaldehyde** is substantially increased, in some cases by up to a factor of 10. Not surprisingly, **ethanol** emissions are substantially increased. For modern vehicles (Category 3), acetaldehyde and ethanol exhaust emission levels are usually very low, typically well below 1 mg/km over the regulatory cycle and essentially zero as soon as the catalyst has been fully warmed up.

Various other unregulated emissions have been measured in some studies, including higher aromatics, ammonia, acrolein and other aldehydes, nitrous oxide, etc. Except for higher aromatics, which are generally reduced with ethanol/petrol blends, no significant increases in emissions have been reported for the other unregulated emissions.

6.1.3. Vehicle Evaporative Emissions

Ethanol can impact **evaporative emissions** in three different ways. First, splash blending of ethanol into petrol can increase the vapour pressure (DVPE) and volatility of the petrol blend. Because the DVPE is not usually readjusted for splash-blended fuels, the total mass of vapour in equilibrium with liquid in the vehicle's fuel tank can be higher than for the base petrol and must be controlled by the evaporative emissions control system, specifically by the activated carbon canister. Second, because of its relative polarity, ethanol is adsorbed more readily by the activated carbon than are volatile hydrocarbons and it also desorbs more slowly. The presence of ethanol can reduce the “working capacity” of the carbon canister, effectively reducing the volume of the canister that is available for controlling evaporative emissions.

Third, ethanol can increase permeation through some plastic and elastomeric components found in the vehicle's fuel system. This can increase the emissions of both ethanol and especially aromatic hydrocarbons through evaporation and leaks in the fuel system materials. To reduce this effect, fluorocarbon polymers are now widely used in fuel system components while multilayer coatings are used in plastic fuel tanks to reduce fuel permeation.

More significant problems can occur in the vehicle's fuel system if the materials used are not compatible with higher ethanol concentrations. For example, some metal parts can experience accelerated corrosion in the presence of ethanol and trace water levels leading to misfueling or leakage [2].

Recent studies on modern vehicles show that evaporative control systems can generally cope with ethanol blends, depending on the DVPE and the ambient temperature. One European vehicle test showed that evaporative emissions only increased on ethanol/petrol blends having DVPE well above 70 kPa.

6.1.4. Atmospheric Reactions

The **Specific Reactivity (SR)** and **Ozone-Forming Potential (OFP)** of exhaust and evaporative emissions depend on the composition of NMOG emissions and the reactivity factors of individual compounds comprising the NMOG. Limited studies suggest that ethanol has little effect on the SR or OFP of exhaust emissions. The same is true for the SR of evaporative emissions, but OFP may be increased due to higher mass of hydrocarbon emissions with splash blends of ethanol in petrol.

6.1.5. Tank-to-Wheels (TTW) CO_2 Emissions

TTW CO_2 emissions are not significantly affected by ethanol because the EMS in modern vehicles automatically corrects the AFR to the stoichiometric point. Thus any benefit in engine efficiency due to the leaning affect of ethanol is lost. In general, the volumetric fuel consumption increases in proportion to the ethanol concentration of the ethanol/petrol blend and this effect becomes more evident to the driver as the ethanol concentration increases. Although these changes may be important to the driver, they are small effects compared to the differences in Well-to-Tank (WTT) and Well-to-Wheels (WTW) CO_2 emissions, which depend on the source and manufacturing pathway for the ethanol component.

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8. Glossary

AFR	Air-Fuel Ratio
ASVP	Air Saturated Vapour Pressure
CO	Carbon Monoxide
CPC	Condensation Particle Counter
CRC	Coordinating Research Council (USA)
CRM	Certified Reference Material
CWD	Cold Weather Driveability
DI	Driveability Index or Indices
DISI	Direct Injection Spark Ignition
DVPE	Dry Vapour Pressure Equivalent
E5,…, E25	Percentage ethanol in petrol/ethanol blend (5%,…, 25%)
E70	% of sample evaporated at 70°C
E100	% of sample evaporated at 100°C
E150	% of sample evaporated at 150°C
ELPI	Electrical Low Pressure Impactor
EMS	Engine Management System
EN228	European standard for unleaded petrol containing up to 5% v/v ethanol
EPEFE	European Programme on Emissions, Fuels, and Engine Technologies
ETBE	Ethyl Tertiary-Butyl Ether
FBP	Final Boiling Point
FFV	Flex Fuel Vehicle
FVI	Flexible Volatility Index
GC	Gas Chromatography
GDI	Gasoline Direct Injection
GFC	Groupement Français de Coordination
HC	Hydrocarbons
HFH	Hot Fuel Handling
HWD	Hot Weather Driveability
IMEP	Indicated Mean Effective Pressure
LCCG	Light Catalytically Cracked Gasoline
LIMS	Laboratory Information Management System
MIR	Maximum Incremental Reactivity
MOR	Maximum Ozone Reactivity
MPFI	Multi-Point Fuel Injection
MTBE	Methyl Tertiary-Butyl Ether
NEDC	New European Driving Cycle

NMOG	Non-Methane Organic Gases
NOx	Nitrogen oxides
OFP	Ozone Forming Potential
PFI	Port Fuel Injected
PM	Particulate Mass or Matter
PN	Particle Number
POCP	Photochemical Ozone Creation Potential
POM	Polycyclic Organic Matter
PONA	Paraffins-Olefins-Naphthenes Analysis
PZEV	Partial Zero Emissions Vehicle
RVP	Reid Vapour Pressure
SD	Standard Deviation
SHED	Sealed Housing Evaporative Determination
SR	Specific Reactivity
T10E	Temperature at which 10% of sample has evaporated
T50E	Temperature at which 50% of sample has evaporated
T90E	Temperature at which 90% of sample has evaporated
TBA	Tertiary-Butyl Alcohol
THC	Total Hydrocarbons
TTW	Tank-to-Wheels
UKAS	United Kingdom Accreditation Service
VLI	Vapour Lock Index
VOC	Volatile Organic Compounds
WTT	Well-to-Tank
WTW	Well-to-Wheels

9. General References

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10. APPENDIX 1
Statistical Design of the Ethanol/Petrol Blending Study

10.1. Introduction

The objective of the test programme is to determine what happens to the volatility of the ethanol/petrol blend, specifically DVPE, E70, and E100, when ethanol is splash blended into a wide range of base petrols.

The E70 of such a blend can be written as

- E70(blend) = (1 – c) × E70(base fuel) + c × B.E70(EtOH) (Eqn A1)

where c ($0<c<1$) is the final concentration of ethanol in the blend and B.E70(EtOH) is its *Blending E70*. It is postulated that the B.E70(EtOH) will depend on the concentration of ethanol in the blend and the base fuel volatility and composition. The study will thus seek explanatory models of the form:

- B.E70(EtOH) = $b_0 + b_1x_1 + b_2x_2 + b_3x_3 + \ldots + b_{11}x_1^2 + b_{12}x_1x_2 + \ldots + b_{00}c + b_{01}cx_1 + \ldots$ (Eqn A2)

where x_1, x_2, x_3, … are base fuel properties, such as E70, E100, DVPE, aromatics, olefins, MTBE, ETBE contents, etc and b_0, b_1, b_{11}, b_{00}, etc are empirical parameters to be estimated from the statistical analysis of the results.

Similar methods will be used to model the E100 of the ethanol/petrol blends.

10.2. Experimental Design

The test programme has been organized into three key stages using the principles of statistical experimental design:

- Selection of the base fuels
- Selection of the test blends
- Determination of the test order

In addition, a pilot study was conducted prior to the main blending programme in order to evaluate the effect of water content on the blending behaviour of ethanol.

10.2.1. Selection of the base fuels

In order to efficiently fit models such as Eqn A2, the base fuel matrix needs to be constructed so that the properties of interest x_1, x_2, x_3, etc. span a wide range and are as orthogonal as possible (that is, are as uncorrelated as possible). The matrix should also allow non-linear responses to be identified.

Designing and blending fuel matrices is challenging as these typically contain a mixture of physical (E70, E100, DVPE, etc.), chemical (aromatics, olefins, ethers, etc.), and performance (octane, etc.) parameters. This makes it difficult to control one parameter without affecting the others. There are also a number of physical constraints, for example:

- E70 < E100
- aromatics + olefins + paraffins + ethers = 100 %v/v (for base petrol fuels)

The fuel matrix must span as wide a range of petrol properties as possible without becoming unrealistic. Some base fuels outside the EN228 limits would be considered if these helped produce more reliable models. Indeed, non-compliant base fuels might produce compliant blends after ethanol has been added.

The seven key base fuel properties and property ranges to be studied are shown:

Property	Minimum	Maximum
DVPE	50kPa	90kPa
E70	20%	56%
E100	35%	71%
Aromatics	20%	45%
Olefins	5%	20%
MTBE	0%	22%
ETBE	0%	22%

Performance measures such as octane were not included because these were not expected to affect E70 or E100.

A number of additional constraints were imposed to keep the base fuels realistic and allow them to be blended from typical refinery streams. Thus, the base fuel fraction evaporating between 70°C and 100°C was constrained between 15% and 35%, i.e.:

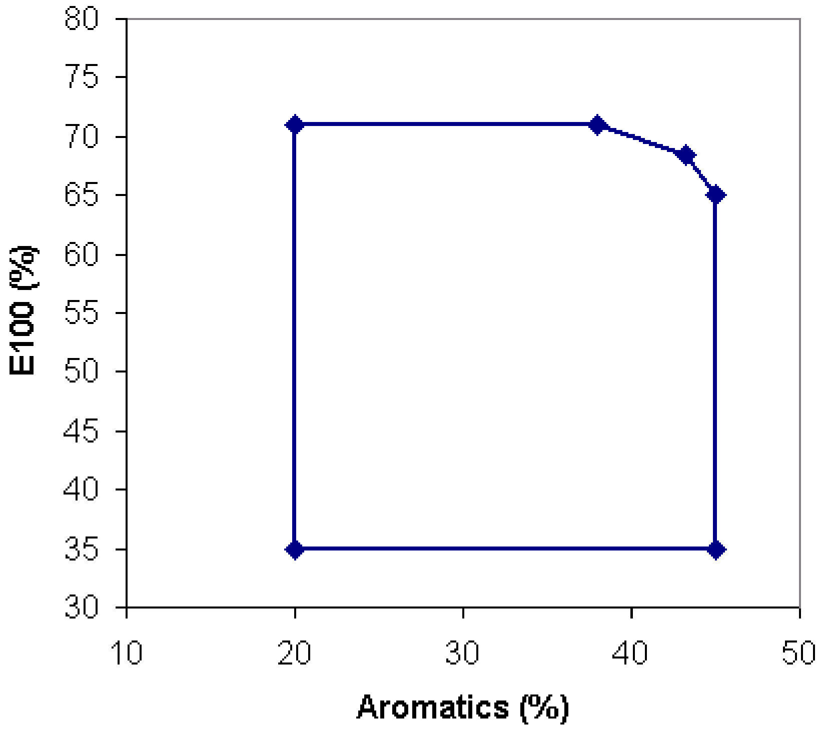
$$15\% \leq E100 - E70 \leq 35\%$$

Blending high aromatic content fuels with a high E100 was also a problem, with realistic upper bounds found to be:

$E100 \leq 65$ @ 45% aromatics
$\text{Aromatics} \leq 38$ @ $E100 = 71$

The region that was considered feasible to blend is shown in **Figure A1-1**.

Figure A1-1 Feasible blending region for aromatics and E100



It was decided that only one ether (ETBE or MTBE) would be used in any base fuel as the two are seldom used together in commercial blends. It was also decided that 50% of base fuels would contain no ether to ensure that the base fuel matrix did not contain a disproportionate number of oxygenated blends.

A number of statistical techniques exist for finding experimental design matrices with good orthogonality properties. For example, one could use a fractional replicate factorial design, giving each of the 7 factors a fixed number of levels (e.g. 3 or 4) and testing some subset of the 3^7 or 4^7 combinations. However there would be problems handling the constraints on E70 & E100 and on MTBE & ETBE; many combinations would need to be excluded which would unbalance the design.

Another alternative was to seek a D-optimal design. This involves choosing a set of fuels from a list of candidates that allows a multiple regression model to be fitted as efficiently as possible. The drawback with this approach is that it assumes the model is known *a priori*. In practice, it is difficult to predict which terms will be important and which will not, particularly when squared and cross-product terms might be expected to appear. Space filling designs, which are evenly spaced across the constrained 7-dimensional design space, are less sensitive to the choice of model (see [8] for more details).

A preliminary study for the tender suggested that a design matrix with around 60 base fuels would be appropriate. The first step was to construct a 49-fuel sub-matrix as an orthogonal resolution-3 1/343 fraction of a 7×7×7×7×7 factorial in pseudo factors A, B, C, D and E. This design was generated using the KEYFINDER program [5,6].

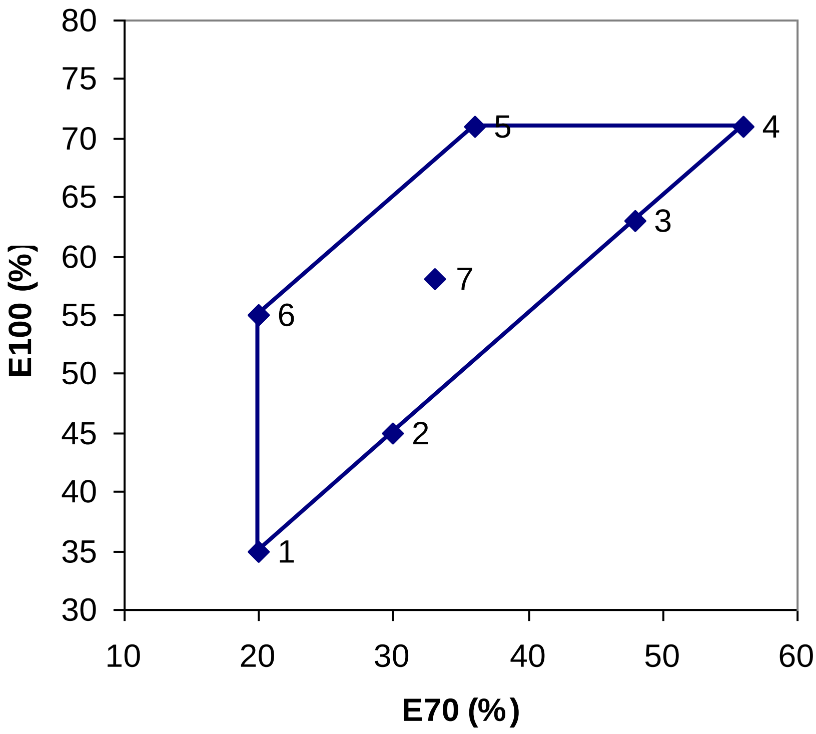
Base fuel properties were then assigned as per **Table A1-1**. The levels of the pseudo factors A, B and C define the aromatic and olefin concentrations and the DVPE respectively in each of the 49 base fuels.

Table A1-1 Base fuel properties corresponding to the 7 levels of pseudo factors A, B, C, D, and E

Factor	**Level**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
A	Aromatics	20	24.2	28.3	32.5	36.7	40.8	45
B	Olefins	5	7.5	10	12.5	15	17.5	20
C	DVPE	50	56.7	63.3	70	76.7	83.3	90
D	E70	20	30	48	56	36	20	33
	E100	35	45	63	71	71	55	58
E	MTBE	0	0	0	0	0	11	22
	ETBE	0	0	0	11	22	0	0

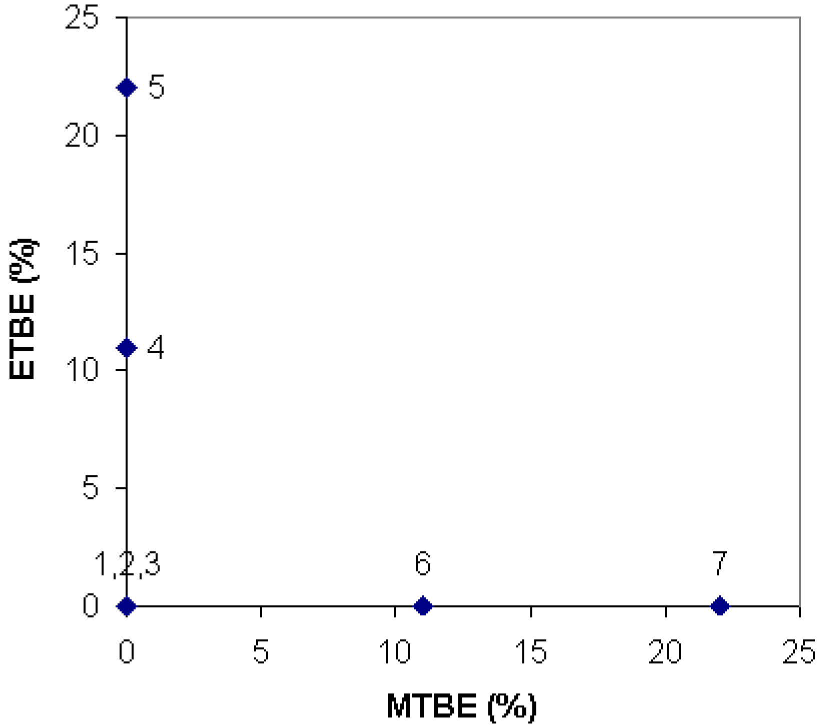
The 7 levels of pseudo factor D provide 7 evenly spaced combinations of levels of E70 and E100, meeting the constraints discussed above. These are depicted in **Figure A1-2**.

Figure A1-2 Values of E70 and E100 corresponding to the 7 levels of pseudo factor D in Table A1-1.



The 7 levels of pseudo factor E similarly define the concentrations of MTBE and ETBE in the 49 base fuels. These are shown in **Figure A1-3** where it can be seen that 3 of the 7 levels contain no ether at all and no fuel blends contain both MTBE and ETBE. This ensures that 21 of the 49 base fuels, just less than half, will be pure hydrocarbons.

Figure A1-3 Concentrations of MTBE and ETBE corresponding to the 7 levels of factor E in Table A1-1



The 49 fuel sub-matrix did involve 2 fuels with aromatics (= 45%) and E100 (= 71%) levels which were outside the feasible region shown in **Figure A1-1**. These were replaced by fuels with target values of aromatics = 43.2% and E100 = 68.4%, the point nearest the top right corner in that figure.

While fractional replicates of 7×7×7×7×7 factorial designs have good orthogonality and space-filling properties, they may not necessarily span the design region very well. Most of the design points will lie in the interior of the 5-dimensional pseudo factor design region, with few points in the corners or on the edges. The same applies when the points are expanded into the 7-dimensional design region using **Table A1-1**. However, not all fractions are the same.

To improve the efficiency of the design even further, the order of the entries in each row of **Table A1-1** was randomized in turn (without changing the tested combinations of E70 & E100 and MTBE & ETBE). The randomized table was then used to produce a new design in the 7 factors of interest (aromatics, olefins, DVPE, E70, E100, MTBE, and ETBE).

After adjusting the high E100 and aromatics points as described above, each proper factor was scaled to the range [-1,1]. The D-optimality criterion D = $|\mathbf{X}'\mathbf{X}|^{-1}$ was then calculated for a model with all linear terms and 20 of the 21 possible linear×linear cross-products, the exception being MTBE×ETBE which is always zero. Here **X** is the 49 × 27 design matrix with each row corresponding to a fuel and each column to a term in the model. This process was repeated 1000 times and the set of randomizations with the lowest value of D was chosen as the final design sub-matrix.

In order to improve the design further an additional 11 fuels were added. These were selected from a large set of candidates which were evenly spread across the design region and included all possible corners. In order to achieve 30 pure hydrocarbon fuels in the final design, only one MTBE and one ETBE containing fuel was selected, the other nine being pure hydrocarbons.

The 11 additional fuels were selected using the D-optimality algorithm of Mitchell [9] using PROC IML code in SAS® [10]. Squared terms were now added to the model assumed when calculating D. The 11 fuels added to the matrix were generally in the corners or on the edges of the design region.

The final base fuel matrix is tabulated in **Table A1-3**.

The correlation matrix for base fuels in the final design matrix is shown in **Table A1-2**. It can be seen that all the correlations are close to zero apart from those between (a) E70 and E100 which have a high degree of mutual dependency (see **Figure A1-2**) and (b) MTBE and ETBE where there is negative correlation as the two ethers cannot appear together.

Table A1-2 Correlation matrix for base fuels in final design

	ARO	**OLE**	**DVPE**	**E70**	**E100**	**MTBE**	**ETBE**
ARO	1.000						
OLE	-0.031	1.000					
DVPE	0.060	-0.062	1.000				
E70	-0.172	-0.039	-0.064	1.000			
E100	-0.107	-0.090	-0.068	0.758	1.000		
MTBE	0.071	-0.051	-0.065	-0.016	-0.003	1.000	
ETBE	-0.057	-0.051	-0.065	0.049	0.064	-0.292	1.000

In practice, it will not be possible to blend fuels with the exact predetermined properties listed in **Table A1-3**. The values listed should therefore be considered as targets for the blenders. The base fuel properties should be measured accurately after the fuels have been blended. The measured values will then be used in the subsequent statistical analysis.

10.2.2. Selection of the test blends

The original tender specifically requested that ethanol be tested at 5%, 10%, and 25% v/v in each base fuel. The base fuel also needs to be characterized.

However, as was discussed in **Sections 2 and 3**, the distillation properties of ethanol/petrol blends are known to depend in a non-linear way on ethanol content. For this reason, it was recommended that data also be collected on ethanol/petrol blends at two additional ethanol contents, namely 15% and 20%. The marginal cost was relatively small and these extra measurements provided valuable information on the behaviour of ethanol between 10 and 25 %v, leading to more robust blending models. This proposal was accepted so that ethanol could be tested at 5, 10, 15, 20, and 25% v/v ethanol in each base fuel.

Table A1-3 Unrandomized base petrol matrix

Fuel	ARO	OLE	DVPE	E70	E100	MTBE	ETBE
1	28.3	20.0	56.7	36.0	71.0	0.0	0.0
2	28.3	17.5	70.0	48.0	63.0	0.0	11.0
3	28.3	5.0	50.0	33.0	58.0	0.0	0.0
4	28.3	15.0	83.3	30.0	45.0	0.0	0.0
5	28.3	10.0	76.7	20.0	35.0	22.0	0.0
6	28.3	7.5	90.0	56.0	71.0	11.0	0.0
7	28.3	12.5	63.3	20.0	55.0	0.0	22.0
8	43.2	20.0	70.0	56.0	68.4	22.0	0.0
9	45.0	17.5	50.0	20.0	55.0	11.0	0.0
10	43.2	5.0	83.3	36.0	68.4	0.0	22.0
11	45.0	15.0	76.7	48.0	63.0	0.0	0.0
12	45.0	10.0	90.0	33.0	58.0	0.0	11.0
13	45.0	7.5	63.3	30.0	45.0	0.0	0.0
14	45.0	12.5	56.7	20.0	35.0	0.0	0.0
15	36.7	20.0	50.0	30.0	45.0	0.0	11.0
16	36.7	17.5	83.3	20.0	35.0	0.0	0.0
17	36.7	5.0	76.7	56.0	71.0	0.0	0.0
18	36.7	15.0	90.0	20.0	55.0	22.0	0.0
19	36.7	10.0	63.3	36.0	71.0	11.0	0.0
20	36.7	7.5	56.7	48.0	63.0	0.0	22.0
21	36.7	12.5	70.0	33.0	58.0	0.0	0.0
22	20.0	20.0	83.3	48.0	63.0	11.0	0.0
23	20.0	17.5	76.7	33.0	58.0	0.0	22.0
24	20.0	5.0	90.0	30.0	45.0	0.0	0.0
25	20.0	15.0	63.3	20.0	35.0	0.0	11.0
26	20.0	10.0	56.7	56.0	71.0	0.0	0.0
27	20.0	7.5	70.0	20.0	55.0	0.0	0.0
28	20.0	12.5	50.0	36.0	71.0	22.0	0.0
29	24.2	20.0	76.7	20.0	55.0	0.0	0.0
30	24.2	17.5	90.0	36.0	71.0	0.0	0.0
31	24.2	5.0	63.3	48.0	63.0	22.0	0.0
32	24.2	15.0	56.7	33.0	58.0	11.0	0.0
33	24.2	10.0	70.0	30.0	45.0	0.0	22.0
34	24.2	7.5	50.0	20.0	35.0	0.0	0.0
35	24.2	12.5	83.3	56.0	71.0	0.0	11.0
36	40.8	20.0	90.0	20.0	35.0	0.0	22.0
37	40.8	17.5	63.3	56.0	71.0	0.0	0.0
38	40.8	5.0	56.7	20.0	55.0	0.0	11.0
39	40.8	15.0	70.0	36.0	71.0	0.0	0.0
40	40.8	10.0	50.0	48.0	63.0	0.0	0.0
41	40.8	7.5	83.3	33.0	58.0	22.0	0.0
42	40.8	12.5	76.7	30.0	45.0	11.0	0.0
43	32.5	20.0	63.3	33.0	58.0	0.0	0.0
44	32.5	17.5	56.7	30.0	45.0	22.0	0.0
45	32.5	5.0	70.0	20.0	35.0	11.0	0.0
46	32.5	15.0	50.0	56.0	71.0	0.0	22.0
47	32.5	10.0	83.3	20.0	55.0	0.0	0.0
48	32.5	7.5	76.7	36.0	71.0	0.0	11.0
49	32.5	12.5	90.0	48.0	63.0	0.0	0.0
50	45.0	5.0	50.0	20.0	53.0	22.0	0.0
51	20.0	5.0	50.0	38.0	71.0	0.0	22.0
52	45.0	5.0	90.0	20.0	53.0	0.0	0.0
53	20.0	20.0	50.0	20.0	35.0	0.0	0.0
54	20.0	5.0	90.0	38.0	71.0	0.0	0.0
55	20.0	20.0	90.0	20.0	35.0	0.0	0.0
56	45.0	20.0	90.0	20.0	53.0	0.0	0.0
57	20.0	20.0	50.0	56.0	71.0	0.0	0.0
58	45.0	5.0	90.0	20.0	35.0	0.0	0.0
59	45.0	20.0	50.0	20.0	53.0	0.0	0.0
60	20.0	5.0	70.0	56.0	71.0	0.0	0.0

10.2.3. Test order

Measurements of E70 and E100 by EN ISO 3405 [7] are subject to measurement error with the repeatability *r* varying as fuel properties and the shape of the distillation curve vary; typical values for *r* are 2 to 3% for E70 and 1.5 to 2.5% for E100 (and higher for some high ethanol concentration blends, see **Appendix 5**). Therefore it was decided that each fuel would be tested in triplicate. Single measurements will be made for other blend properties.

The primary interest is in the differences between the E70 and E100 of ethanol blends and the E70 and E100 of the base fuel. Therefore, the eighteen measurements on the base fuel and ethanol blends were carried out within a short time interval on the same piece of equipment at the same laboratory.

The typical test order for a particular base fuel was:

Block 1	E10 - Base - E25 – E15 - E20 - E5
Block 2	E20 - E10 - E5 - Base - E15 - E25
Block 3	E25 - E5 - E15 - E20 - Base - E10

The measurements are conducted in three blocks of six, with each block testing the base fuel and the 5 ethanol blends in a different randomized order. Each block was completed by the same operator in a single day. Different operators carried out blocks 2 and 3 and different random orders were used for each base fuel.

The analyst conducting Block 1 also measured the DVPE, density and water content (base and E25) using the same randomized test order.

The base fuels themselves were tested in a randomized order and the final design for testing is given in **Table A1-4**.

Table A1-4 Final randomized test design (base fuel numbers in Column 2 are as listed in Table A1-3; entries in this table show the order in which the various ethanol concentrations were to be tested)

		BLOCK 1						**BLOCK 2**						**BLOCK 3**					
TEST	FUEL	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
1	31	10	5	0	20	15	25	20	0	10	15	5	25	0	5	15	10	20	25
2	36	5	15	0	10	25	20	25	5	10	15	0	20	10	0	5	20	15	25
3	37	0	20	15	10	5	25	15	5	10	25	20	0	15	25	10	0	5	20
4	48	5	15	0	10	25	20	25	20	5	0	10	15	5	20	0	15	10	25
5	44	0	25	20	10	15	5	15	10	5	20	25	0	0	5	15	10	20	25
6	1	5	25	10	0	15	20	15	0	20	25	10	5	0	25	5	20	15	10
7	24	10	5	20	15	25	0	20	0	25	10	15	5	5	20	15	25	0	10
8	47	0	15	5	25	10	20	15	10	5	0	25	20	25	10	20	15	0	5
9	17	10	0	25	15	20	5	0	10	20	5	15	25	0	15	5	20	25	10
10	50	10	15	20	0	25	5	0	25	20	10	15	5	15	0	25	20	5	10
11	19	20	15	25	0	10	5	25	20	5	0	10	15	10	25	15	0	5	20
12	58	15	0	5	25	10	20	0	25	10	15	5	20	10	15	5	25	20	0
13	28	20	15	25	5	10	0	0	5	20	15	25	10	20	0	5	15	25	10
14	2	10	0	5	25	15	20	25	5	0	20	10	15	0	5	25	10	15	20
15	41	10	20	0	5	25	15	10	15	25	20	5	0	20	0	10	15	5	25
16	55	25	15	10	5	0	20	10	20	25	5	0	15	20	15	5	25	0	10
17	5	25	5	20	0	15	10	5	15	25	20	10	0	15	5	10	25	20	0
18	40	25	15	5	10	0	20	10	0	5	15	20	25	0	5	15	25	20	10
19	6	15	20	10	25	0	5	25	5	10	15	0	20	15	0	10	25	20	5
20	52	25	10	20	15	5	0	10	25	15	5	0	20	15	20	25	10	0	5
21	4	10	15	25	20	0	5	15	20	5	10	0	25	10	5	20	0	25	15
22	30	0	25	10	5	15	20	20	10	15	0	5	25	5	0	10	15	20	25
23	33	15	0	20	10	25	5	15	25	5	20	0	10	20	25	5	0	10	15
24	60	15	20	0	10	5	25	10	15	0	20	25	5	10	20	0	25	5	15
25	23	15	5	25	20	0	10	25	20	5	15	10	0	0	10	5	15	25	20
26	42	0	5	15	20	25	10	15	10	25	0	20	5	20	0	5	15	25	10
27	9	10	25	20	5	0	15	20	10	25	15	0	5	10	0	25	15	20	5
28	27	15	25	0	5	20	10	10	15	0	25	5	20	5	15	20	0	10	25
29	13	25	10	15	0	20	5	25	10	5	0	15	20	25	0	10	5	20	15
30	10	10	15	20	0	25	5	25	0	15	10	20	5	10	15	25	0	20	5
31	35	5	20	0	15	10	25	20	5	0	25	10	15	25	0	10	5	15	20
32	45	5	10	0	15	20	25	0	10	15	20	5	25	20	0	10	15	5	25
33	39	0	5	20	15	10	25	10	15	5	20	25	0	20	15	10	0	5	25
34	12	10	15	5	20	25	0	5	20	0	25	15	10	5	20	0	15	10	25
35	26	25	20	5	10	0	15	5	10	15	20	25	0	5	15	10	0	20	25
36	32	20	25	15	0	10	5	15	0	20	25	5	10	0	25	5	20	15	10
37	16	15	5	20	25	10	0	0	5	10	20	25	15	10	20	5	15	25	0
38	51	5	10	0	25	15	20	20	5	25	0	10	15	20	15	25	10	5	0
39	54	5	0	20	25	15	10	5	15	20	0	10	25	5	15	20	25	0	10
40	11	5	25	15	10	20	0	10	0	20	25	5	15	10	5	25	20	0	15
41	14	25	20	5	0	15	10	25	5	15	10	20	0	5	20	25	0	10	15
42	20	20	0	5	25	10	15	5	0	15	20	10	25	25	15	10	0	5	20
43	46	15	20	25	10	5	0	0	10	20	15	25	5	20	5	0	10	25	15
44	18	20	10	5	25	15	0	15	10	25	0	5	20	15	10	5	20	0	25
45	59	10	25	0	5	15	20	15	25	0	20	10	5	15	0	5	25	10	20
46	57	25	15	20	5	0	10	0	25	20	10	5	15	20	15	10	25	5	0
47	53	25	5	15	20	0	10	15	25	10	0	20	5	0	15	20	5	25	10
48	3	20	0	15	5	25	10	5	0	10	20	15	25	0	25	15	10	20	5
49	56	25	0	10	5	20	15	20	0	15	10	5	25	20	5	15	0	25	10
50	21	20	0	15	10	5	25	15	10	20	0	5	25	15	0	25	20	5	10
51	7	5	10	25	15	20	0	0	15	10	5	25	20	15	10	20	5	0	25
52	49	10	5	15	20	0	25	20	10	25	5	0	15	5	15	10	0	20	25
53	15	20	5	0	15	25	10	0	25	15	20	5	10	0	20	10	25	15	5
54	34	25	20	10	5	15	0	0	25	5	15	20	10	20	10	0	5	15	25
55	43	0	10	5	25	15	20	0	20	5	15	25	10	5	25	10	0	20	15
56	25	0	5	10	20	25	15	10	15	25	0	20	5	5	10	20	25	0	15
57	8	10	25	20	15	0	5	25	20	10	5	0	15	5	0	25	20	15	10
58	29	0	5	10	15	25	20	10	25	5	15	0	20	15	25	0	5	20	10
59	22	0	15	25	10	5	20	25	15	0	10	5	20	25	20	15	5	0	10
60	38	15	5	10	25	0	20	0	5	20	10	25	15	5	25	20	0	15	10

11. APPENDIX 2
Fuel Blending and Analytical Methods

Shell Research Ltd. operates an extensive analytical laboratory at the Thornton Technology Centre near Chester in the UK. The laboratory provides standard accredited analytical services to the Stanlow refinery which is located next door, as well as standard and specialised analytical services to the research and development activities of Shell Research Ltd. In total, Analytical Technology employs more than 80 people at the Thornton site.

The fuels testing activities within the Analytical Technology Group at Thornton are accredited to the standard ISO 17025 "General requirements for the competence of testing and calibration laboratories". The accreditation is provided via the sole UK National accreditation body "UKAS - United Kingdom Accreditation Service" recognised by the UK government (laboratory accreditation number 1158). This is a rigorous standard with the highest recognition for testing and calibration activities and as such, provides a high level of confidence in the integrity of the data provided by accredited laboratories. Accreditation documents can be checked at:

http://www.ukas.org/testing/lab_detail.asp?lab_id=846&location_id=&vMenuOption=3

In addition, the laboratory participates in Shell’s global fuels proficiency testing programme (GFPS - Global Fuels Proficiency Scheme) where the current performance (2007 & 2008) of the Analytical Technology Group is categorised as excellent.

Analytical Technology also uses third-party accredited laboratories for testing in certain circumstances. There are no plans to use third-party laboratories within this project, but the option could be taken in the event of resource limitations.

Blending of specialty fuels is performed within the Automotive Fuels Technology Group. This expertise has primarily been developed in order to produce the necessary test fuels needed for product development. Facilities exist for the blending on laboratory scale (1 to 10 litres) and vehicle/fleet testing scale (10,000 to 50,000 litres). A matrix of refinery and chemical components are routinely stocked to allow accurate blending of fuels to varied specifications, including the de-correlation of multiple fuel properties. (An example of a set of typical gasoline test fuels blended in this facility in given in [11].)

Accurate blending to target properties is achieved through individual expertise combined with a predictive model. This allows the blend recipe to be accurately formulated and the correct fuel blend to be achieved first time. Within the Automotive Fuels Technology Group at Thornton, a laboratory team of more than 10 technicians and a blending team of more than 10 technicians support approximately 40 scientists in their research and development activities.

The characterisation of the base petrol fuels and ethanol/petrol blends involves measurements of distillation (by 1% increments including E70 and E100), vapour pressure (DVPE), density, and molecular composition (aromatics, olefins, paraffins, and ethers). The methods and instruments employed for these four measurements are given in the table below.

Measurement	Method	Instrument
Vapour Pressure (DVPE)	IP 394 EN 13016-1 Determination of Air Saturated Vapour Pressure (ASVP) and calculated Dry Vapour Pressure Equivalent (DVPE) Method for the determination of the total pressure, exerted *in vacuo*, by volatile, low viscosity petroleum products, components, and feedstocks containing air.	Equipment Used: 81000-2 Setavap 2 Vapour Pressure Tester An automated instrument for the measurement of the vapour pressure of gasoline, solvents, light crude oils, and other similar products using the “mini” test method. A sample is injected through a septum into a fixed volume chamber that is maintained at 37.8°C ± 0.1°C. The pressure is automatically measured at one minute intervals until three readings are within 0.1 kPa, which determines the end of the test. Test temperature 38.7°C (100°F) +/- 0.1°C. Pressure range 0 to 200kPa +/- 0.5kPa. Pressure resolution 0.1kPa. Accuracy Check: Daily using n-heptane as reference material See also: www.stanhope-seta.co.uk
Distillation	IP 123 EN ISO 3405: Determination of distillation characteristics at atmospheric pressure Laboratory method for the determination of the distillation characteristics of light and middle distillates derived from petroleum with initial boiling points above 0ºC and end-points below approximately 400ºC, utilizing either manual or automated equipment.	Equipment Used: PAC OptiDist™ Analyser The OptiDist™ is the state-of-the-art Optimal Solution for performing atmospheric distillation offering highest precision and ease of use. The OptiDist™ measures the volatility of liquid petroleum products including biofuels. The OptiDist™ automatically sets the optimal distillation conditions for any sample through the unique heating optimizer technology. It delivers up to 2 times better precision for all common distillation samples. Optical measurement of sample volume with accuracy of +/- 0.1ml. Calibration: CRM 2 times/year and standard equipment calibrations See also: www.paclp.com

Measurement	Method	Instrument
Density	IP 365 EN ISO 12185: Determination of density: oscillating U-tube method Method for the determination of the density of crude petroleum and related products using an oscillating U-tube density meter. The density range is within 600 kg/m^3 to 1100 kg/m^3 for samples that can be handled as single-phase liquids at the test temperature and pressure.	Equipment Used: Anton Paar/DMA 4500 Density Meter Provides density measurement to 4 decimal places through the temperature range 0ºC to 90ºC, based on oscillating U-tube method. Includes viscosity correction for all sample viscosities. Calibration of temperature measurement is traceable to international standards. Automatic data transfer to LIMS system. Range 0 to 3 g/ml. Accuracy +/-0.00005 g/ml. Sample throughput 10 to 30/hour. Accuracy Check: Once per week using filtered boiled water See also: www.anton-paar.com
Molecular Composition	ASTM D6839 EN 14517 Standard test method for hydrocarbon types, oxygenated compounds and benzene in spark ignition engine fuels by gas chromatography Method providing the quantitative determination of saturates, olefins, aromatics and oxygenates in spark ignition engine fuels by multi-dimensional gas chromatography. The method is applicable to finished petrol with total aromatics contents up to 50% and total olefins contents from about 1.5% up to 30%.	Equipment Used: AC Reformulyzer® M3 The sample is introduced into the Reformulyzer® M3, which consists of switching valves, columns, an olefin hydrogenation catalyst and an ether/alcohol trap, all operating at various temperatures. The valves are actuated at predetermined times to direct portions of the sample to appropriate columns and traps. As the analysis proceeds, the columns separate portions sequentially into groups of different hydrocarbon types that elute to a flame ionization detector. Each hydrocarbon type can be reported either by carbon number or as a total. Calibration: AC qualitative standard once per month and various other specific certified standards as required See also: www.reformulyzer.com/

Measurement	Method	Instrument
Water Content	UK 3367 (in-house method) Water in various chemical materials	Equipment Used: Metrohm 831 Karl Fischer Coulometer Accuracy Check: using 5µl of H_2O once per day

The methods selected for this study are those allowed by the EN 228 specification for European petrol. In the event of a discrepancy in any result, the reference method specified in the EN 228 method will be used, if the reference method is different from those specified in the table above.

12. APPENDIX 3
Project Structure

CONCAWE is a non-profit making, scientific association that has been in existence since 1963. The governing body of the Association is the General Assembly on which all CONCAWE Member Companies are represented. The General Assembly elects a Board of Directors to manage the Association and a Scientific Council assists the Board in matters related to the scientific and technical direction of the Association.

The permanent CONCAWE Secretariat is based in Brussels and is headed by a Secretary General who is assisted by six Technical Coordinators. The Secretariat is responsible for coordinating CONCAWE's research activities.

The activities are distributed among a number of management groups that propose research programmes and manage agreed projects. Project work is normally carried out by a special task force (STF) or by an *ad hoc* group, with the assistance of external consultants and contractors for specialized tasks. These groups are composed of Member Company experts as well as Secretariat staff. Where actual testing is involved, appropriate research groups, either inside or outside of the Member Companies, are contracted to complete the test work. A formal contract is executed between the CONCAWE Association and the designated research group that specifies roles and responsibilities, deliverables, timing, and costs.

In this area of research, a CONCAWE Special Task Force (FE/STF-24) is responsible for providing technical support to CONCAWE Member Companies on specifications and CEN-related activities. The FE/STF-24 task force meets about six times per year to review the status of on-going research programmes and to plan future activities. The task force consists of the CONCAWE Technical Coordinator and about eighteen active technical experts representing about sixteen Member Companies. The activities of FE/STF-24 are stewarded by the Fuels Quality and Emissions Management Group (FEMG). For this study, the technical experts in FE/STF-24 acted as project advisors and the progress of the work was periodically reviewed by FEMG.

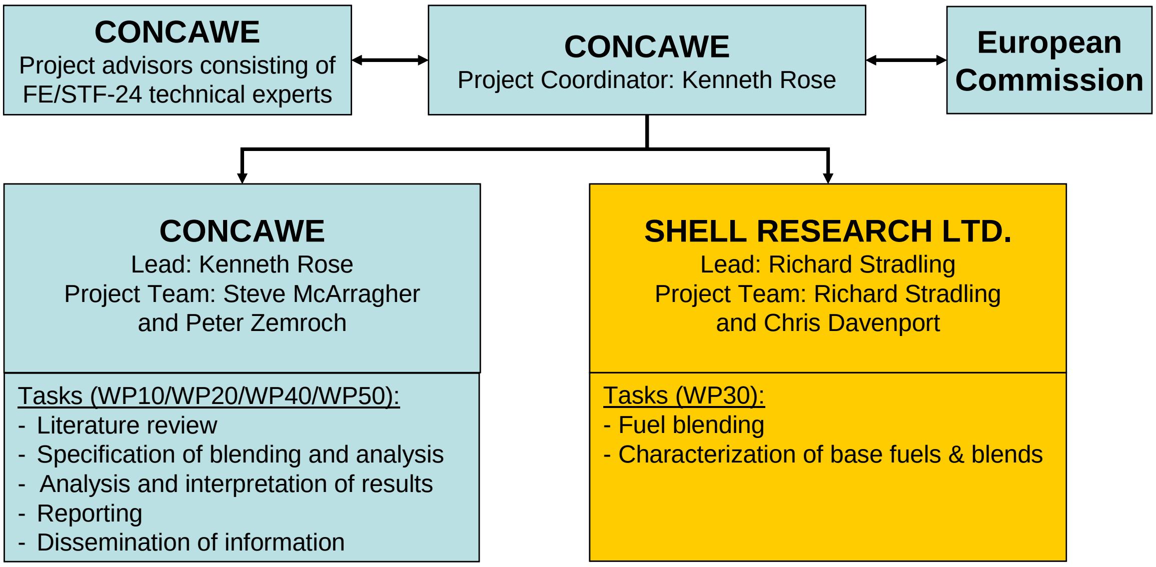
The BEP525 Project was carried out by CONCAWE and its partner, Shell Research Ltd., as shown in **Figure A3-1.** The CONCAWE Project Coordinator was responsible for coordinating work to design the fuel blend matrix and specify the physical and chemical analyses to be carried out on the base petrol fuel, the ethanol blendstock, and respective blends of the base petrol fuel and ethanol. He was assisted in this task by two temporary consultants and the FE/STF-24 project advisors.

Information on the fuel matrix design and required analytical measurements was provided to SHELL who was responsible for acquiring appropriate refinery blendstocks, blending the base petrol fuels to the design specifications, and completing the required measurements as specified by CONCAWE. The measurement results were returned to CONCAWE for statistical analysis, interpretation of the results, and preparation of the Interim and Final reports.

CONCAWE has in place standard agreements and procedures (under Belgian law) for tendering, bidding, and contracting research projects. CONCAWE used its competitive bidding procedures to select SHELL as its partner for this project. Both organizations share a long history of fruitful cooperation, including similar contractual relationships in the recent past.

Exchange of information between partners took place through tele- and web-conferences as well as through project team meetings at SHELL's laboratory.

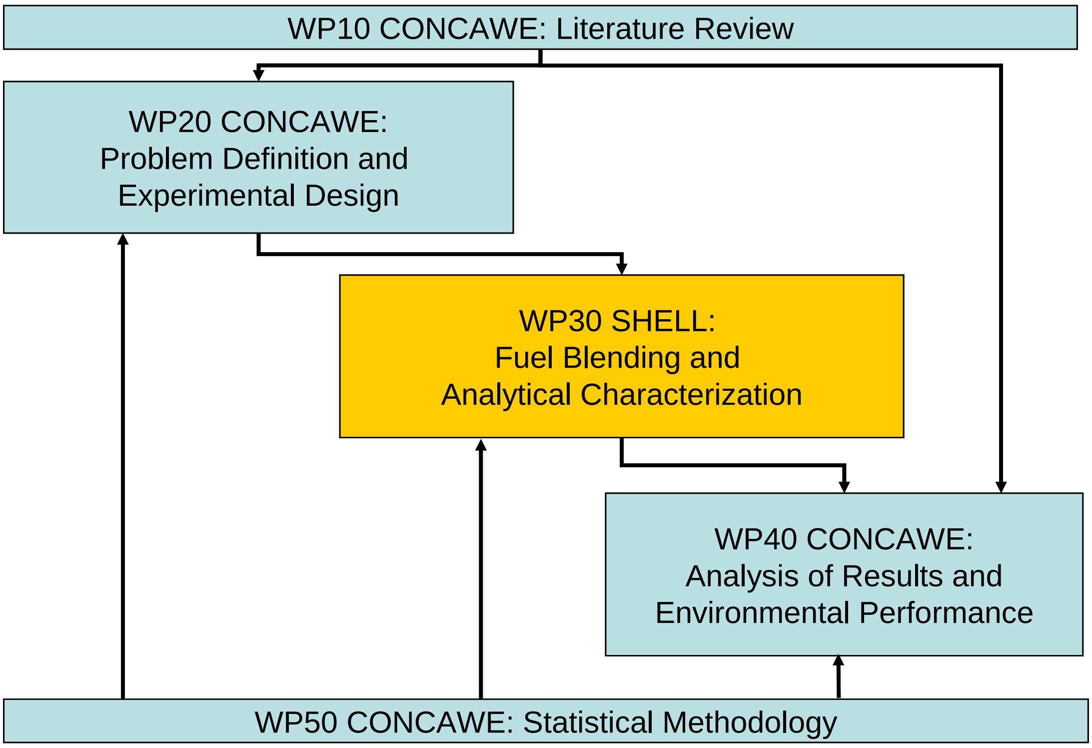
Figure A3-1 Project Management Structure



The Project Task Structure is shown in **Figure A3-2** and the following task descriptions address the work that was requested by the tender proposal, including:

- an extensive literature review in the EU and beyond (WP10)
- a detailed analysis of the technical problems faced (WP20)
- a detailed characterisation of the base petrol, both winter and summer variances (WP30)
- a detailed characterisation of the bioethanol (WP30)
- a detailed characterisation of the volatility behaviour of both the base petrols and their corresponding blends with bioethanol (WP30)
- an analysis of the environmental performance of such blends (WP40)
- a detailed description of the statistical methodology (or other analysis) to be used to evaluate the data (WP50)

Figure A3-2 Project Task Structure



13. APPENDIX 4
Project Plan and Timeline

13.1. Literature Review (WP10)

Task number	WP10	**Start date or starting event:**	M01 to M11
Participant ID	CONC		

Objective:

- Complete a literature review on the current status of petrol blending with ethanol and other oxygenates as well as the impact of these oxygenates on petrol volatility and vehicle performance.

Description of Work:

In this Work Package, CONCAWE will complete an extensive literature review on petrol blending with ethanol and other oxygenates. This review will cover published literature obtained from its own archives, acquired from Member Company experts, and identified through external search engines. Key literature will be reviewed from the US's Coordinating Research Council (CRC), ASTM, CEN, and DGMK as well as from recent published studies in Australia, Minnesota, and other sources.

The following elements will be reviewed:

- The impact of ethanol and other oxygenates on petrol volatility
- The impact of petrol volatility on vehicle performance

In-house and publicly available databases will be scanned for relevant key words and hits will be assessed for relevance to the project and scientific soundness. A literature review on ethanol blending into petrol and its effects on petrol properties will be prepared.

Task Descriptions:

- WP10-Task 1: A literature review on (1) the impact of ethanol on the volatility of ethanol/petrol blends and (2) the impact of volatility on vehicle driveability performance will be integrated into the Interim and Final Reports

13.2. Problem Definition and Experimental Design (WP20)

Task number	WP20	**Start date or starting event:**	M01 to M02
Participant ID	CONC		

Objectives:

- Complete a detailed analysis of the technical problems faced in blending ethanol/petrol fuels

Description of Work:

Ethanol is known to impact the volatility of ethanol/petrol blends, especially at low ethanol concentrations. In addition to the ethanol concentration in the final blend, volatility changes also depend on the properties of the petrol fuel, including the DVPE, distillation, aromatics content, and olefins content. The use of other oxygenates, such as MTBE or ETBE, can also have an impact on the volatility of the final blend.

In this Work Package, the CONCAWE partner will use in-house and publicly-available information to analyze the technical problems associated with the blending of ethanol/petrol blends (supported by work carried out in WP50).

Most importantly, the results from this analysis will include a detailed fuel design matrix and specifications for the analytical characterisation of these fuel blends that will communicated to the Shell partner for action in WP30.

Task Descriptions:

- WP20-Task 1: The results of this problem analysis will provide the specifications for the fuel blending and analytical characterisation tasks to be performed by the SHELL partner in WP30 and will be integrated into the Interim and Final Reports.

13.3. Fuel Blending and Analytical Characterisation (WP30)

Task number	WP30	**Start date or starting event:**	M03 to M08
Participant ID	SHELL		

Objectives:

- Blend base petrol fuels and ethanol/petrol blends meeting the expectations of the fuel design matrix carried out in WP20.
- Analyze the volatility and related properties of these blends as defined in WP20.

Description of Work:

In this Work Package, the Shell partner will implement the fuel design matrix developed in WP20 and prepare laboratory samples of the base petrol fuels and ethanol/petrol blends. The samples will be prepared from typical refinery streams using in-house blending expertise. The samples will then be characterized for volatility and related properties as defined in WP20.

Task Descriptions:

- WP30-Task 1: Base petrol fuel blends meeting the expectations of the fuel design matrix carried out in WP20. The results of this work will be integrated into the Interim Report.

- WP30-Task 2: Ethanol/petrol fuel blends meeting the expectations of the fuel design matrix carried out in WP20. The results of this work will be integrated into the Interim Report.

- WP30-Task 3: Analytical characterisation of the volatility and related properties of the base petrol and ethanol/petrol blends as defined in WP20. The results will be integrated into the Final Report.

13.4. Analysis of Results and Environmental Performance (WP40)

Task number	WP40	**Start date or starting event:**	M04 to M11
Participant ID	CONC		

Objectives:

- Complete an analysis of the environmental performance of ethanol/petrol blends in the range E5 to E25 vol%.

Description of Work:

In this Work Package, the CONCAWE partner will analyze the impact of ethanol on the environmental performance of ethanol/petrol blends. This will be done in two parts with the first part based on a survey of published and in-house literature and the results of this assessment will be included in the Interim Report.

The second part will be a detailed interpretation of the results from WP30 as well as an interpretation of these results on vehicle driveability performance and on vehicle emissions. The results of this assessment will be included in the Final Report.

Task Descriptions:

- WP40-Task 1: A preliminary analysis of the impact of ethanol on environmental performance of ethanol/petrol blends will be based on a survey of published and in-house literature and will be integrated into the Interim Report.
- WP40-Task 2: The results obtained from the interpretation of the volatility study will be analyzed for the environmental performance of ethanol/petrol blends in the E5 to E25 range. This analysis will be integrated into the Final Report.

13.5. Statistical Methodology (WP50)

Task number	WP50	**Start date or starting event:**	M01 to M11
Participant ID	CONC		

Objectives:

- Complete a detailed description of the statistical methodology used to analyze the data

Description of Work:

Along with the actual fuel blending and analysis carried out in WP30, the statistical methodology forms the scientific underpinning for this project. In this Work Package, the CONCAWE partner will be responsible for assessing the statistical issues related to the overall project, including:

- An assessment of the relative importance of different fuel properties on volatility of ethanol/petrol blends,
- Statistical design of the base petrol and ethanol/petrol blends, based on this assessment,
- Analysis of the results of the laboratory fuel blending and analysis carried out in WP30, and
- An interpretation of these results on the impact of volatility changes due to ethanol blending on the environmental performance of these fuels in vehicles.

Task Descriptions:

- WP50-Task 1: The properties of a designed fuel matrix will be delivered to the Shell partner for action in WP30.

- WP50-Task 2: A detailed description of the statistical methodology will be integrated into the Interim and Final Reports.

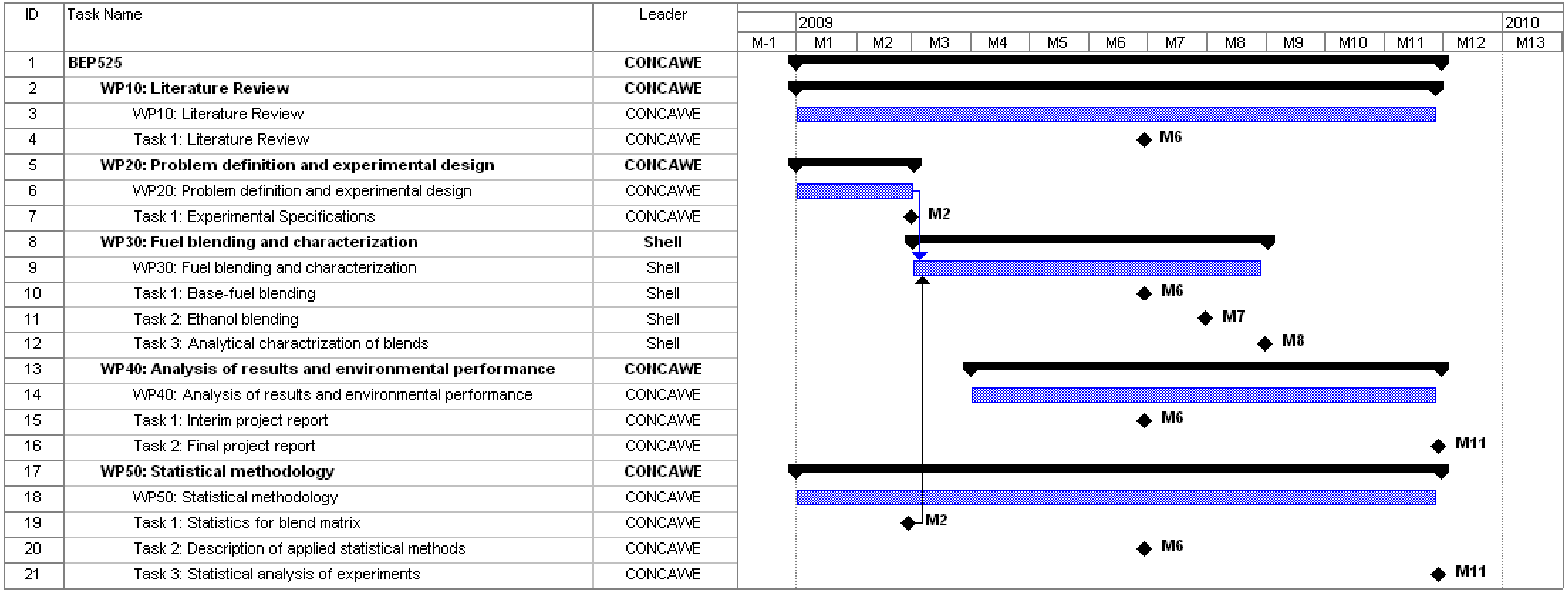
- WP50–Task 3: A detailed statistical analysis of the results of the fuel blending and characterisation activities will be integrated into the Final Report.

13.6. Project Deliverables

The requested project deliverables are the Interim and Final Reports which will contain the information shown below.

No.	Deliverable Name	Contents	Due	Contractor
1	Interim Report	o Literature review on the impact of ethanol on the volatility of ethanol/petrol blends and on vehicle driveability o Description and rationale for the fuel design matrix o Specifications and rationale for the analytical characterisation of the fuel blends o Preliminary data on blended fuels and their analytical characterisation o Preliminary analysis of the potential impact of ethanol on the environmental performance on ethanol/petrol blends based on published data o Description of the statistical methods used in the design of the fuel matrix	M06	CONC
2	Draft Final Report	All items shown above, updated with new information as appropriate, plus: o Composition and volatility data on all blended fuels o Analysis of the environmental performance of ethanol/petrol blends based on published and measured data o Detailed description of the statistical methods applied to the analysis of the fuel blends and volatility data	M11	CONC
3	Final Report	Draft Final Report including improvements, if requested by the Commission	M12	CONC

13.7. Project Timeline and Task Description



ID	Task Name	Leader
1	**BEP525**	**CONCAWE**
2	**WP10: Literature Review**	**CONCAWE**
3	WP10: Literature Review	CONCAWE
4	Task 1: Literature Review	CONCAWE
5	**WP20: Problem definition and experimental design**	**CONCAWE**
6	WP20: Problem definition and experimental design	CONCAWE
7	Task 1: Experimental Specifications	CONCAWE
8	**WP30: Fuel blending and characterization**	**Shell**
9	WP30: Fuel blending and characterization	Shell
10	Task 1: Base-fuel blending	Shell
11	Task 2: Ethanol blending	Shell
12	Task 3: Analytical charactrization of blends	Shell
13	**WP40: Analysis of results and environmental performance**	**CONCAWE**
14	WP40: Analysis of results and environmental performance	CONCAWE
15	Task 1: Interim project report	CONCAWE
16	Task 2: Final project report	CONCAWE
17	**WP50: Statistical methodology**	**CONCAWE**
18	WP50: Statistical methodology	CONCAWE
19	Task 1: Statistics for blend matrix	CONCAWE
20	Task 2: Description of applied statistical methods	CONCAWE
21	Task 3: Statistical analysis of experiments	CONCAWE

14. APPENDIX 5
Precision of E70 and E100 Measurements

It is difficult to obtain accurate values for E70 in fuels having high ethanol concentrations. This is because the distillation curves of the ethanol/petrol blends are unusually flat in the 70-80°C distillation range due to the formation of azeotropes between ethanol and the hydrocarbons comprising the blends [2]. The E70 values are especially affected by azeotrope formation because of the similarity of the specification temperature (70°C) and the normal boiling point of ethanol (78.4°C).

In this study, E70 and E100 were estimated from distillation curves that had been measured in triplicate using a PAC OptiDist™ Analyser. The measurements were completed according to standards IP 123/EN ISO 3405 using the automated method. The precision of Txx numbers obtained by this method is given in the standard method (**Table A5-1**) as:

Table A5-1 Repeatability (r) and reproducibility (R) of IP 123/EN ISO 3405 for ethanol/petrol blends having different RVP values [Ref A5-1]

For Group 1 Blends with RVP ≥ 65.5kPa			**For Group 2 Blends with RVP < 65.5kPa**		
Percent Evaporated	Repeatability r (^{o}C)[14]	Reproducibility R (^{o}C)[15]	Percent Recovered	Repeatability r (^{o}C)	Reproducibility R (^{o}C)
IBP	3.9	7.2	IBP	3.5	8.5
			2	3.5	2.6 + 1.92 S
5	2.131 + 0.673 S	4.397 + 1.998 S	5	1.1 + 1.08 S	2.0 + 2.53 S
10	1.691 + 0.673 S	3.337 + 1.998 S	10	1.2 + 1.42 S	3.0 + 2.64 S
20	1.131 + 0.673 S	3.337 + 1.998 S	20 to 70	1.2 + 1.42 S	2.9 + 3.97 S
30 to 70	1.131 + 0.673 S	2.617 + 1.998 S			
80	1.131 + 0.673 S	1.677 + 1.998 S	80	1.2 + 1.42 S	3.0 + 2.64 S
90	1.131 + 0.673 S	0.717 + 1.998 S	90 to 95	1.1 + 1.08 S	2.0 + 2.53 S
95	2.531 + 0.673 S	2.617 + 1.998 S			
FBP	4.4	8.9	FBP	3.5	10.5

In these equations, S is the slope of the distillation curve (°C/%v/v) at the evaluated temperature. The precision of Exx numbers is then obtained by dividing the precision of the corresponding Txx number by the slope, i.e.:

- $r(E70) = r(T_{E70}) / S$, $R(E70) = R(T_{E70}) / S$ (Eqn A5-1)

Example:

Figure A5-1 shows the middle portion of one of the measured distillation curves for a Group 2 Base Fuel #19 and its 25% v/v ethanol splash blend which is Group 1. In this example, the measured E70 values are 34.9% for the base fuel and 49.5% for the 25% v/v ethanol/petrol blend.

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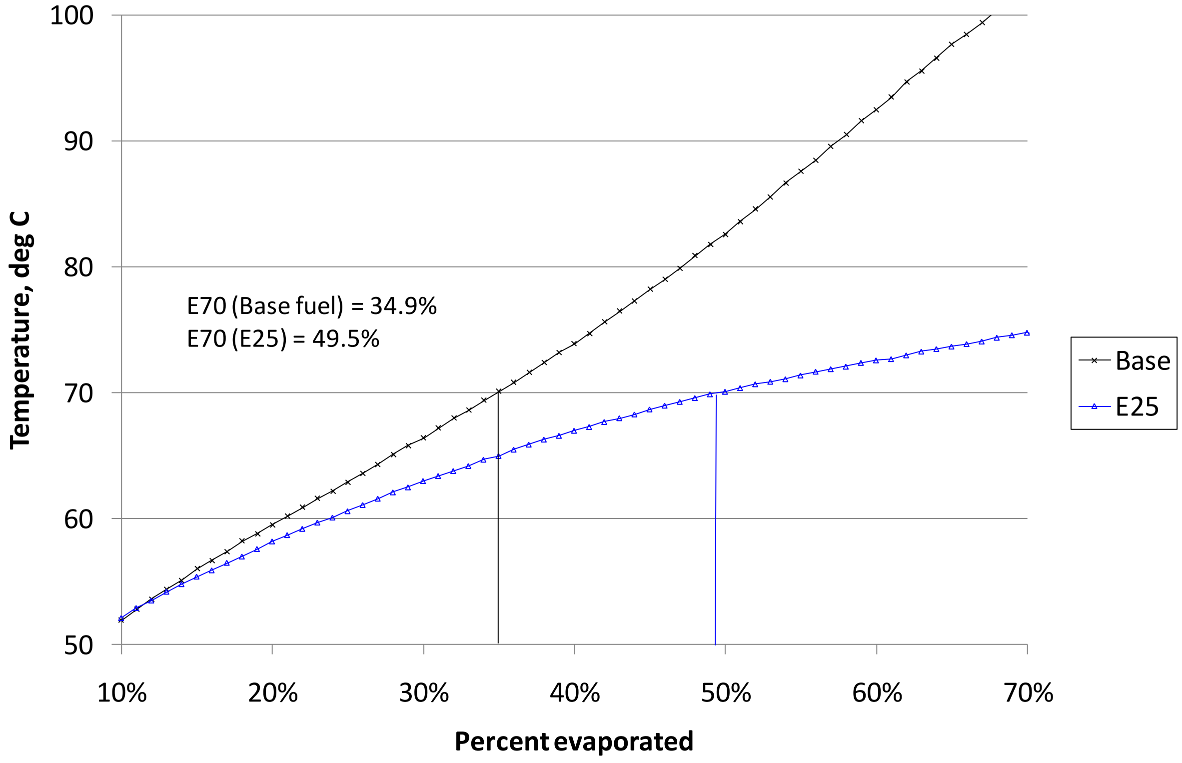
[14] Repeatability (r): The value equal to or below which the absolute difference between two single test results on identical material obtained by the same operator at the same laboratory using the same equipment in a short interval of time may be expected to lie with a probability of 95%.

[15] Reproducibility (R): The value equal to or below which the absolute difference between two single test results on identical material obtained by operators in different laboratories using the standardized test method may be expected to lie with a probability of 95%.

Figure A5-1 Example of two distillation curves for base fuel #19 and its 25%v/v ethanol splash blend



For the base fuel measurement, the slope of the distillation curve at E70 = 34.9% is approximately 0.75°C/%v/v, so:

- r (at $T_{34.9}$) = 1.2 + 1.42 x 0.75 = 2.26
- R (at $T_{34.9}$) = 2.9 + 3.97 x 0.75 = 5.88

Thus:

- r (E70) = 2.26 / 0.75 = 3.02
- R(E70) = 5.88 / 0.75 = 7.84

For the corresponding 25% v/v ethanol/petrol blend, the slope at E70 = 49.5% is much flatter (0.27°C/%v/v) and so:

- r (at $T_{49.5}$) = 1.131 + 0.673 x 0.27 = 1.31
- R(at $T_{49.5}$) = 2.617 + 1.998 x 0.27 = 3.16

And:

- r (E70) = 1.31 / 0.27 = 4.86
- R(E70) = 3.16 / 0.27 = 11.7

Thus, the precision of E70 measurements is about 50% worse for the 25% v/v ethanol/petrol blend than for the base fuel, because of the flattening of the distillation curve due to ethanol addition and azeotrope formation.

The 25% v/v ethanol blends do in fact lie outside of the scope of EN ISO 3405 [Ref A5-1] which states: “The method is only applicable to petroleum products incorporating a minor constitution of components from non-petroleum origin, but the precision data may not apply in all cases”. The ASTM D86 standard [Ref A5-2] similarly restricts the scope of the D86 method to gasolines containing 10% v/v ethanol or less.

With a reproducibility (R) as high as 12%, the measured values of E70 of 25% v/v ethanol/petrol blends by EN ISO 3405 (or ASTM D86) are clearly very sensitive to small changes in measurement conditions.

The E100 measurements pose less of a problem because the slopes of the distillation curves are generally steeper at 100°C, regardless of the ethanol concentration.

Future work should investigate other measures of volatility that would be more precise and more appropriate for petrol containing higher ethanol concentrations.

Appendix 5 References:

Ref A5-1 International Standard EN ISO 3405. Petroleum products – determination of distillation characteristics at atmospheric pressure

Ref A5-2 ASTM International Standard D86-07b. Standard test method for distillation of petroleum products at atmospheric pressure

15. APPENDIX 6
Assessment of Environmental Performance

Specific references related to ethanol and environmental performance can be found in **Section 15.7**.

15.1. Regulated Exhaust Emissions

Regulated exhaust emissions from vehicles comprise carbon monoxide (CO), hydrocarbons (HC), Volatile Organic Compounds (VOCs), nitrogen oxides (NOx), Particulate Matter (PM), and Particle Number (PN) (See **Section 15.3**).

The quantitative measurement of hydrocarbons from vehicles is a complicated and specialized task because there are a wide range of hydrocarbons emitted. European legislation requires these to be measured as Total Hydrocarbons (THC) while, in the USA, they are regulated as Non-Methane Organic Gases (NMOG). The NMOG measurement does not include methane which can be a substantial part of total HC exhaust emissions. Hence, European and US emissions standards cannot be directly compared.

The main effect of ethanol on engine operation is to make the air/fuel ratio (AFR) of the mixture leaner. This is because the oxygen in the ethanol (or other oxygenate) molecule increases the oxygen concentration in the air/fuel mixture. A 10% v/v ethanol/petrol blend contains about 3.7% m/m oxygen which can change the AFR. The effect, however, depends on the sophistication of the engine technology which has been defined below in four different categories[16]:

Category 1: Older engines without exhaust aftertreatment catalysts that operated with fixed calibration carburettors or simple fuel injection systems. These engines run significantly leaner at all conditions on ethanol/petrol blends.

Category 2: First-generation ‘3-way catalyst’ systems having an oxygen sensor and a rudimentary engine management system (EMS) to control the AFR to exactly stoichiometric during normal running conditions. (Stoichiometric control is necessary in order for the 3-way catalyst to simultaneously control the emissions of CO, HC, and NOx.) Because the EMS exactly controls the AFR, the presence of ethanol in the petrol is not expected to have a leaning effect on the AFR.

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[16] These categories do not represent industry-accepted terms but are used in this section to clarify the impact of ethanol/petrol blends on different vintages of engine/vehicle technology.

Under cold-starting conditions, however, the EMS does not operate and the engine intentionally runs rich (more fuel than normally required) to ensure good driveability performance until the engine and catalyst are fully warmed up. Thus, the leaning effect of ethanol on the AFR does occur during cold-starting and warm-up conditions. This is beneficial since the highest exhaust emissions will occur before the 3-way catalyst becomes fully warmed-up and operational.

Category 3: Modern engines having a Multi Point Fuel Injection (MPFI) system, complex EMS, and more sophisticated exhaust aftertreatment systems. In this category, the EMS includes “adaptive learning” where the control system slowly “learns” the stoichiometric AFR of the fuel in the tank and corrects for changes during subsequent operation, including cold starts. The primary input to the EMS is the oxygen sensor in the exhaust system that informs the EMS of the actual engine-out combustion mixture. Thus, these modern systems are not expected to be sensitive to the presence of ethanol in the petrol but this is not always the case.

Category 4: The latest engine technology is Gasoline Direct Injection (GDI, also Direct Injection Spark Ignition (DISI)) where fuel is injected directly into the cylinder rather than into the inlet manifold. This approach provides less time for vaporisation of the injected fuel mixture and very sophisticated EMS with adaptive learning are used. Of course, the exhaust aftertreatment system is also quite sophisticated and fully optimized to the engine and vehicle design in order to achieve the desired emissions level.

There are usually considered to be two generations of GDI engines that depend on how the injected air/fuel mixture is guided toward the spark plug for ignition. In the first generation approaches, the air/fuel mixture is typically guided to the spark plug by means of a specially designed piston bowl (so-called ‘wall-guided’) or by a combination of the piston bowl design and intake port (so-called ‘air-guided’). Second generation approaches (so-called ‘stratified charge’) inject the air-fuel mixture into the top of the combustion chamber and directed toward the spark plug. In this approach, the air/fuel mixture is richer near the spark plug and leaner near the combustion wall. Most GDI engines today use first generation approaches although the more complicated second generation approaches are starting to appear on some higher-end vehicles. Because of their design features, first generation approaches are not expected to be very sensitive to ethanol while there is not yet enough data available on second generation GDI engines.

Figure 36 (in **Section 6**) shows the approximate regulated emissions levels for HC + NOx that correspond to the four categories of vehicle technology described above. Hydrocarbons plus NOx was chosen for this comparison because early EU and US emissions regulations focused on these emissions due to their contribution to smog and ozone formation. In the USA, emission limits that were low enough to require aftertreatment catalysts were introduced in 1975 and have been progressively reduced since that time. In Europe, however, catalysts were only required from 1992 at which point the technology quickly moved to Category 3. There is some overlap between different categories and US and European limits are not directly comparable because of different test cycles etc. This figure does show, however, how emission limits have dropped by more than 95% in 30 years with the introduction of new engine technology. At the same time, fuel specifications have changed to enable these new technologies, with the most significant change being the introduction of low-sulphur and sulphur-free petrol and diesel fuels.

This categorization approach has been used to better understand the effect of low-level ethanol/petrol blends on vehicle emissions. Since the average lifetime of European vehicles is about 12-14 years, most of the Category 1 and 2 vintage vehicles are no longer significant contributors to the on-road fleet while Category 4 vehicles have just started to enter the light-duty fleet.

Ethanol does have other effects on emissions. Ethanol has a high latent heat of evaporation so that ethanol blends are more difficult to vaporise in the inlet system of the engine, which can degrade driveability and increase emissions. Ethanol forms constant boiling point azeotropes with hydrocarbons which substantially affects fuel volatility. Partially combusted ethanol also forms acetaldehyde which is a photochemically reactive compound, and is designated as an “air toxic” in US legislation.

There have been many studies over the years to assess the effects of low concentration ethanol blends on exhaust emissions. The main studies are summarised in **Table A6-1**, which shows the average percentage change in emissions found for different vehicle technology categories. Clearly, there is a wide variation in results and it is not possible to directly compare studies carried out by different groups, because the vehicles, test cycles, and ethanol/gasoline blends are all somewhat different.

It is possible, however, to use a “weight of evidence” approach in order to draw some general conclusions from all of the available data. That is, general trends can be inferred from the published studies even though details regarding the vehicles, fuels, and driving cycles may be different from one report to another.

The published studies typically measure percentage changes for 5 to 10% v/v ethanol in petrol on emissions although a few studies have tested petrol blends containing up to 20% v/v ethanol. All of the observed changes in **Table A6-1** are expressed as a percentage of the baseline emissions in the same study. The absolute emissions varied from one study to the next depending upon the emission standard and the category of engine technology.

For non-catalyst vehicles (Category 1), ethanol substantially reduces CO emissions with smaller reductions in HC emissions, as shown in particular by the older Australian Orbital studies [11,12]. At the same time, ethanol significantly increases NOx by about 10% in Category 1 vehicles.

Similar percentage changes in emissions have been reported for early catalyst vehicles (Category 2) tested on ethanol/petrol blends. In general, CO emissions are reduced by 10-20%, HC or NMOG by 5-10%, while NOx is increased by more widely varying amounts from 5-30%. One of these Australian studies [12], however, showed much greater effects of ethanol after 80,000 km durability. This was attributed to higher catalyst operating temperatures on ethanol blends which greatly increased the deterioration factors.

For advanced catalyst (Category 3) vehicles, the effects of ethanol are generally (but not always) smaller and more variable, but usually show the same directional change. Clearly absolute effects will be much lower for these modern low-emissions vehicles but it is surprising that significant effects of ethanol are still seen for sophisticated modern vehicles with advanced electronics. However, most of the emissions occur during cold start before the catalyst has warmed up to operating temperature, and with the electronic control system in “open loop” mode.

There is little information available in the published literature on new GDI (Category 4) vehicles, with only one Canadian study [23] on one test vehicle. Although the results are limited on this new technology, the study appears to give broadly similar results on the GDI vehicle to previously tested Category 3 vehicles.

Table A6-1 Summary of literature studies: effect of ethanol in petrol on regulated exhaust emissions

				Vehicles		% Change in Exhaust Emissions			
Programme	**Reference**	**Year**	**Fuel^1**	**Number**	**Technology Category**	**CO**	**THC**	**NMOG**	**NOx**
AQIRP Auto/Oil (USA)	1	1990	10%S	20 USA (1989)	2	-13.4	-	-4.9	+5.1
US EPA	29	1994	10%M	36 USA – 20 Normal	2	-8.6	-7.3	-	+5.7
				16 (1986-1990) - 16 High E		-25.3	-19.3		NS
US EPA	30	1994	10%M	39 USA – 27 Normal	2	-7.3	NS	-	NS
				12 (1986-1990) - 12 High E		-12.1	NS		NS
CARB Study	4	1998	10%S	12 USA (1991-1995)	2-3	-7	+8	+8	+17
Toyota Study	5	2000	9%S	9 LEV/ULEVs USA	3	-6	-	-0.3	+5.5
US EPA & Alaska Study	3	1998	10%(S)	11 USA (1977-1994) at – 24°C	1-2	-21	-14	-	-5
				3 USA (1988-1994) at -7°C		-8	-7		-1
				11 USA (1977-1994) at -21°C		-27	-24		-6
				11 USA (1977-1994) at -41°C		-17	-14		+6
Thailand Petroleum Authority	31	1999	(7.5) 15(M)	5 Catalyst (1994-1996)	2	-32	-6		+15
				1 Non-catalyst (1993)	1	-9	NS		+12
AEAT study for UK DTLR (special cycles)	6	2002	10%S	5 Euro 3	3	-20.8	?	-	NS
Swiss EMPA study	7	2002	5%S	1 Euro 3	3	-7	-8.4	-	+14.3
Shell Study	8	2002	5, 10%M	3 Euro 3 - 5%	3	-7	NS	-	+28
				10%		-21			+42
ADEME Study	10	2003	5, 10%S	3 MPI Euro 3	3	?	?		?
				1 DISI Euro 3					
Orbital Engine Company (Australia)	11	2003	20%	5 New (2002) Urban	2	-29	-30		+48
				5 New (2002) Highway	2	-48	-25		unclear
				4 Old (1985-1993) Urban	1	-70	-4		+9
				4 Old (1985-1993) Highway	1	-76	-10		+10
Orbital Engine Company (Australia)	12	2004	20%	2x5 (2001) New Australia 80,000km	2	-13	-12		+30
					2	+19	+33		+82
IDIADA Study	13	2003	5-10%	1 2003 Euro 3	3	-6	-13	-	0
Fortum Study	14	2004	10%M	10 1999 – 2002	3	NS	NS		NS
			vs ETBE	Euro 3					
Westerholm, Egeback, Rehnlund, Henke	17	2004	Up to 15%	Review of various studies		NS	NS	NS	NS
Niven (Australia)	18	2005	10, 85	Review of previous studies		↓	↓	↓	↑
Coordinating Research Council (US CRC) E67	19	2006	5, 7, 10	12 CA (USA) LEV-SULEV	3	-6 to -18^2	NS	+14	+5 to -12^2
Environment Canada Study	21	2002	10, 15, 20	5 (1999-2001)	2-3	-12 to -49		NS	??
Environment Canada Study	22	2006	10, 20	3 (1998–2003) at 20°C	3	-15 to -73	**	**	-77
				1 DISI (2000) at 20°C	4	-3 to -55	-35	-39	+???
				3 (1998–2003) at -10°C	3	?	**	**	-145
				Overall statistical analysis		-16	+9	+14	NS

NOTES:
1. 10%S = 10% v/v ethanol splash blend; 10%M = 10% v/v ethanol matched volatility
2. depends on volatility, T50 and T90
NS = not significant
**** THC increased with 10% ethanol, decreased with 20% ethanol**
?? Results were variable and difficult to interpret
Arrows in this table represent directional trends

15.2. Unregulated Exhaust Emissions

The US EPA classifies a number of organic compounds as “air toxics”: benzene, formaldehyde, acetaldehyde, 1,3-butadiene and “polycylic organic matter (POM)”. In US regulations, vehicle emissions of these “toxics” are not directly regulated but are controlled through fuel specifications (by means of the so-called ‘simple’ and ‘complex’ models). There have been a number of studies that have measured the exhaust emissions of these compounds. POM, however, is not easily defined and has generally not been measured in great detail.

Many studies on unregulated emissions have now been completed and the results vary substantially as shown in **Table A6-2**. However, the same “weight of evidence” approach can be used to draw some general conclusions from the reported results.

Benzene emissions are generally reduced with ethanol blends. Engine-out benzene has been shown to originate almost entirely from unburned benzene and from partially burned aromatics in the fuel. Ethanol normally reduces the petrol’s aromatics content. This can occur either by simple dilution for splash blends or by reblending the base petrol to take advantage of ethanol’s high octane number. Reblending can have a substantially larger impact on benzene emissions than simple dilution. The CRC [19] and Environment Canada [22,23] studies showed somewhat higher benzene emissions although the test fuels used in these studies were blended to have essentially constant benzene and aromatics levels. In the Environment Canada studies, benzene and aromatics levels of the summer grade ethanol blends were much higher than for the base petrol.

1,3-butadiene emissions are either unaffected or are reduced with ethanol/petrol blends. Again, there are exceptions such as the CRC study and the Environment Canada study which showed a significant increase in 1,3-butadiene emissions with ethanol/petrol blends. For the CRC study, this was consistent with the 14% increase in NMOG (see **Table A6-1**). It should be noted, however, that these results only apply to fuels with high T90E levels. There is no clear explanation for the Environment Canada study results, which were very variable and generally not statistically significant.

Formaldehyde emissions have generally been shown to be unaffected by ethanol content. This is not surprising because formaldehyde is not a partial combustion product of ethanol. **Acetaldehyde** however is easily formed by partial combustion of ethanol, so very substantial increases in acetaldehyde emissions have been seen at up to a factor of 10 higher values. However, this is one case where percentage changes can be misleading because mass emissions of acetaldehyde are very low for modern catalyst vehicles (Categories 3 or 4). Levels are well below 1 mg/mile, over the full emissions test cycles, and essentially zero once the catalyst is fully warmed up.

Not surprisingly, unburned **ethanol** emissions are also significantly increased, though here again emission levels from hydrocarbon fuels are essentially zero so large percentage increases are misleading. Emission rates from modern vehicles are of the order of a few mg/mile during cold start operation and well below 1 mg/mile once the catalyst has been fully warmed up.

Various other unregulated emissions have been measured in some studies, including higher aromatics, ammonia, acrolein and other aldehydes, nitrous oxide etc. However, no significant effects have been found except for aromatics which are generally reduced with ethanol for the same reasons as they are for benzene.

Table A6-2 Summary of effects of low concentrations of ethanol on unregulated exhaust emissions

				Vehicles		% Change in Exhaust Emissions				
Programme	Reference	Year	Fuel[1]	Number	Technology Category	Benzene	1,3-butadiene	formaldehyde	acetaldehyde	Ethanol
AQIRP Auto/Oil Study (USA)	1	1990	10%S	20 USA (1989)	2	-11.5	-5.8	+19	+159	-
US EPA and SWRI	28	1990	10%M	5 USA (1974-1990)	1-2	↓	NS	NS	↑	-
US EPA	29	1994	10%M	36 USA – 19 Normal (1986-1990) - 15 High E	2	-27.2 -42.4	No report	NS NS	+89 +138	
US EPA	30	1994	10%M	39 US – 27 Normal (1986-1990) - 12 High E	2	-29.4 -36.3	NS NS	NS NS	+54 +64	
CARB Study	4	1998	10%S	12 US (1991-1995)	2-3	Total toxics +9% Potency weighted toxics -1%				
US EPA & Alaska Study	3	1998	10%(S)	11 US (1977-1994) at – 24°C 3 US (1988-1994) at -7°C 11 US (1977-1994) at -21°C 11 US (1977-1994) at -41°C	1-2	-13.6 -20.1 -26.5 -13.4	NS	NS	+156 +453 +261 +316	-
Thailand Petroleum Authority	31	1999	(7.5) 15(M)	5 catalyst (1994-1996) 1 non-catalyst (1993)	2 1	-1.7 -3.2	NS +5.3	+37 +61	+231 +295	
AEAT Study for UK DTLR (special cycles)	6	2002	10%S	3 EURO 3	3	-	-27.6	NS	+514	-
Shell Study	8	2002	5, 10%M	3 EURO 3 - 5% 10%	3	-	-	-	+100 +230	-
ADEME Study	10	2003	5, 10%S	3 MPI EURO 3 1 DISI EURO 3	3 4	-	-	-	?	-
Orbital Engine Company (Australia)	11	2003	20%	5 New (2002) Urban 5 New (2002) Highway 4 Old 1985-93 Urban 4 Old 1985-93 Hway	2 2 1 1	-40 -20	-?? -15	NS NS	~+1000 +700	- -
Orbital Engine Company (Australia)	12	2004	20%	2x5 (2001) Base Australia 80,000km	2	NS NS	NS NS	-60 +49	+250 +610	-
IDIADA Study	13	2003	5-10%	1 2003 Euro 3	3	-13.6	-1.3	-68	-36	>+100
Coordinating Research Council (US CRC) E67 Project	18	2006	5, 7, 10	12 California LEV - SULEV	3	+18	+22	NS	+73	-
Fortum Study	14	2004	10%M vs ETBE	10 EURO3 (1999–2002)	3	-22	-15	NS	+180	
Westerholm, Egeback, Rehnlund, Henke	17	2004	Up to 15%	Review of various studies		↓	-	↑	↑↑	-
Niven (Australia)	18	2005	10, 85	Review of previous studies		↓	↓↑	↓↑	↑	↑↑
Environment Canada Study	22	2002	10, 15, 20	5 (1999-2001)	2-3					
Environment Canada Study	23	2006	10, 20	3 (1998–2003) at 20°C 1 DISI (2000) at 20°C 2 (1998–2003) at -10°C Overall Statistical Analysis	3 4 3	? ? ? +15	? ? ? +16	+NS NS NS	-845 +400+ +108	+170 +300 >1000 -

NOTES:
1. 10%S = 10% v/v ethanol splash blend; 10%M = 10% v/v ethanol matched volatility
NS = not significant
?? Results were variable and difficult to interpret
Arrows in this table represent directional trends

15.3. Particulate Emissions

Exhaust emissions of **Particulate Matter** (PM) are increasingly a concern for human health. PM emissions from gasoline engines are normally very low and difficult to measure, although somewhat higher PM emissions have been measured from DISI vehicles. There is however increasing concern about “ultrafine” or “nano-particles” (below 1 micron) which can be produced in large numbers. These are normally counted as total or solid Particle Number (PN) emissions rather than being weighed gravimetrically as are PM emissions.

A recent European study [32] showed that DISI vehicles produced 4–11 mg/km PM over the NEDC cycle. Conventional gasoline vehicles produce emissions <3 mg/km which is near the limit of detection of gravimetric methods. Solid PN were measured with an Electrical Low Pressure Impactor (ELPI) which showed that diesel vehicles produced ~10^{14} particles/km, DISI vehicles were a factor of 10-20 below that, while conventional gasoline vehicles were at least two orders of magnitude (~10^{11} particles/km) lower than those from DISI vehicles and similar to diesel vehicles equipped with particulate traps. Unfortunately, this programme did not look at the effect of ethanol on particulates.

Several studies have been carried out to determine the effects of ethanol on PM and PN emissions, as shown in **Table A6-3** and **Figures A6-2, A6-3,** and **A6-4**. The overall conclusion from this limited study was that both PM and PN emissions are reduced with ethanol blends. The Environment Canada study [22] did show some increases in both emissions but the results were quite variable, as shown in **Figure A6-4**.

Table A6-3 Summary of effects of low concentrations of ethanol on particulate exhaust emissions

				Vehicles		% Change in Exhaust Emissions			
						PM	Particle Number		
							CPC^1	CPC	
Study	Reference	Year	Fuel*	Number	Technology Category	Filter	W/O TD^2	With TD^2	ELPI^3
EPA and Alaska Dept. Env. & Cons.	27	1997	10	EPA – 3 (1987-1994)	2	↓	-	-	-
				5 (1977-1994)	1-2	↓			
AEAT Study for UK DTLR (special cycles)	6	2002	10%S	3 EURO 3	3	-39	See Fig A6-2	-	↓
EMPA Study (Switzerland)	7	2002	5%S	1 EURO 3	3	-	-8	-18	
Westerholm, Egeback, Rehnlund, Henke	17	2004	Up to 15%	1 (1985) Cat at 22°C	2	NS	-	-	
				-5°C		-11			
Fortum Study	14	2004	10%M	3 EURO3 (1999–2002)	3	-27 to -65	-	-	-
			vs ETBE						
Environment Canada Study	22	2006	10, 20	3 (1998–2003) at 20°C	3	↑NS	NS	-	NS
				1 DISI (2000) at 20°C	4	↑	NS		NS
				3 (1998–2003) at -10°C	3	↑NS	NS		NS

NOTES:
***10%S = 10% v/v ethanol splash blend**
***10%M = 10% v/v ethanol matched volatility**
NS = not significant
Arrows in this table represent directional trends

Definitions:
1. Condensation Particle Counter
2. Thermal Desorber
3. Electrostatic Low Pressure Impactor

Figure A6-2 CPC PN emissions on gasoline and E10 over a cold start cycle (AEA [6])

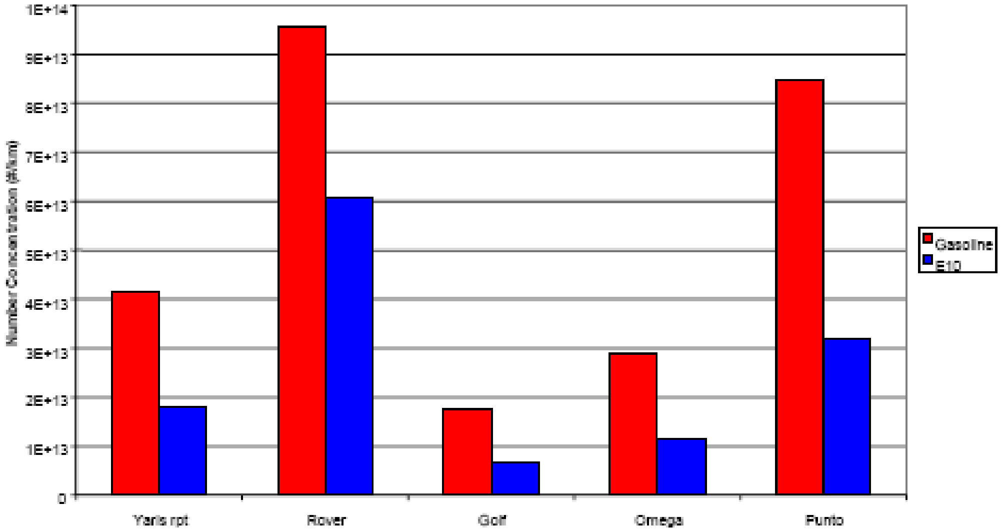


Figure A6-3 CPC Particle emissions (with and without Thermal Desorber) on gasoline and E5 over NEDC (EMPA [7])

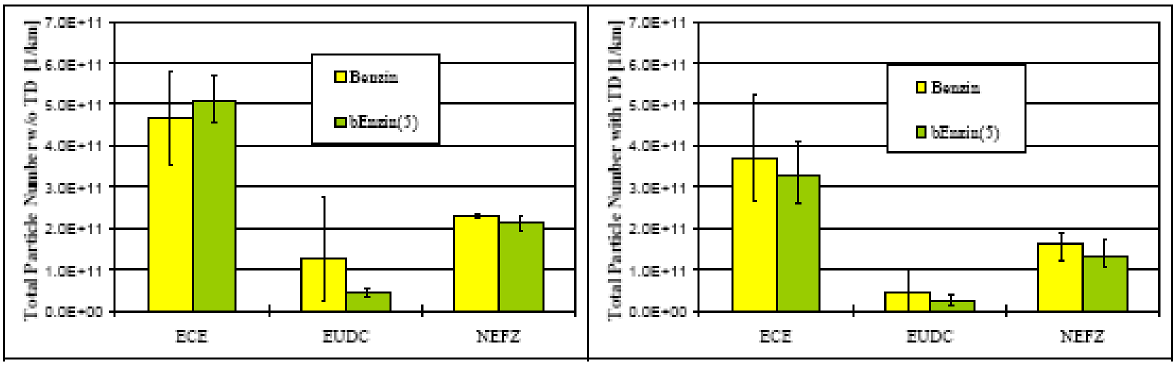
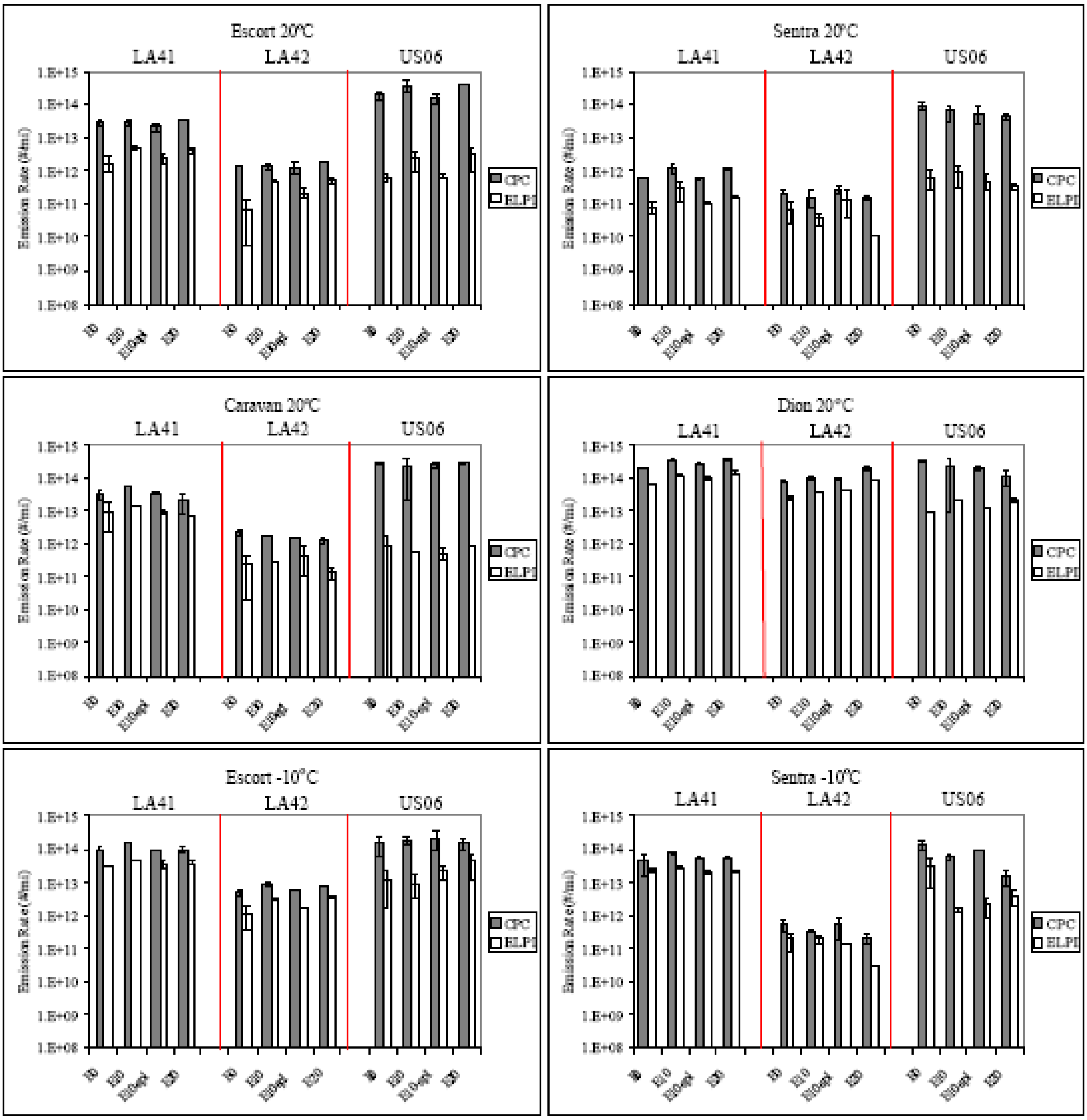


Figure A6-4 Average PN emission rates measured using the CPC and ELPI ± 1 standard deviation (note: logarithmic scale) (Environment Canada Study [22])



15.4. Evaporative Emissions

The use of ethanol/gasoline blends can affect several aspects of evaporative emissions:

- Increased volatility of the blends, especially DVPE and E70 if not controlled, will increase the amount of vapour that the evaporative control system must minimize.
- Compared to most hydrocarbon molecules in petrol, ethanol has different adsorption and desorption characteristics in carbon canisters and may remain as a “heel” in the active carbon, reducing the working capacity of the carbon canister.

- Ethanol is a polar molecule and may increase permeation through plastics and elastomers used in vehicle fuel systems.

These issues are considered in more detail below.

Vapour Generation

The mass of vapour generated will be different during normal driving (Running Losses), when the hot vehicle is resting after use (Hot Soak losses), and when the cold vehicle is resting overnight and experiencing atmospheric temperature fluctuations (Diurnal Emissions). The vapour generation will depend on the fuel system design, the permeability of the fuel system components, the fuel's volatility, and the temperature. Evaporative control systems with carbon canisters must be designed to cope with this mass of vapour under all conditions.

Work done by CONCAWE [34] in the 1980s on vehicles without evaporative emission control systems showed that Reid Vapour Pressure (RVP) was the only fuel variable that significantly affected the mass of Hot-Soak and Diurnal emissions. A linear increase in evaporative emissions with increasing RVP was seen in this study but a subsequent study on cars with evaporative control systems [35] showed an exponential effect of both RVP and measurement temperature. Unfortunately, neither of these programmes tested ethanol blends although the first study did include methanol/TBA and MTBE blends with matched volatility. Some tests showed no effect of oxygenates on evaporative emissions so that the conclusion was that only RVP was important. The second CONCAWE study [35] estimated vapour emissions from uncontrolled vehicles and late 1980s canister equipped vehicles on a 93 kPa fuel at 28°C as:

	Hot Soak g/test	Running Loss g/km	Total Daily Loss* g/day
Uncontrolled cars	8.0	1.06	64.2
Controlled cars	0.9	0	3.1

*TDL = 3.4*Hot Soak + 35*Running Loss

Diurnal emissions were not measured in this work, but other work has shown that they are the most important source of emissions for vehicles fitted with canisters. In a recent test programme run at the EU's Joint Research Centre in Ispra [36], total diurnal emissions were calculated from the weight gain of the carbon canister. The following results were obtained for one vehicle tested using the EU diurnal test procedure on a 60 kPa fuel (A) and on two 5% v/v ethanol blends, one with matched volatility (A5E) and one prepared by splash blending (A5S).

Fuel	A	A5E	A5S
DVPE (kPa)	60.1	59.7	67.1
Ave. Diurnal Emissions (g/test)	18.8	21.5	22.8

In an extension of this programme [38], diurnal emissions up to 50 g/test were measured for higher volatility/temperature combinations but this work did not cover ethanol blends.

In the USA, a study in the 1980's [37] investigated emissions from gasoline/alcohol blends. The results showed that a gasoline blend with a methanol/TBA mixture gave lower mass hot soak and diurnal emissions than did a hydrocarbon-only gasoline even though both fuels had very similar distillation curves. A mathematical model of evaporation from fuel systems was developed that predicted this behaviour and showed that it was due to lower vapour pressures of oxygenated fuels at the test temperatures and the lower molecular weights of the vapours generated by these fuels. Increased emissions from gasoline/alcohol blends in other test programmes were shown to be due to their higher volatility. This work did not look at ethanol alone, although a methanol/ethanol blend was modelled. It is expected that ethanol blends would behave in the same way, however.

Thus it would appear that the use of ethanol does not increase the mass of evaporative emissions for blends at the same volatility levels as hydrocarbon-only fuels. However, most ethanol blends are more volatile than hydrocarbon fuels and it is the increase in DVPE and front-end volatility due to splash blending that can increase the evaporative emissions.

Canister adsorption and desorption

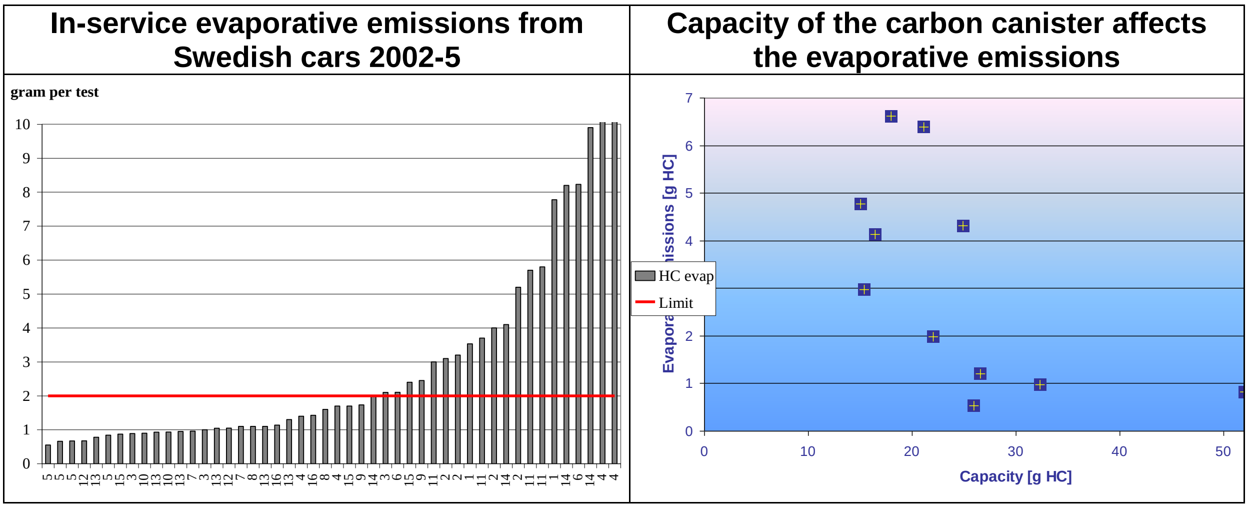
All modern vehicles are fitted with activated carbon canisters that are used to adsorb gasoline vapour emissions from the fuel system. These canisters must of course be designed with sufficient capacity to absorb all vapours generated during normal operation, and a purging system to draw these vapours into the engine and burn them. However, the "working capacity" of a canister is only around 40–50% of its total equilibrium absorption capacity and is heavily dependent on canister design and purge conditions. A "heel" of material that cannot easily be desorbed from the carbon can accumulate over a few operating cycles. Larger hydrocarbon molecules are less easily desorbed so the average molecular weight of the heel increases over time. For a typical one litre canister, this heel of adsorbed material is about 60-90g with a working capacity of 50-60 g of vapour. The canister working capacity must be adequate to adsorb all hot soak and diurnal emissions. If this is not the case, then vapour "breakthrough" can occur and the excess fuel vapour will be emitted to the atmosphere.

Ethanol is more easily adsorbed on activated carbon than butane and other hydrocarbons. For this reason, it has been suggested that an ethanol heel may build up significantly reducing the canisters working capacity. Work at the University of North Dakota [2] showed that there were increased levels of ethanol in the breakthrough vapour from canisters, and a longer time to breakthrough. However, recent work by MeadWestVaco [39] on modern activated carbons showed that ethanol is easily desorbed even though it is more readily absorbed than butane. Subsequent aging tests showed no significant loss of the canister's working capacity over 500 load/purge cycles.

The JEC study [36] on the effect of ethanol on evaporative emissions did not reach clear conclusions on this question due to problems with the test procedure. It was observed that there was a clear effect of DVPE but not of ethanol as such on evaporative emissions. The canister conditioning procedure used for this programme allowed the canister weight to build up over successive tests, which may have been due to increased hydrocarbon loading or a build-up of ethanol.

Thus, although ethanol is more easily adsorbed, it does not appear to build up a long term heel. However in-service testing in Sweden [40] has shown reduced working capacity of canisters on vehicles that fail the evaporative emissions test, which may be due to the use of ethanol blends in Sweden (see **Figure A6-5**). Of the 50 vehicles tested between 2002 and 2005, 40% (20 vehicles) exceeded the limit value of 2g/test. This can be compared to the results from a similar German programme where only 2 of the 19 vehicles tested (10%) failed the test. The difference was thought to be due to the ethanol content of the market fuels in both testing regions at the time of this study.

Figure A6-5: Swedish in-service evaporative emissions testing [40]



In-service evaporative emissions from Swedish cars 2002-5

Capacity of the carbon canister affects the evaporative emissions

Permeation

Historically, fuel tanks, lines and carburettors were made of metal, with only a few flexible hoses to connect them, so permeation was not an issue. For modern vehicles however, fuel tanks are generally made from high-density polyethylene (HDPE), and fuel lines and other components from a range of plastics and elastomers.

Hydrocarbons can permeate through polymers and elastomers because permeation is a function of the solubility of the molecule in the polymer and its diffusion rate through the polymer, which is driven by the concentration gradient. The size and shape of the molecule is important because smaller molecules can pass more easily through the “spaces” between polymer molecules.

Thus, straight chain molecules are expected to permeate more rapidly through polymeric materials than branched chain or cyclic molecules. Neat ethanol has relatively poor solubility in HDPE. In ethanol/gasoline mixtures, however, aromatic molecules in the gasoline have good solubility in HDPE and can increase the permeation of both aromatics and ethanol through the polymer by increasing the spacing between polymer molecules.

Permeation rates are measured with standard test fluids, e.g. ASTM Fuel C which is a 50/50 mixture of iso-octane and toluene. **Table A6-4** shows measured permeation rates through various fuel system materials for Fuel C and a 10% ethanol blend. Nitrile Butadiene Rubber (NBR) and Nylon showed high permeation rates as did the fluorosilicone rubber. The other materials are all fluoropolymers which show much lower permeation rates although almost all polymers show very substantial increases when ethanol is blended into the fuel.

Table A6-4 Average permeation rate (g x mm)/(m^2 x day) for different materials [42]

Material	ASTM Fuel C	10% Ethanol	% Increase
NBR (33% ACN)	669	1028	54
FVMQ (Fluorosilicone)	455	584	28
HNBR (44% ACN)	230	553	140
Nylon 12	5.5	24.0	336
FKM GLT (65% F)	2.6	14.0	438
FKM GFLT (67% F)	1.8	6.5	261
FKM A200 (66% F)	0.8	7.5	838
FKM B70 (66% F)	0.8	6.7	738
FKM B200 (68% F)	0.7	4.1	486
FKM GF (70% F)	0.7	1.1	57
PFA 1000LP	0.1	0.03	-40
FEP 1000L	0.03	0.03	0
ETFE 1000LZ	0.03	0.1	67

A major study was carried out by the US CRC [20] on behalf of the California Air Resources Board (CARB) to investigate the effects of ethanol on permeation through vehicle fuel systems. They removed the complete fuel systems from 10 vehicles dating from 1978 to 2001, mounted them on test rigs and measured permeation rates. The fuels tested included a hydrocarbon-only fuel, a 10% MTBE blend and a 5.9% ethanol blend with volatilities matched as closely as possible. Results showed that the ethanol blend increased total permeation emissions for all vehicle fuel systems. Even the non-ethanol part of the emissions was higher than for Fuel A (MTBE blend) or Fuel C (hydrocarbon only). The average increase in permeation was about 45% compared to the hydrocarbon-only fuel.

An extension of this work [21] looked at the effects of higher concentration ethanol blends on five modern low-emission fuel systems. All of these vehicles had much lower emissions, with the highest only around 1.5g/day, similar to the lowest result in the previous study. Again, ethanol increased permeation from all vehicles, although Rig 12 (from a PZEV) showed very low emissions and only a small effect of ethanol on permeation.

Clearly, ethanol does have an impact on permeation. However, modern fuel systems are increasingly manufactured from newer materials that are compatible with higher ethanol concentrations. Fuel hoses are often composite materials with a fluorocarbon inner layer to control permeation and a polymeric outer layer to give greater flexibility. Fuel tanks are typically made from HDPE to facilitate molding and reduce vehicle weight but with multiple internal layers of another polymer in contact with the fuel to control permeation.

Overall Effect on Evaporative Emissions

A number of studies looked at the overall effect of ethanol blends on vehicle evaporative emissions, including all the effects described above. Only the major studies are reviewed here.

The 1992 US AQIRP programme [1] looked at the effect of RVP and 10% ethanol on ten 1989-model US vehicles equipped with activated carbon canisters. The study showed that splash blending of ethanol increased the diurnal emissions by 30% and hot soak emissions by 50%. Several vehicles were found to have higher than expected levels of toluene in the measured emissions suggesting that fuel permeation or leakage might be important.

Another US EPA study [3] at around the same time showed that, for one vehicle, diurnal emissions from a matched volatility 8% ethanol blend were 45% higher than from the base hydrocarbon fuel at low temperatures but 43% lower at higher temperatures (22–35°C). Hot soak emissions from the two fuels were similar at low and intermediate temperatures but again the ethanol blend had 20% lower emissions at 32°C.

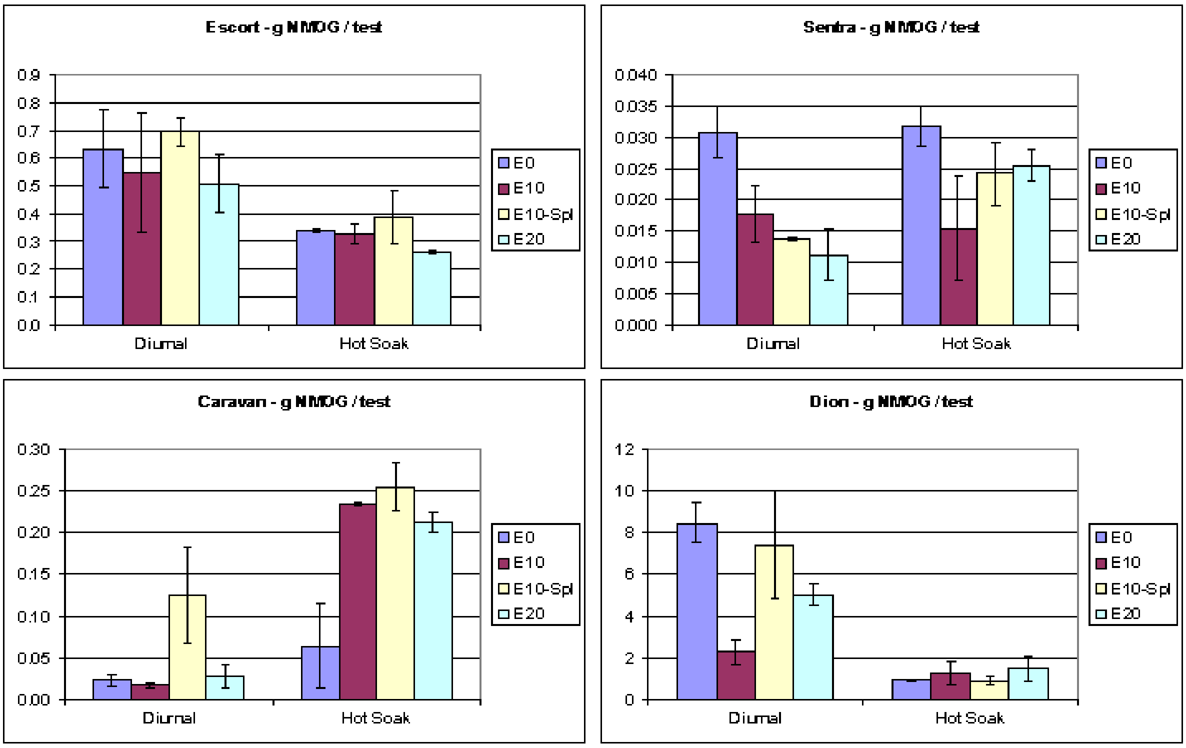
A CARB study [4] reported in 1998 tested six US vehicles on a base fuel and splash blends using 10% ethanol and 11% MTBE. The ethanol splash blend increased diurnal and hot-soak emissions on all vehicles tested. Running losses were not measured. Simple average emissions increased as shown in **Table A6-5**. Total evaporative emissions calculated using the CARB Emission Inventory process, including modelled running loss figures, increased by 54% (THC) and 84% (NMOG).

Table A6-5 Percentage change in THC and NMOG emissions from a 10% ethanol/petrol blend (53.9kPa RVP) compared to an 11% MTBE/petrol blend (47.5kPa RVP) [4]

Emission	Hot Soak	24h Diurnal	24-48h Diurnal
THC	58%	65%	86%
NMOG	89%	69%	84%

A more recent Canadian study [23] tested four 1998-2003 US vehicles on 10 and 20% matched volatility ethanol blends and a 10% ethanol splash blend. The study showed (**Figure A6-6)** that evaporative emissions on the matched volatility blends were similar to, or lower than on the base fuel for three of the four vehicles. One vehicle showed higher hot-soak emissions. The 10% ethanol splash blend gave higher emissions on two vehicles but lower emissions on the other two.

Figure A6-6 Diurnal and hot-soak NMOG emissions from four US vehicles [23]



The first Australian study [11] measured evaporative emissions from five modern and four older vehicles on a 20% ethanol splash blend. For the modern vehicles, emission levels were very low, all below 0.5 g/test total. Diurnal emissions were lower with the ethanol blend for three vehicles, higher for one, and unchanged for one. Hot soak emissions increased for all vehicles on the E20 blend, however. Overall, the 5-car mean total emissions increased by 8%.

For the older vehicles, diurnal emissions increased in two of the oldest vehicles, one substantially, but decreased for the two more recent vehicles. Hot soak emissions increased for all four vehicles on the E20 blend. The second phase of the study [12] was a durability test on the five modern vehicles. All vehicles tested on base fuel and E20 fuels gave evaporative emissions below 1g/test even after 80,000 km. There was no difference in diurnal emissions between base and E20 fuels, but hot soak emissions increased by ~80%. The results were quite variable, however, and this result was not statistically significant.

The only substantial European work was the JEC study [36] carried out by the EU's JRC with EUCAR and CONCAWE. Seven modern European cars were tested on 5 and 10% splash blends and matched volatility blends. The test protocol did not require that the canister be returned to a constant weight before each test, so canister loading increased with the number of tests making the interpretation of results difficult.

In this study, the hot soak emissions were small, generally below 10% of total emissions, with diurnal emissions comprising the other 90%. DVPE was the only fuel variable to clearly affect emissions, with high volatility ethanol splash blends having DVPE ~75kPA giving much higher emissions than the other fuels with DVPE in the range 60-70kPa. Some diurnal tests carried out with the canisters vented outside of the measurement SHED gave similar emissions to the standard test, although levels were low, generally below 1g/test. This result suggested that leakage or permeation could be making an important contribution.

Overall, it is clear that ethanol does affect evaporative emissions. Although ethanol itself does not increase the total mass of emissions generated from the fuel system, the increase in DVPE caused by ethanol splash blending does. Ethanol is strongly absorbed in activated carbon canisters but is also readily desorbed, although a little more slowly than are light hydrocarbons. Finally, ethanol can increase permeation through some plastic and elastomer components. Materials that are resistant to this permeation have been developed and are widely used in the USA. Some Australian work [12] showed that canisters can cope with ethanol fuels and maintain their performance over long periods. However, Swedish testing [40] suggested that this may not always be true for vehicles in-service.

15.5. Atmospheric Reactivity and Ozone Forming Potential

The formation of ground-level ozone is a serious air pollution concern in many areas. Ozone is not emitted directly but is formed from the photochemical reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NOx). Many different types of VOCs are emitted into the atmosphere by vehicles and each will react at different rates and with different reaction mechanisms. These differences in effects on ozone formation are referred to as the ozone "reactivities" of the VOCs.

Because of the reaction times involved, peak ozone concentrations often occur far downwind of the precursor emissions. Therefore, ozone is a regional pollutant that can impact a wide area. Due to the time scale involved in the production of ozone and the differences in reactivity of different hydrocarbon species, it is not possible to calculate “ozone emissions” from vehicles. It is possible, however, to report the Specific Reactivity (SR = gO_3/gNMOG) and Ozone Forming Potential (OFP = gO_3/km) of hydrocarbon emissions. These values are derived from speciated hydrocarbon analysis data and reactivity factors for each species.

In the USA, MIR (Maximum Incremental Reactivity) or MOR (Maximum Ozone Reactivity) factors are used, depending on the NOx level present while POCPs (Photochemical Ozone Creation Potential factors) have been developed for Europe. POCPs for a few typical gasoline hydrocarbons are shown in **Table A6-6**. Clearly, methane is very unreactive for ozone formation which is why hydrocarbon emissions are measured as Non-Methane Organic Gases (NMOG) in the USA. For other compounds, POCPs vary between 10 and 130. The POCP value for ethanol is relatively low at 38.6 while acetaldehyde (formed from ethanol) is higher at 64.1. The compounds with the highest SR factors are olefins or alkenes and some heavier aromatics.

Table A6-6 POCP values for selected organic compounds

Compound	POCP	Compound	POCP	Compound	POCP
Methane	0.6	Benzene	21.8	Methanol	13.1
Propane	17.6	Toluene	63.7	Ethanol	38.6
n-Butane	35.2	m-xylene	110.8	n-butanol	61.2
But-1-ene	107.9	p-xylene	101.0	MTBE	15.2
Trans-Hex-2-ene	107.3	Ethylbenzene	73	ETBE	21.4
1-3 Butadiene	85.1	1,3,5 Trimethyl benzene	138	Formaldehyde	51.9
Isoprene	109.2	Cyclohexane	29.0	Acetaldehyde	64.1

Several of the emission studies referred to above have calculated SR and OFP of both exhaust and evaporative hydrocarbon emissions and some results are summarised in **Table A6-7**.

Table A6-7 Effect of ethanol on specific reactivity (SR) and ozone forming potential (OFP) of emissions

				Vehicles		% change in reactivity of exhaust emissions			
Programme	**Ref**	**Date**	**Fuel***	**Number**	**Tech level**	**Exhaust SR**	**Exhaust OFP**	**Evap SR**	**Evap OFP**
US AQIRP Auto/Oil Study	1	1990	10%S	20 1989 US	2	NS	-5	+30 -18	NS +50
CARB Study	4	1998	10%S	12 1991-5 US	2-3	-	+7	-	+23
Swiss EMPA Study	7	2002	5%S	1 EURO 3	3	+6	+16	-	-
Fortum Study	1	2004	10%M vs ETBE	10 1999 – 2002 EURO 3	3	-	NS	-	-
Environment Canada Study (at +20 and -10°C)	23	2006	10, 10S, 20	3 1998 – 2003 20°C 1 2000 DISI 20°C 2 1998 – 2003-10°C	3 4 3	NS -25 NS	NS -38 NS	NS NS -	+20* NS -

* for E10 splash blend only

The US AQIRP [1] study showed that the use of 10% ethanol reduced both exhaust SR and OFP slightly, but this result was not statistically significant. Evaporative emission results showed a 30% increase in SR of diurnal emissions but a small reduction in OFP. Hot soak emissions showed a reduction in SR but a 50% increase in OFP. There were wide variations in the evaporative emission results, however, and the paper warned that care should be used when interpreting the data. The CARB study [4] used MIR reactivity factors to calculate OFP of exhaust and evaporative emissions. The study concluded that a 10% ethanol splash blend would increase OFP by 21%. The Environment Canada study [23] also suffered from wide variations in results so small changes measured due to ethanol were generally not significant. An exception was from one DISI vehicle which showed a substantial reduction in SR and OFP of exhaust emissions.

Overall, it appears that ethanol has little effect on SR, with the changes being relatively small and inconsistent. The same is generally true for OFP at constant fuel volatility but increases in OFP of evaporative emissions are generally due to the increase in mass HC emissions caused by the higher DVPE of petrol blends prepared by splash-blending ethanol.

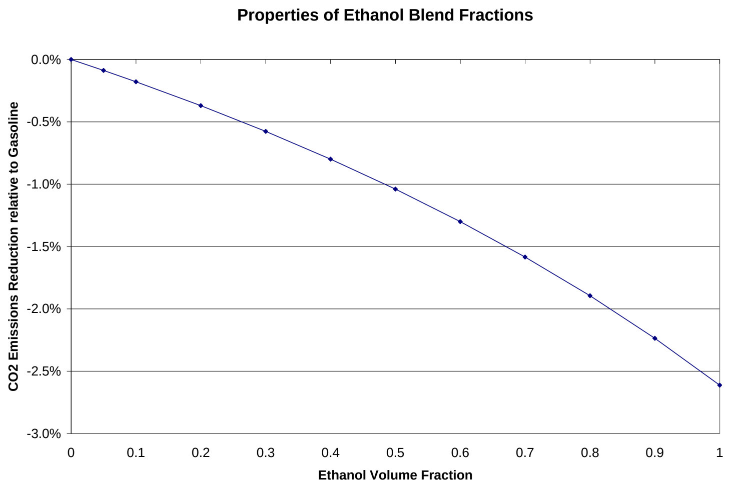
15.6. Tank-to-Wheels CO_2 Emissions

There are little published data on the effect of ethanol on CO_2 emissions as such, although CO_2 emissions are always measured during emissions tests. These results are used to calculate fuel consumption which is generally reported. Care is needed, however, because the fuel consumption calculation formula includes a fuel Carbon Weight Fraction (CWF) term which varies as a function of the ethanol content in the fuel blend. A default CWF for an average hydrocarbon fuel is sometimes mistakenly used for this calculation on ethanol blends. The physical and chemical properties of ethanol differ substantially from those of hydrocarbon gasoline, resulting in several potential routes by which the measured CO_2 emissions and hence fuel consumption of a gasoline engine may be affected:

- Lower Heating Value (LHV) of ethanol, requiring a greater mass of fuel to release a given quantity of energy.
- Greater density of ethanol, requiring a smaller volume of fuel for a given mass.
- Lower CWF and a higher oxygen content for ethanol, reducing the mass of air required to combust a given mass of fuel. This may change the effective mixture strength and thus change the combustion efficiency of the engine.
- Different volatility characteristics and higher heat of vaporisation leading to changes in air/fuel mixing and combustion characteristics.
- Higher octane value of ethanol. This may allow engines capable of optimizing its performance on higher octane blends to operate under more optimised ignition timing at higher loads leading to higher engine efficiency.
- The combination of heating value and mixture strength changes will affect the airflow requirements and hence the throttle setting, which has a strong influence on the overall efficiency of the engine.
- The very high latent heat of vaporisation of ethanol can give a high level of charge air cooling, which increases the air density and the mass in the cylinder. This may also impact the throttle setting.
- Chemical kinetic effects on the laminar flame speed and thus on the combustion efficiency.

Although each of these should be considered when evaluating literature studies, most of these effects are very small. For example, the theoretical total carbon emissions per unit of energy (g/MJ) are slightly lower for ethanol than they are for gasoline. Carbon dioxide emissions are directly related to the total carbon emissions, except for a very small effect due to changes in carbon monoxide and hydrocarbon emissions. For a 100% ethanol fuel, it is estimated that the carbon dioxide emissions will be 2.6% lower than from an un-oxygenated gasoline, assuming that the same energy efficiency is maintained. For an E10 fuel, the reduction in carbon emissions will be about 0.18%, while for E5, the carbon emissions will be about 0.09% lower, as shown in **Figure A6-7.**

Figure A6-7 Relative reduction in carbon dioxide emissions for ethanol/petrol blends compared to petrol



From the studies where CO_2 emissions are specifically reported, the ADEME study [10] showed small but inconsistent changes in emissions for 5 and 10% ethanol blends. The AEA study [6] showed statistically significant reductions in CO_2 for a 5% ethanol blend in some, but not in all, of the four cars tested. The EMPA study [7] showed a ~1% reduction for a 5% ethanol blend in one vehicle, as did the IDIADA programme [13]. The Fortum study [14] also showed about a 1% reduction in CO_2 for ten vehicles comparing a 10% ethanol blend to an ether blend containing 2% oxygen. This result was not statistically significant, however.

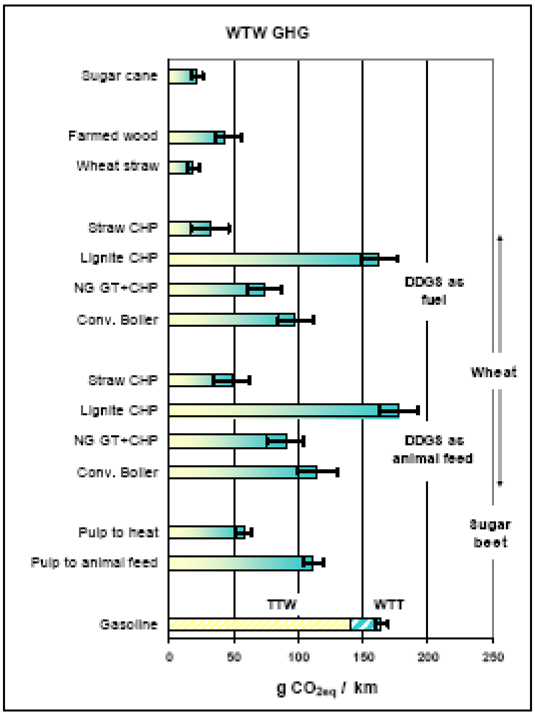
The Environment Canada study [23] which looked at 10 and 20% ethanol blends in four US vehicles including an early DISI car. The study showed no significant effect of ethanol on CO_2 emissions per km. The authors stated that apparently “the effect from the lower energy density of the ethanol blend fuels cancelled out the effect from the lower carbon content per litre of ethanol blend fuel burned.”

The first Australian study [11] showed about a 1% reduction in CO_2 for five modern vehicles tested on a 20% ethanol blend but inconsistent effects for four older vehicles.

A recent JEC study of evaporative emissions on 5 and 10% ethanol blends [24] also measured vehicle exhaust emissions. Although the regulated gaseous emissions data were too variable to draw robust conclusions, CO_2 emissions and fuel consumption data were also analysed. Neither CO_2 emissions nor energy consumption showed any effect of ethanol but the volumetric fuel consumption increased in proportion to the ethanol content of the fuel.

The overall conclusion then is that TTW CO_2 emissions are not affected by ethanol blends, or are very slightly reduced by about 1% or less. This result does not seem to vary with ethanol concentration. In any case the effect on TTW emissions is very small compared to that on Well-to-Tank emissions, which are more difficult to calculate. The recent JEC WTW study [33] showed that there were benefits for WTT emissions leading to substantial benefits in WTW emissions for neat bio-ethanol, depending upon the source material and processing route (**Figure A6-8**).

Figure A6-8 WTW GHG emissions for various ethanol pathways for 2010 vehicles [33]



15.7. Specific References on Ethanol and Environmental Performance

No.	Authors	Title	Reference	Year	% EtOH	Exhaust	Evap
1	US AQIRP	Effects of oxygenated fuels and RVP on automotive emissions – Auto/Oil Air Quality Improvement programme	SAE 920326	1992	10	X	X
2	Grisanti et al. (U of N Dakota)	Gasoline Evaporative Emissions -Ethanol Effects on Vapor Control Canister Sorbent Performance	SAE 952748	1995	10		X
3	Knapp, Stump and Tejeda (US EPA)	The Effect of Ethanol Fuel on the Emissions of Vehicles over a Wide Range of Temperatures	J. Air & Waste Mgmt. Assoc. 48, 646-653, 1998	1998			X
4	California Air Resources Board (CARB)	Comparison of the effects of a fully-complying gasoline blend and a high RVP ethanol blend on exhaust and evaporative emissions	CARB Report (www.arb.ca.gov)	1998	10	X	X
5	B. Crary (Toyota)	Effects of ethanol on emissions of gasoline LDVs	Presentation on CARB website	2000	10	X	X

No.	Authors	Title	Reference	Year	% EtOH	Exhaust	Evap
6	Reading et al. (AEA Technology)	Ethanol Emissions Testing	AEA Technology Report E&E/DDSE/02/021 rev.	2004	10	X	
7	EMPA	Bio-Ethanol Project	EMPA report 202672	2002	5	X	
8	Clarke Groves Crawshaw (Shell)	Introduction of biofuels into gasoline and diesel	4th Int Coll. Fuels TAE Germany, Jan 2003	2003	5,10	X	
9	H. Haskew Associates	Evaporative Emission Effects (Permeation) Created by Ethanol in Gasoline	Submissions to CARB contract 99-04. See www.arb.ca.gov	2003	?		X
10	ADEME	Mesures d'émissions polluantes sur véhicules légers à allumage commandé, alimentés en carburants contenant de l'éthanol et de l'ETBE	ADEME Report ETS 03-046	2003	5,10	X	
11	Orbital Engine Company (Australia)	A Testing Based Assessment to Determine Impacts of a 20% Ethanol Gasoline Fuel Blend on the Australian Passenger Vehicle Fleet	Orbital Phase 1 Report to Environment Australia	2003	20	X	X
12	Orbital Engine Company (Australia)	Market Barriers to the Uptake of Biofuels Study: Testing Gasoline Containing 20% Ethanol (E20)	Orbital Phase 2b report to the Dept of the Environment and Heritage	2004	20	X	X
13	R. Delgado (IDIADA)	Comparison of vehicle emissions at European Union annual average temperatures from E0 and E5 petrol	IDIADA Report LM030411	2003	5	X	X
14	Pentikäinen & Rantanen (Fortum)	The Effect of Heavy Olefins and Ethanol on gasoline Emissions	SAE 2004-01-2003	2004	10	X	
15	R.K. Niven (U of NSW Australia)	Ethanol in Gasoline: environmental impacts and sustainability review article	Renew. and Sustain. Energy Reviews 9 (2005) 535-555	2004	All	X	X
16	Laveskog, Egeback (MTC Sweden)	Addition of small amounts of Alcohol to petrol	MTC Report in Swedish	1999	5,25	X	X
17	Westerholm, Egeback, Rehnlund and Henke	Blending of Ethanol in Gasoline for Spark Ignition Engines – Problem Inventory and Evaporative Measurements (Lit survey and Evap tests)	AVL MTC Report No. MTC 5407	2004-5	5–15	X	X

No.	Authors	Title	Reference	Year	% EtOH	Exhaust	Evap
18	R.K. Niven (U of NSW Australia)	Ethanol in gasoline: environmental impacts and sustainability review article	Renew. and Sustain. Energy Reviews. 9 (2005) 535-555	2005	10,85	X	X
19	Coordinating Research Council (CRC, USA)	Effects of Ethanol and Volatility Parameters on Exhaust Emissions	CRC Report E67 and ES&T 2007, 41, 4059-4064	2006	5.7,10	X	
20	Coordinating Research Council (CRC, USA)	Fuel Permeation from Automotive Systems	CRC Report E65	2004	5.7	X	X
21	Coordinating Research Council (CRC, USA)	Fuel Permeation from Automotive Systems: E0, E6, E10, E20, E85	CRC Report E-65-3	2006	6,10, 20,85		X
22	Aubin and Graham (Environment Canada)	The Evaluation of Gasoline-Ethanol blends on Vehicle Exhaust and Evaporative Emissions–Phase 1	Report for Environment Canada	2002	0–20	X	X
23	Baas and Graham (Environment Canada)	Emissions from 4 Different Light Duty Vehicle Technologies operating on Low Blend Ethanol Gasoline	Environment Canada ERM reports 04-27A, B, C, D and Atmos. Environ. 42, 4498-4516 (2008)	2007	10,20	X	X
24	G. Martini et al. (JEC Consortium)	EUCAR/JRC/ CONCAWE Study on effects of Gasoline Vapour Pressure and Ethanol Content on Evaporative Emissions from Modern Cars	Report EUR 22713 EN and SAE 2007-01-1928	2007	5,10	P	X
25	Klontz et al. (MeadWestVaco)	Effects of Low-Purge Vehicle Applications and Ethanol-Containing Fuels on Evaporative Emissions Canister Performance	SAE 2007–01-7051	2007	10		X
26	US DOE NREL	Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1	Report NREL/TP-540-43543 ORNL/TM-2008/117	2008	10,15,20	X	
27	Mulawa et al.	Effect of Ambient Temperature and E-10 Fuel on Primary Exhaust Particulate Matter Emissions from Light Duty Vehicles	Environ. Sci. Technol. 1997. 31, 1302-1307	1997	10	X	
28	Warner-Selph and Harvey (SWRI & US EPA)	Assessment of unregulated emissions from gasoline oxygenated blends	SAE 902131	1990	10	X	X
29	Mayotte, Lindhjem, Rao, and Sklar (US EPA)	Reformulated Gasoline Effects on Exhaust Emissions: Phase 1 Initial Investigation of Oxygenate, Volatility, Distillation, and	SAE 941973	1994	10	X	

No.	Authors	Title	Reference	Year	% EtOH	Exhaust	Evap
		Sulfur effects					
30	Mayotte, Lindhjem, Rao, and Sklar (US EPA)	Reformulated Gasoline Effects on Exhaust Emissions: Phase 2 Continued Investigation of the Effects of Fuel Oxygenate Content, Oxygenate Type, Sulfur, Olefins and distillation Parameters	SAE 941974	1994	10	X	
31	Thummadetsak, Wuttimongkilchai, Tunyapisetsak, and Kimura (Petroleum Authority of Thailand, JICA)	Effect of gasoline compositions and properties on tailpipe emissions of currently existing vehicles in Thailand	SAE 1999-01-3570	1999	7.5,15	X	
32	Ntziachristos et al.	Overview of the European "Particulates" Project on the Characterization of Exhaust Particulate Emissions from Road Vehicles: Results for Light-Duty Vehicles	SAE 2004-01-1985	2004			
33	JEC Consortium	Well-to-Wheels analysis of future automotive fuels and powertrains in the European context	JRC Report http://ies.jrc.ec.europa.eu/WTW	2007			
34	CONCAWE	An Investigation into Evaporative Emissions from European Vehicles	CONCAWE Report 87/60	1987	-		X
35	CONCAWE	The Effects of Temperature and Fuel Volatility on Vehicle Evaporative Emissions	CONCAWE Report 90/51 Also I Mech E paper C394/028	1990	-		X
36	JEC Consortium	JEC Study on Effects of Gasoline Vapour Pressure and Ethanol content on Evaporative Emissions from Modern Cars	EU JRC Report EUR22713 EN	2007	5,10		X
37	Reddy (General Motors)	Evaporative emissions from Gasolines and Alcohol-Containing Gasolines with Closely Matched Volatilities	SAE 861556	1986	-		X
38	Melios et al. (JRC/CONCAWE)	A vehicle testing programme for calibration and validation of an evaporative emissions model	Fuel, 88, 1504-1512 (2009)	2009			X
39	Clontz et al. (MeadWestVaco)	Effects of low-Purge Vehicle Applications and Ethanol Containing Fuels on Evaporative Emissions	SAE 2007-01-7051	2007	10		X

No.	Authors	Title	Reference	Year	% EtOH	Exhaust	Evap
		Canister Performance					
40	P Åsman and H Johansson (Vägverket Sweden)	Evaporative Emissions Related to Blending Ethanol in Petrol	Vägverket Report to EU (2006)	2006	5		X
41	Coordinating Research Council (CRC, USA)	Fuel Permeation from Automotive Systems	Final Rpt CRC Project E-65 Final Rpt CRC E-65-3	2004-2006	5.8 6,10,20,85		X X
42	Dupont	Fuel-Alcohol Permeation Rates of Fluoroelastomers Fluoroplastics, and Other Fuel Resistant Materials	SAE 920163	1992			X

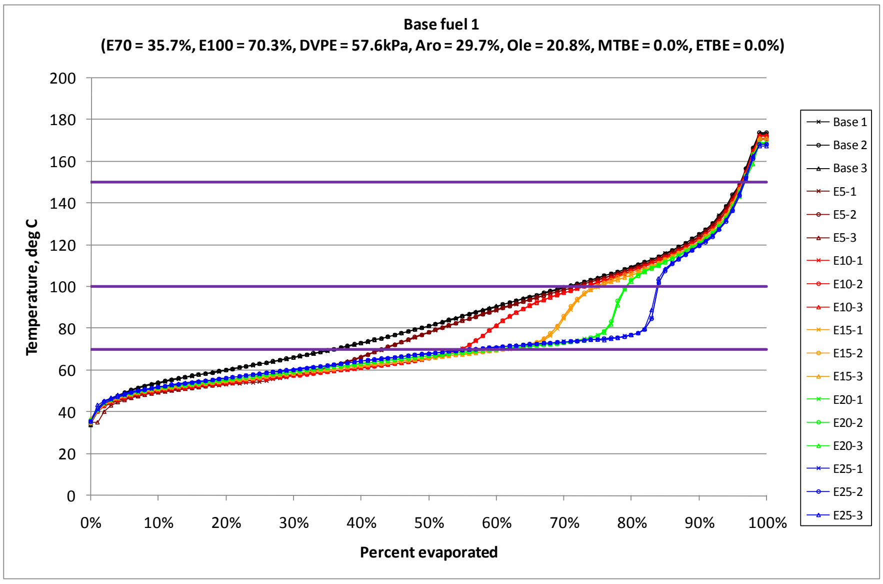
16. APPENDIX 7
Visual categorization of distillation curves

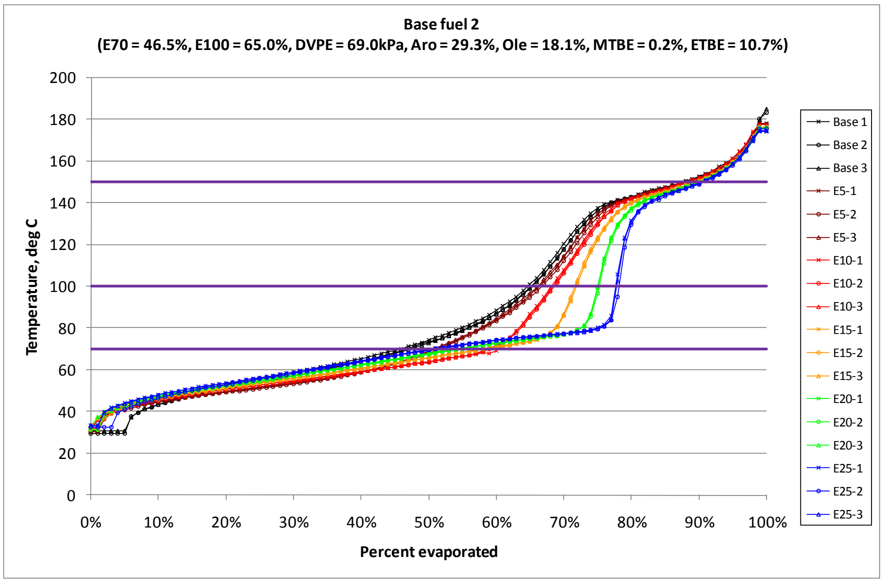
Group	Base Fuel		E70 %	E100 %	E120 %	E150 %	Density kg/m3	DVPE kPa	Aromatics %v	Olefins %v	MTBE %v	ETBE %v	Total ether %v	EtOH %v		Observations on E70/E100
			2	3	4	5	6	7	8	9	10	11	12	13		
		min	17.4	31.7	39.0	60.1	710.7	48.9	19.98	4.30	0.00	0.00	0.00	0.00		
		max	60.2	74.9	93.6	98.0	784.5	92.8	48.23	21.60	22.14	21.73	22.35	1.16		
		mean	32.4	56.1	70.7	85.9	748.3	70.8	33.39	12.35	4.38	3.94	8.32	0.11		
A	3		31.8	60.4	71.5	89.8	736.6	57.7	27.55	5.59	0.00	0.00	0.00	0.00		**Medium E70 and High E100**
A	21		29.4	57.2	72.1	89.4	749.7	70.5	37.30	13.16	0.03	0.00	0.03	0.03		
A	43		33.1	56.2	69.7	87.6	745.6	63.7	31.79	21.60	0.02	0.00	0.02	0.00		
A	48		34.3	72.1	90.0	96.8	744.6	92.8	33.45	7.74	0.15	10.54	10.69	0.15		
A	54		36.0	68.8	83.9	94.3	717.9	90.2	21.50	4.78	0.00	0.00	0.00	0.03		
B	18		29.8	52.6	63.8	78.5	764.2	90.8	38.32	14.83	21.77	0.00	21.77	0.03		**Medium E70 and Medium E100**
B	32		33.4	56.2	64.8	78.7	744.7	60.2	24.67	16.07	10.71	0.00	10.71	0.00		
B	36		20.9	37.9	52.3	71.4	773.0	86.7	42.24	19.79	0.52	21.28	21.80	0.30		
B	41		31.4	55.9	66.2	87.8	769.5	82.8	42.89	7.26	22.12	0.03	22.15	0.05		
B	50		19.8	50.4	66.6	89.2	784.5	51.4	45.73	4.58	21.41	0.00	21.41	0.00		
C	5		21.1	38.5	49.4	72.8	762.0	78.1	30.10	10.36	22.14	0.00	22.14	0.21		**Low E70 and Low E100**
C	34		22.5	39.0	48.1	69.6	743.8	52.6	23.87	8.13	0.00	0.00	0.00	0.00		
C	53		18.4	36.9	47.9	66.4	740.0	50.5	20.40	21.44	0.03	0.00	0.03	0.03		
D	17		44.3	70.4	86.1	96.4	735.1	71.8	38.66	4.69	0.00	0.00	0.00	0.04		**Medium+ E70 and High E100**
D	20		32.1	67.3	78.4	96.7	754.8	58.7	35.38	7.71	0.62	21.73	22.35	0.34		
D	28		37.7	68.1	82.6	95.0	739.9	53.4	22.31	11.78	20.69	0.00	20.69	0.25		
D	46		39.3	72.3	84.4	97.2	750.7	50.1	31.49	15.24	0.50	21.29	21.79	0.27		
D	60		55.2	74.0	82.2	94.6	710.7	71.0	20.24	5.45	0.00	0.00	0.00	0.11		
E	2		46.5	65.0	70.3	87.7	738.3	69.0	29.33	18.10	0.15	10.67	10.82	0.12		**Medium+ E70 and Medium+ E100**
E	22		47.2	61.5	66.2	76.7	729.0	83.7	19.98	21.28	10.14	0.04	10.18	0.00		
E	49		47.0	61.4	66.3	78.1	734.1	90.9	34.08	12.87	0.02	0.00	0.02	0.03		
F	8		47.9	65.5	76.1	96.3	758.7	75.7	38.60	18.85	21.13	0.00	21.13	0.45		**Medium+ E70 and Medium+ E100**
F	11		42.2	60.5	85.5	97.8	751.9	77.7	47.02	15.24	0.00	0.00	0.00	0.00		
F	37		43.7	65.9	89.4	97.7	746.9	64.9	41.99	17.33	0.00	0.00	0.00	0.00		
F	40		40.2	63.9	79.6	97.6	751.4	51.9	41.79	10.12	0.00	0.00	0.00	0.03		
G	6		60.2	71.8	74.7	80.8	731.2	92.3	30.60	7.09	11.19	0.00	11.19	0.06		**Medium+ E70 and High E100**
G	26		54.5	71.7	74.6	86.5	713.7	60.1	20.39	9.56	0.00	0.00	0.00	0.00		
G	31		45.8	63.8	67.2	79.2	743.0	58.9	25.08	4.79	21.74	0.00	21.74	0.00		
G	35		59.0	74.9	77.9	82.0	723.0	84.9	30.34	9.60	0.21	12.40	12.61	0.75		
G	51		41.0	74.9	79.4	88.5	731.0	52.1	20.99	4.67	0.27	21.67	21.94	0.27		
G	57		55.4	73.6	77.5	87.3	717.2	53.8	20.78	21.04	0.03	0.00	0.03	0.06		
H	4		28.2	44.8	59.0	82.6	739.5	86.4	31.66	16.00	0.03	0.00	0.03	0.00		**Low E70 and Low+ E100**
H	13		27.9	47.1	60.4	87.1	765.1	64.1	46.64	7.87	0.02	0.00	0.02	0.04		
H	14		19.7	36.7	49.4	77.9	772.0	59.0	45.62	13.21	0.04	0.00	0.04	0.00		
H	15		27.4	46.6	55.2	79.7	765.3	51.0	38.82	17.90	10.15	0.00	10.15	0.06		
H	16		21.7	31.7	39.0	60.1	762.8	82.4	38.78	16.33	0.02	0.00	0.02	0.00		
H	24		29.4	46.0	58.5	75.1	725.3	88.1	20.71	4.48	0.00	0.00	0.00	0.00		
H	25		19.9	39.2	51.7	71.4	743.2	64.7	20.28	15.55	0.11	10.56	10.67	0.17		
H	42		27.6	45.8	57.1	83.1	766.0	76.9	43.85	12.46	10.89	0.00	10.89	0.05		
H	45		21.3	36.7	44.1	62.0	761.9	71.4	33.43	4.77	10.92	0.00	10.92	0.04		
I	27		21.0	53.1	72.2	85.4	733.2	70.6	20.99	7.55	0.00	0.00	0.00	0.05		**Low E70, Medium E100, and High E120**
I	47		20.7	51.5	78.1	91.9	748.2	79.5	35.03	10.18	0.02	0.00	0.02	0.00		
I	52		20.3	50.7	84.2	95.1	764.8	90.3	46.67	4.30	0.00	0.00	0.00	0.03		
I	56		23.3	46.7	86.1	95.9	764.0	90.0	45.53	19.62	0.00	0.00	0.00	0.00		
J	33		28.2	49.6	56.5	63.3	752.5	69.7	25.00	10.24	0.74	20.81	21.55	0.30		**Low+ E70, Medium E100, and Low E120/E150**
J	44		27.4	45.2	50.7	68.9	767.8	58.4	33.44	17.63	21.57	0.00	21.57	0.05		
K	7		17.7	55.6	75.8	92.0	753.5	60.3	27.99	12.89	0.69	21.26	21.95	0.27		**Low E70 and Medium E100**
K	29		23.4	53.0	73.2	84.9	737.0	73.1	22.63	20.64	0.00	0.00	0.00	0.00		
K	38		17.4	55.5	77.5	93.4	767.7	54.1	42.03	4.92	0.14	10.62	10.76	0.13		
K	59		21.5	50.0	81.0	94.3	766.7	54.3	46.03	20.87	0.00	0.00	0.00	0.04		
L	55		23.2	35.1	51.0	74.0	733.4	91.5	21.18	21.02	0.19	0.00	0.19	1.16		**Low E70 and Low E100**
L	58		21.2	33.0	44.0	77.3	766.2	85.9	47.06	4.44	0.00	0.00	0.00	0.00		
M	1		35.7	70.3	87.4	96.1	737.4	57.6	29.67	20.76	0.03	0.00	0.03	0.04		**Medium E70 and High E100**
M	19		34.9	67.7	91.9	97.4	754.5	64.1	38.94	10.18	10.08	0.00	10.08	0.00		
M	30		35.8	70.0	89.8	97.0	725.0	89.6	28.29	17.09	0.00	0.00	0.00	0.00		
M	39		37.8	63.4	93.6	98.0	750.5	70.9	46.44	14.52	0.00	0.00	0.00	0.00		
N	9		20.2	54.5	79.8	93.9	775.3	48.9	44.97	16.87	10.40	0.00	10.40	0.00		**Medium E70 and Medium E100**
N	10		30.9	63.0	91.7	97.4	762.5	83.7	43.73	4.55	0.47	21.11	21.58	0.32		
N	12		29.7	55.2	81.5	94.9	766.7	88.7	48.23	10.19	0.13	10.96	11.09	0.18		
N	23		30.4	59.2	76.6	94.8	735.5	74.7	20.99	12.98	0.59	21.52	22.11	0.33		

This table shows an arrangement of the 60 sets of distillations, as shown in **Appendix 8**, into 14 homogenous groups A, B, C, …, N such that all the sets within a group follow the same distinctive pattern. The grouping is based purely on a visual assessment. The properties of the 60 base fuels are tabulated in the middle 12 columns. General comments regarding the range of base fuel E70 and E100 values within each group are given in the last column.

17. APPENDIX 8
Distillation Curves

Figure A8-1 Distillation Curves 1-3





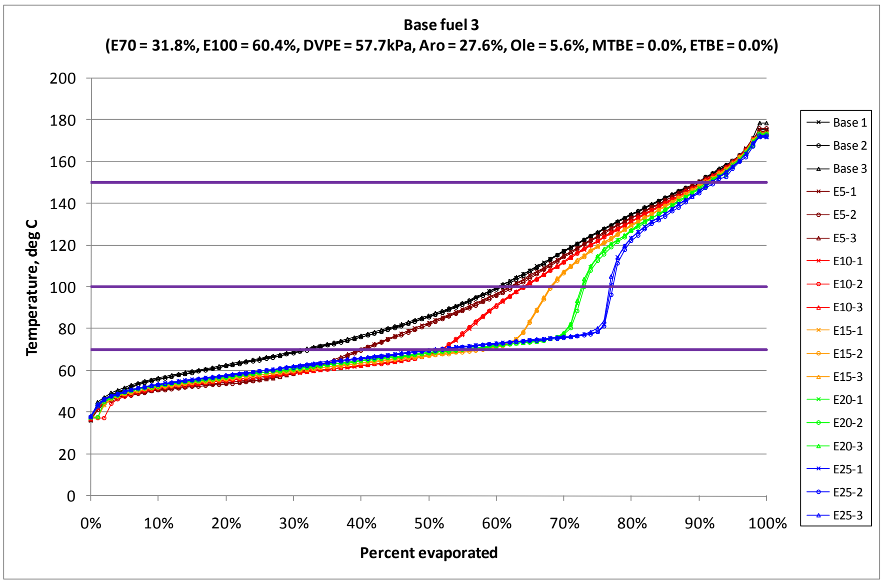
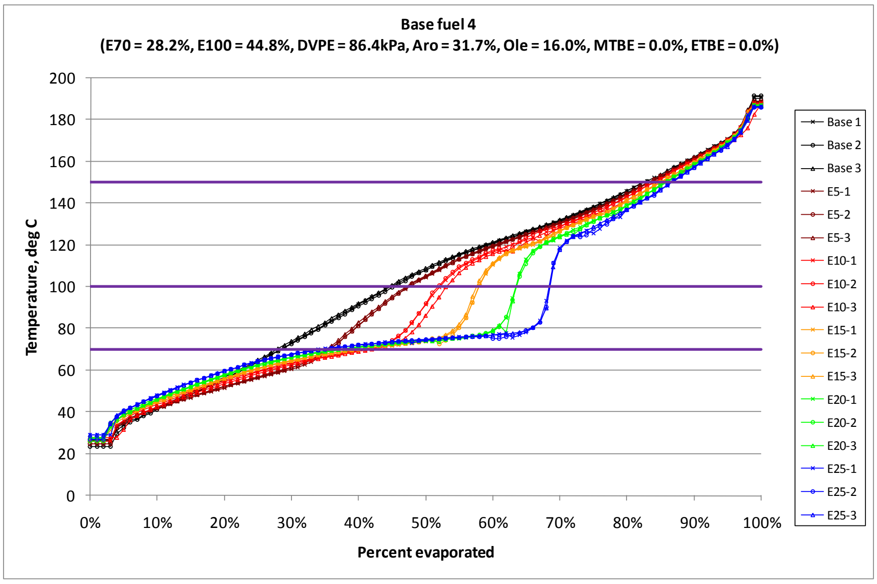
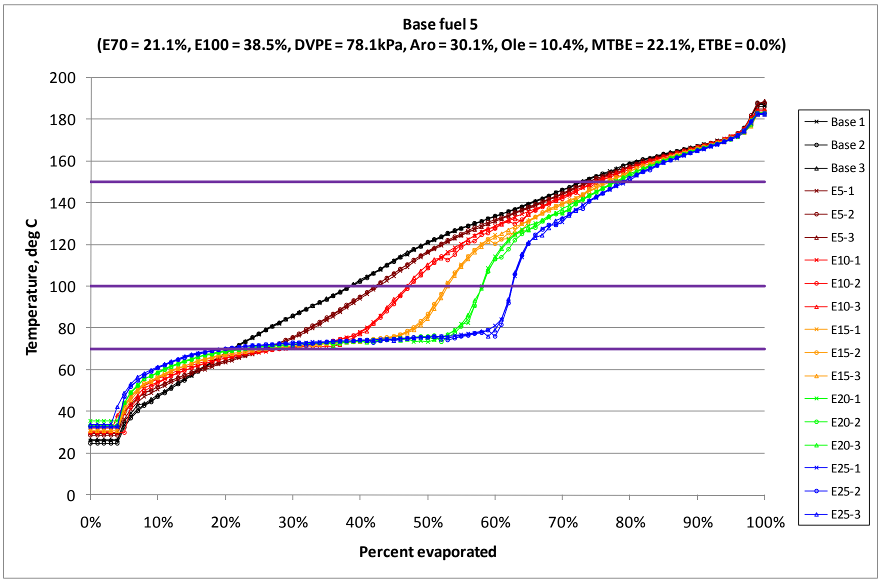


Figure A8-1 Distillation Curves 4-6





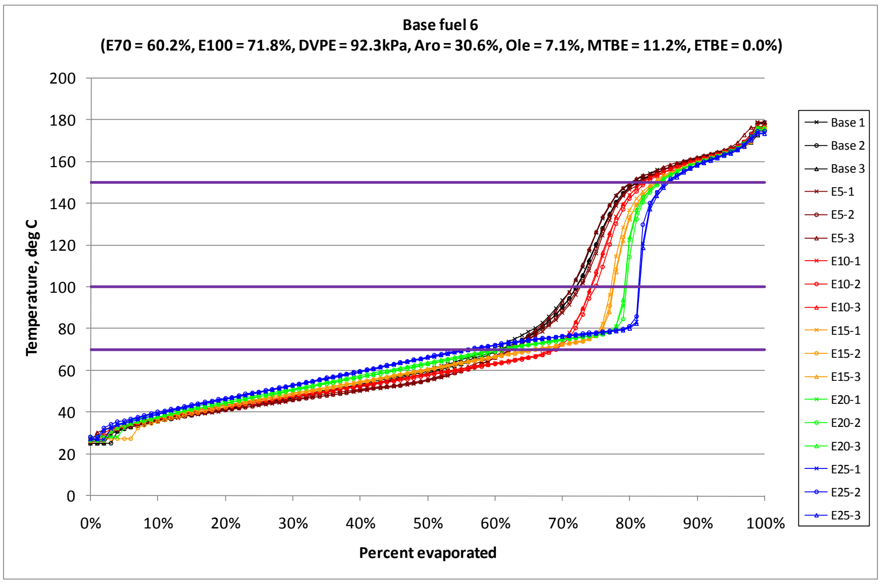
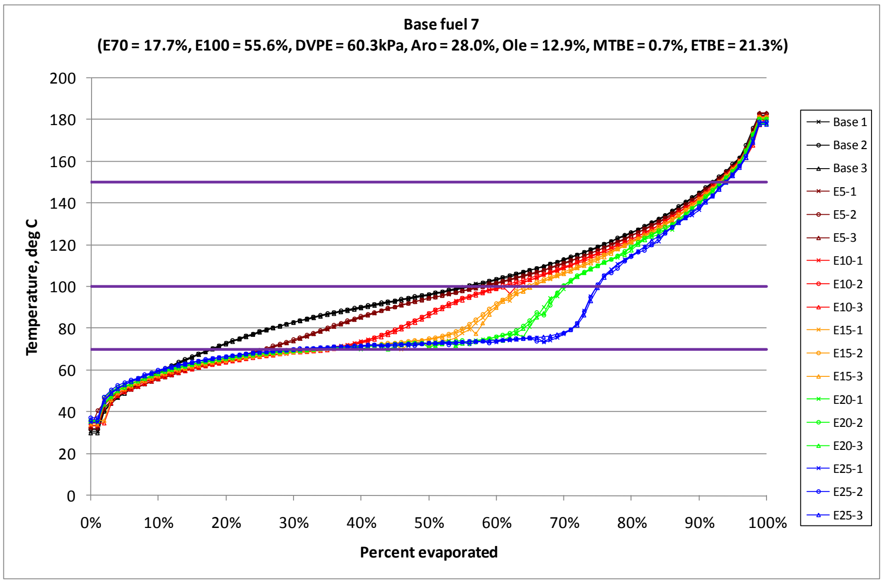
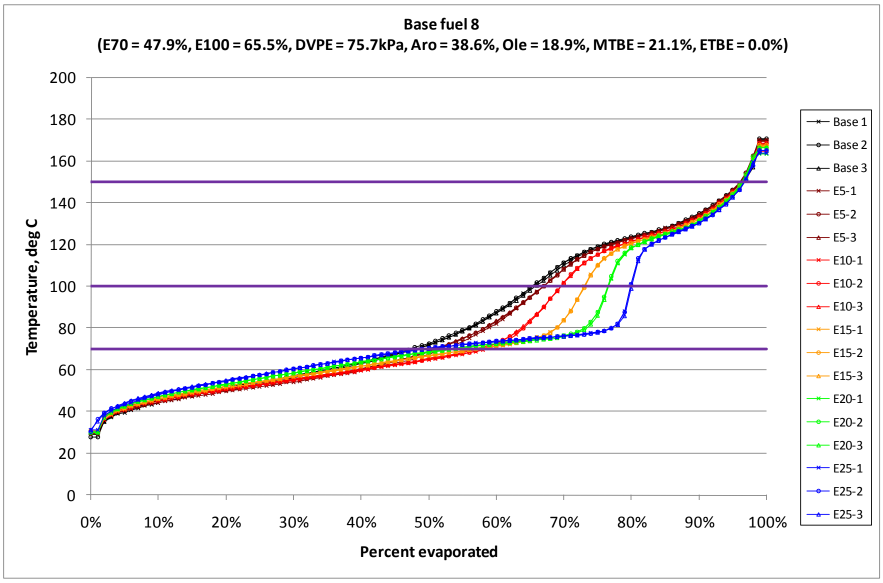


Figure A8-1 Distillation Curves 7-9





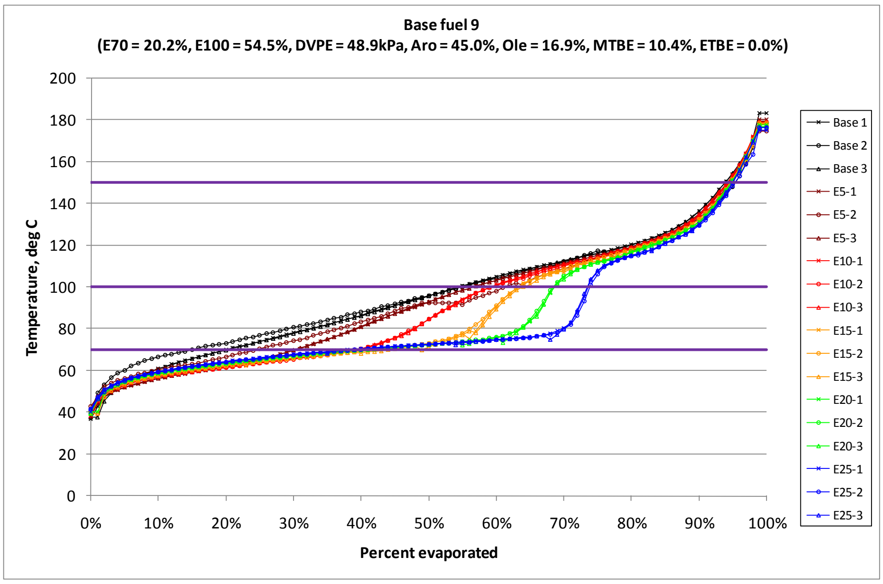
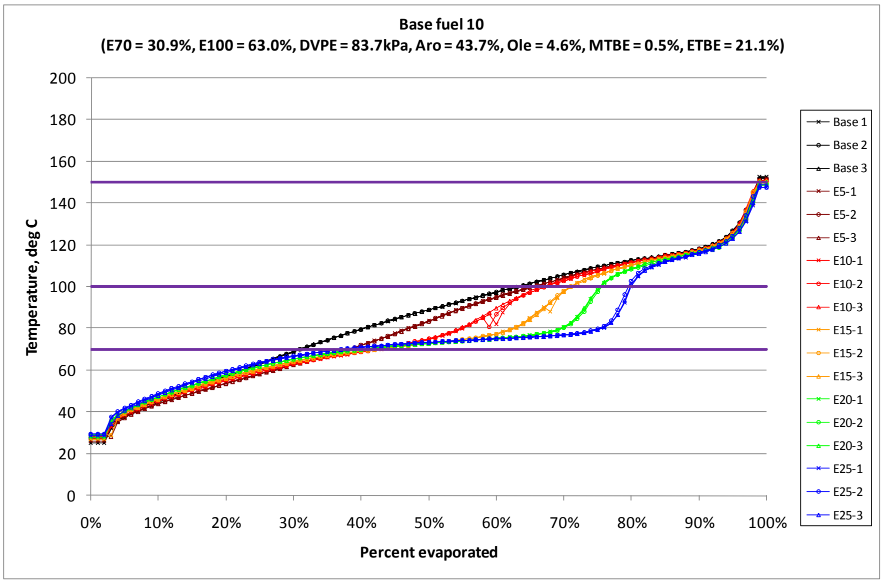
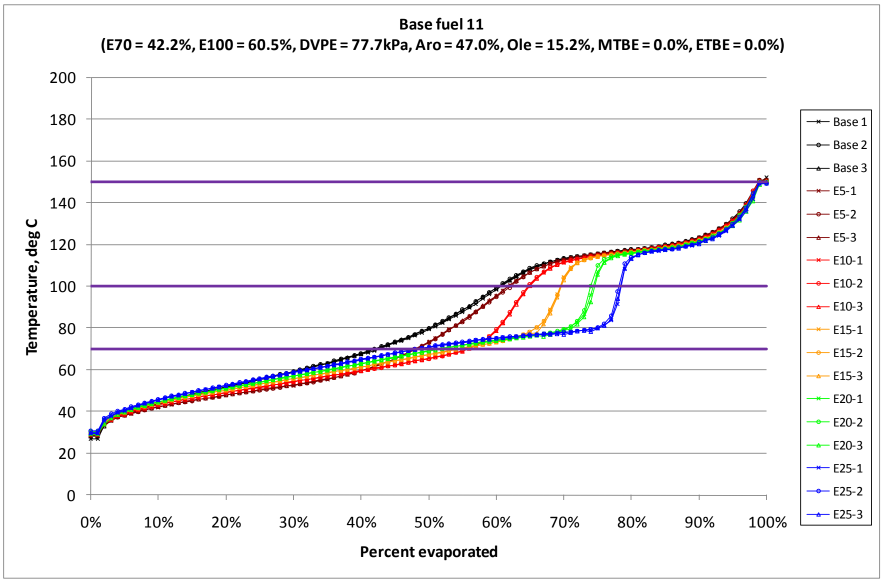


Figure A8-1 Distillation Curves 10-12





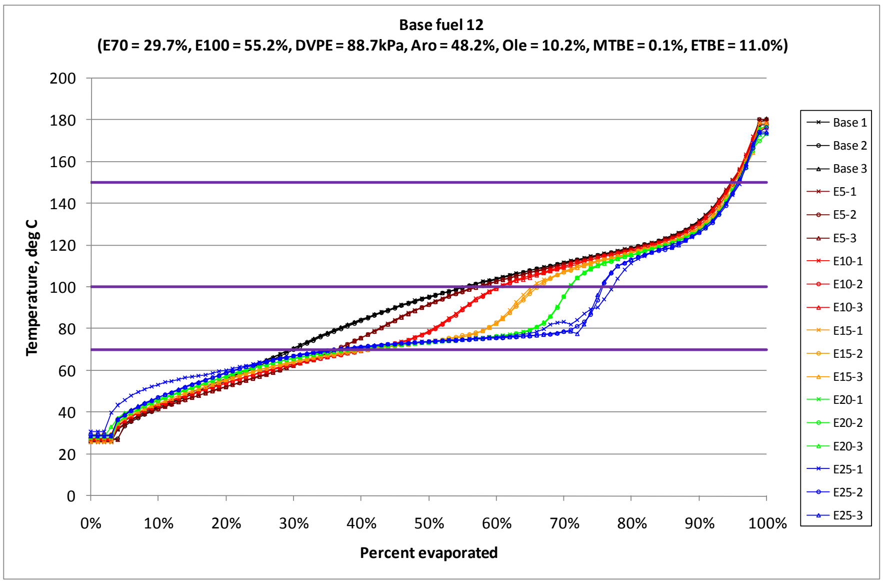
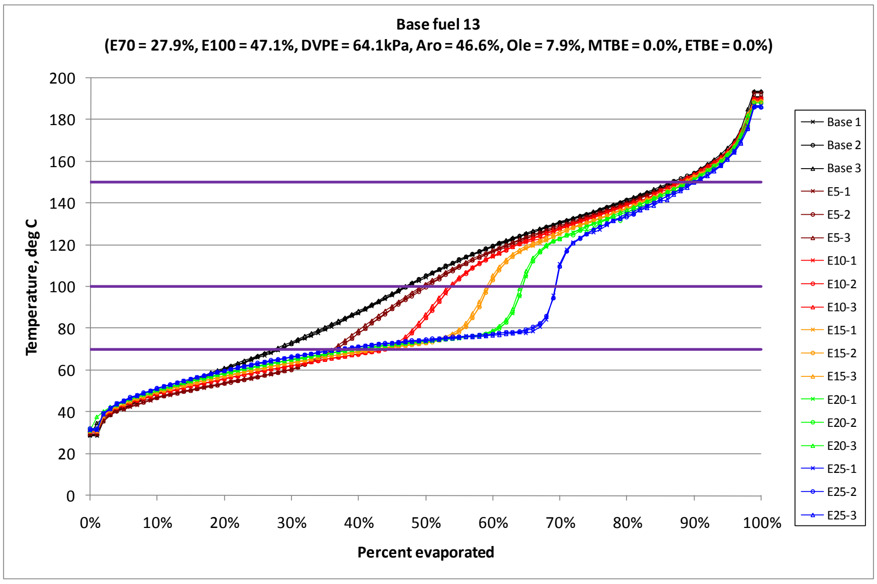
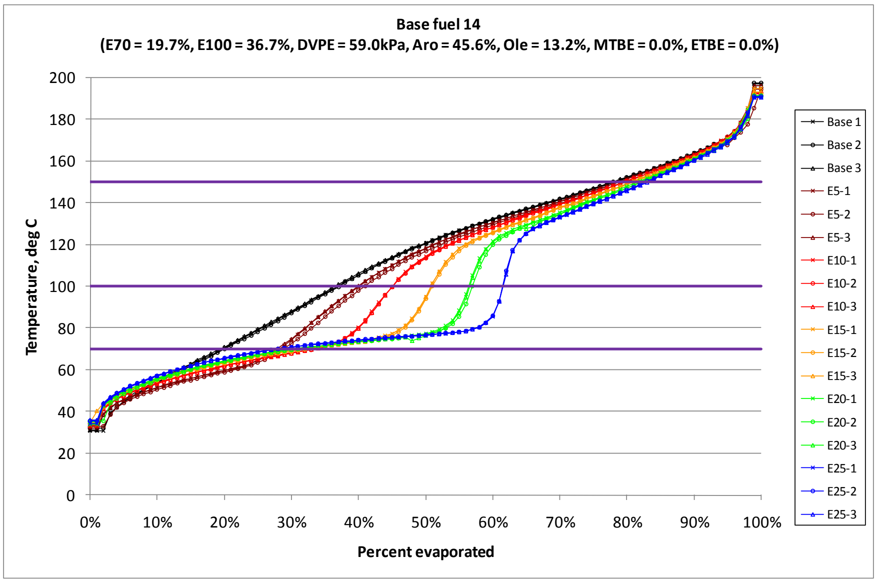


Figure A8-1 Distillation Curves 13-15


Base fuel 13
(E70 = 27.9%, E100 = 47.1%, DVPE = 64.1kPa, Aro = 46.6%, Ole = 7.9%, MTBE = 0.0%, ETBE = 0.0%)


Base fuel 14
(E70 = 19.7%, E100 = 36.7%, DVPE = 59.0kPa, Aro = 45.6%, Ole = 13.2%, MTBE = 0.0%, ETBE = 0.0%)

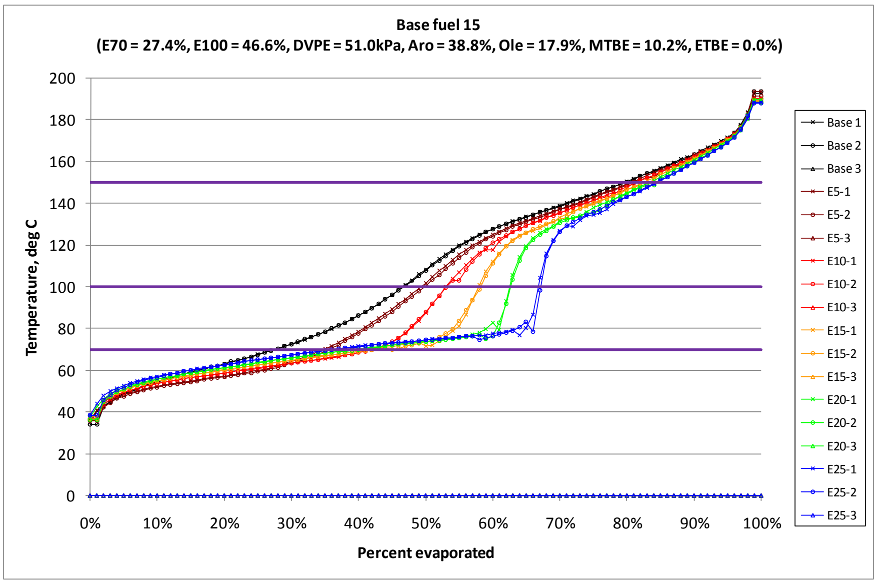
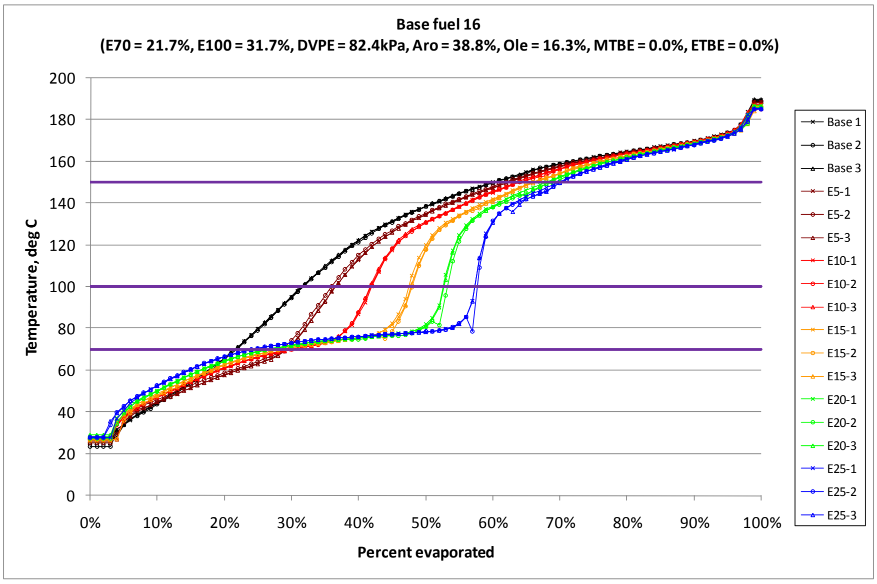
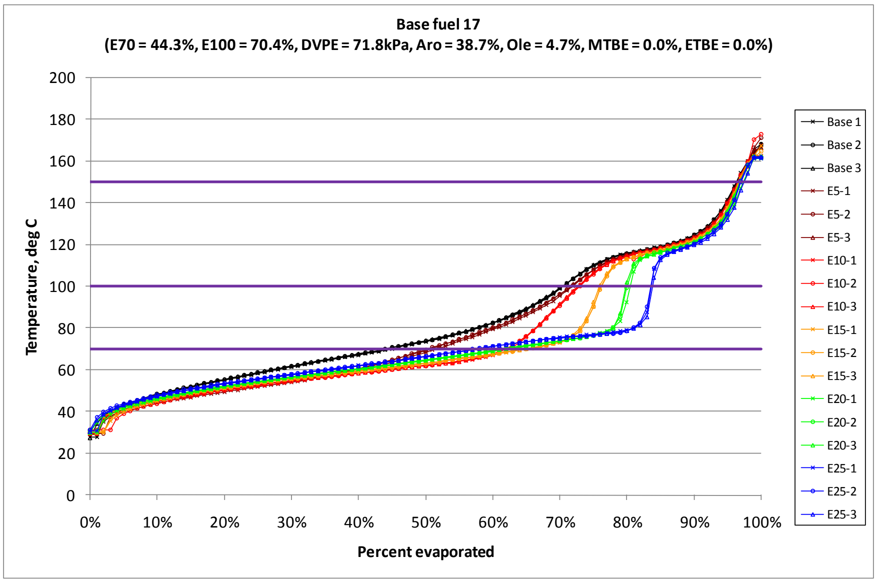

Base fuel 15
(E70 = 27.4%, E100 = 46.6%, DVPE = 51.0kPa, Aro = 38.8%, Ole = 17.9%, MTBE = 10.2%, ETBE = 0.0%)

Figure A8-1 Distillation Curves 16-18





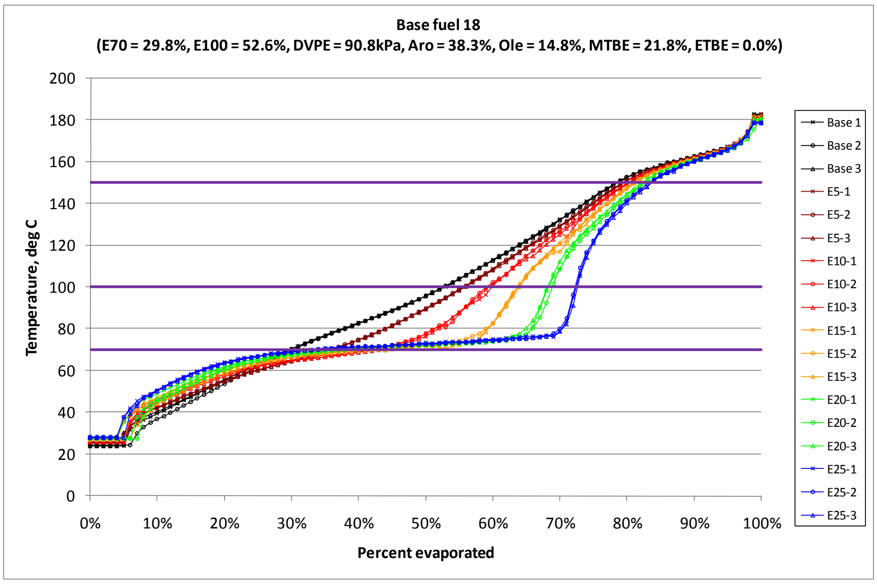
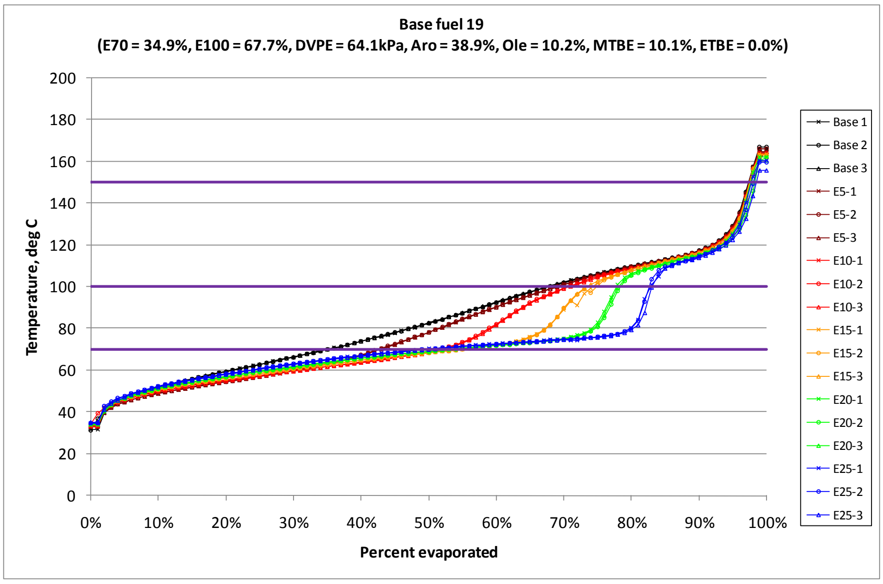
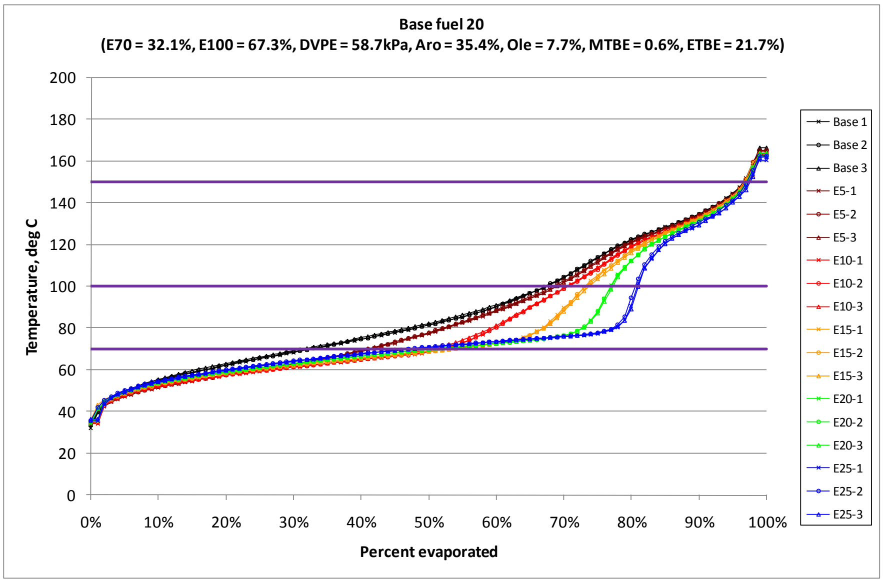


Figure A8-1 Distillation Curves 19-21





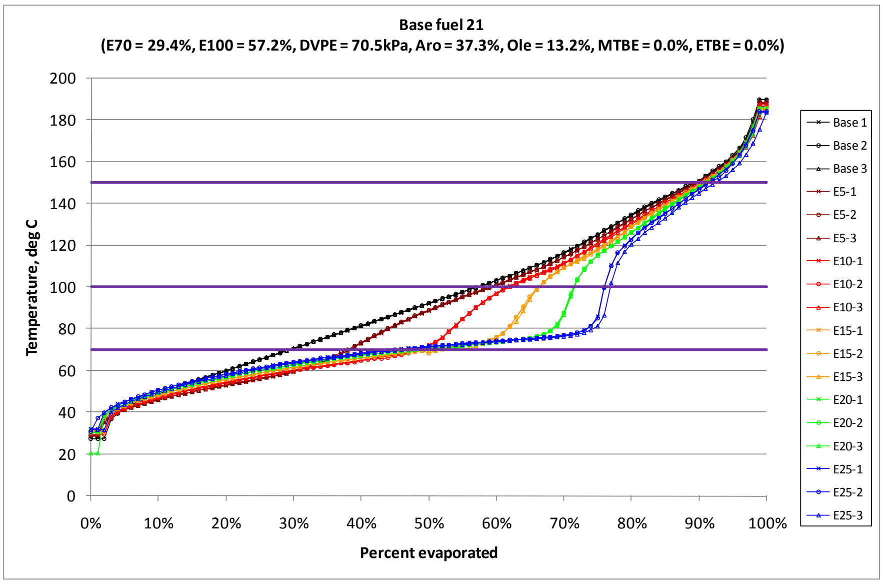


Figure A8-1 Distillation Curves 22-24

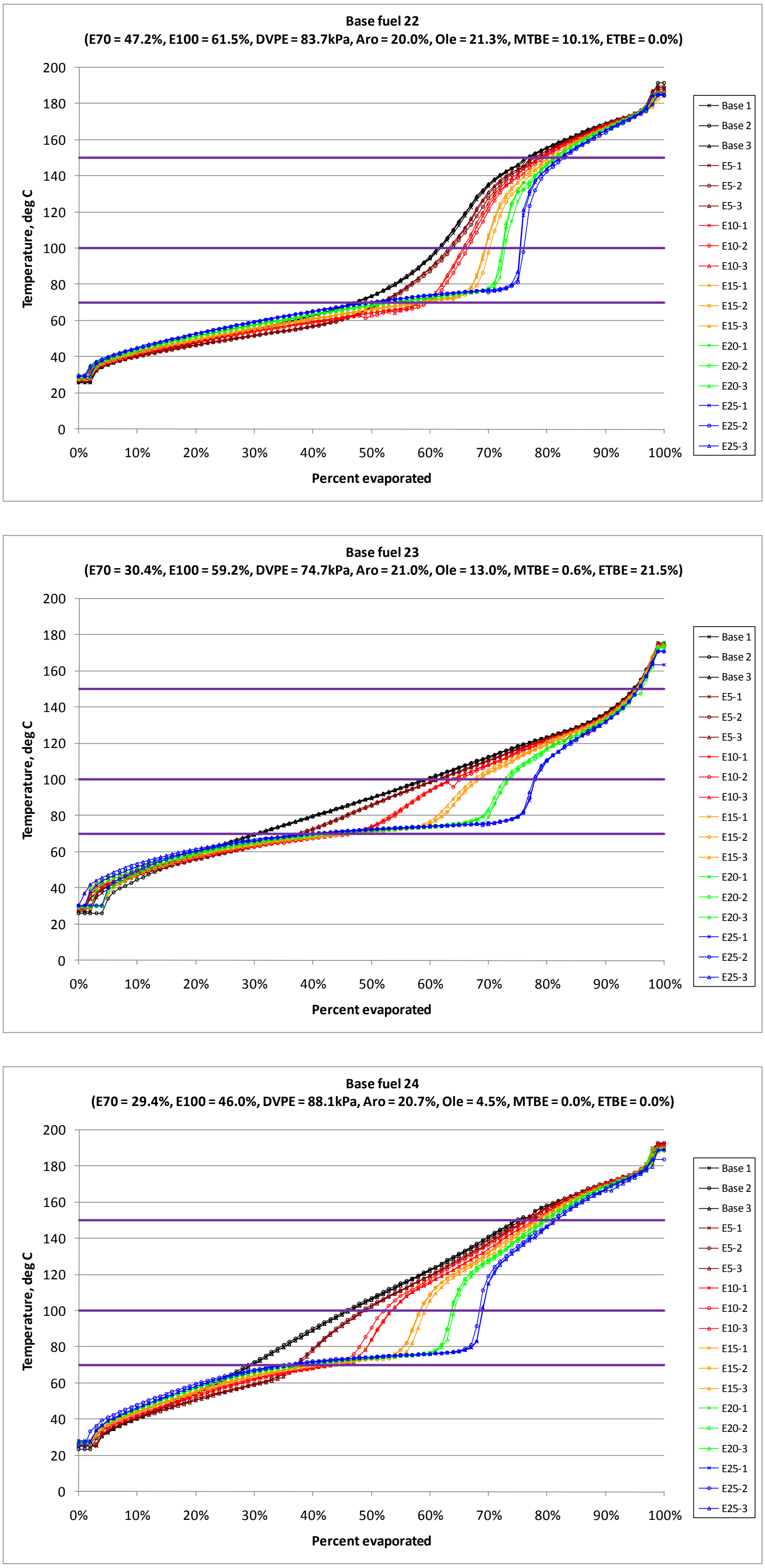
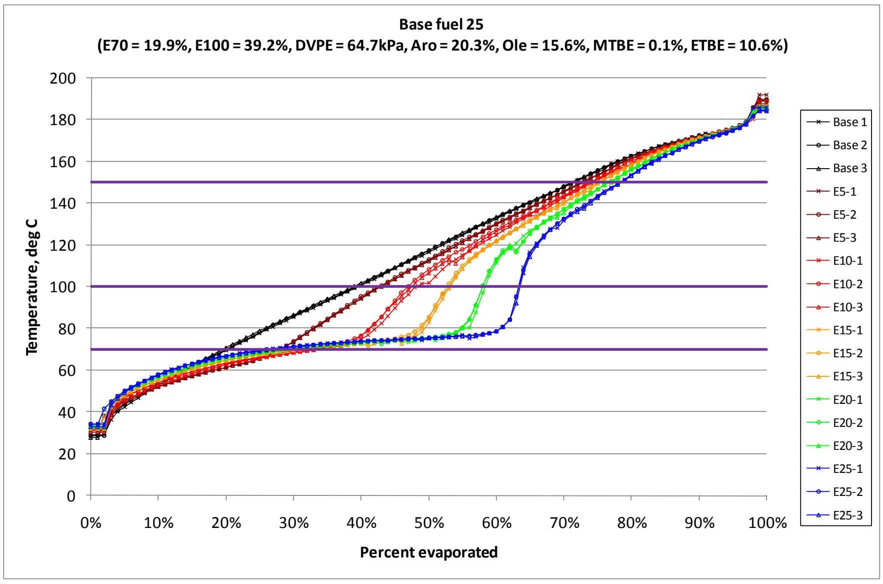
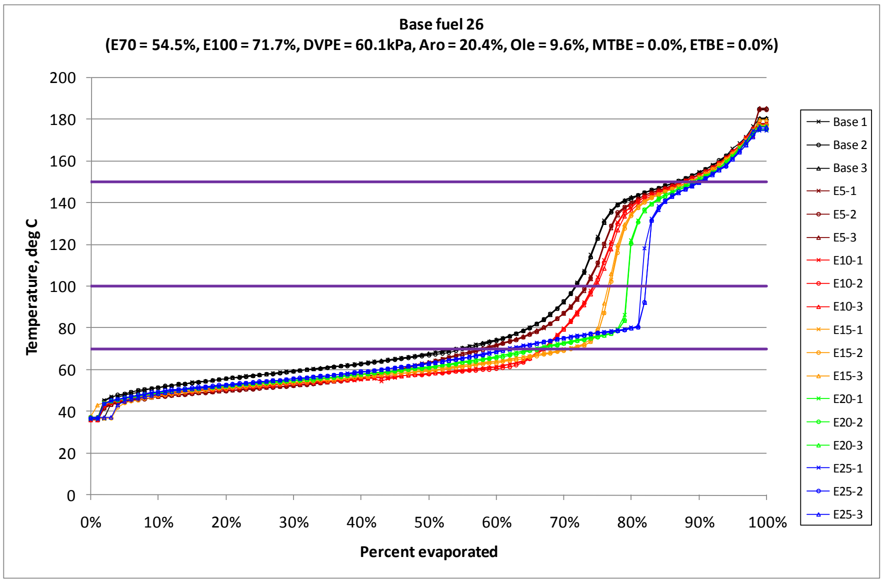


Figure A8-1 Distillation Curves 25-27





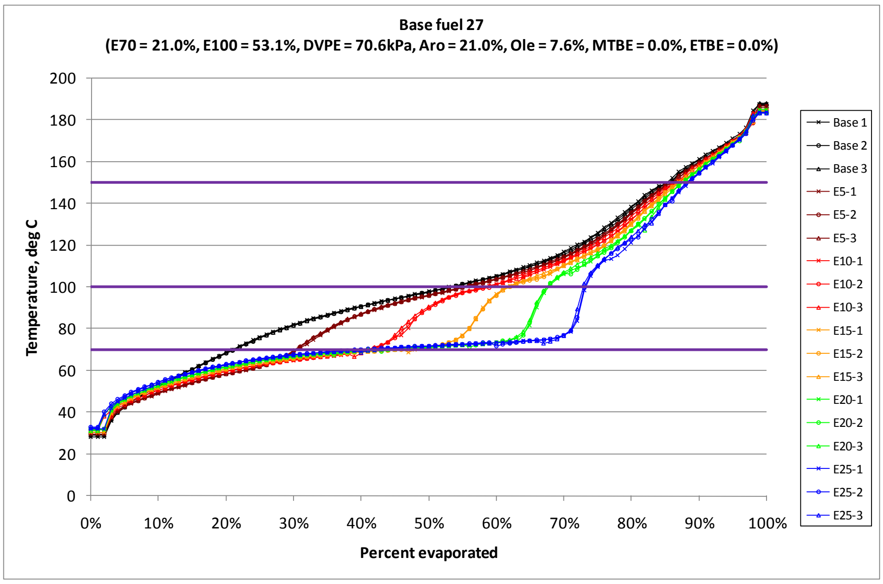
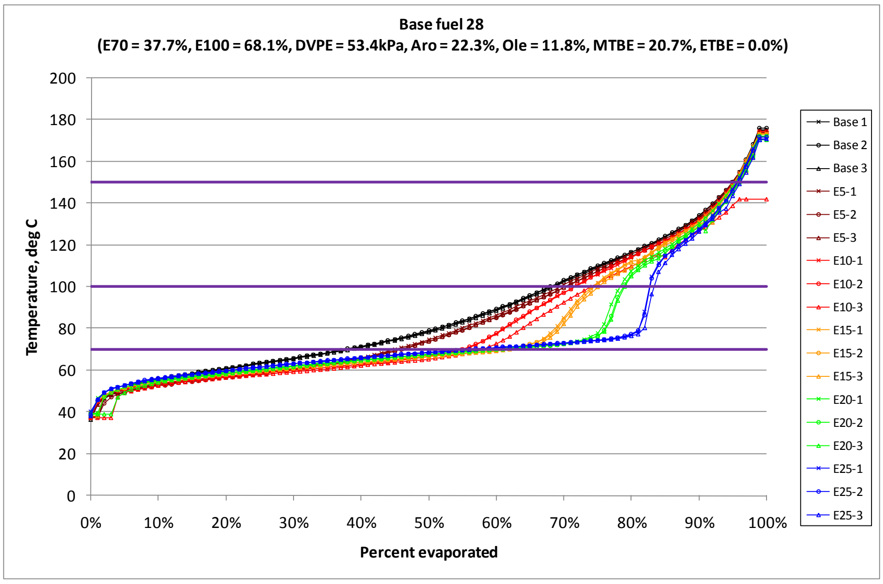
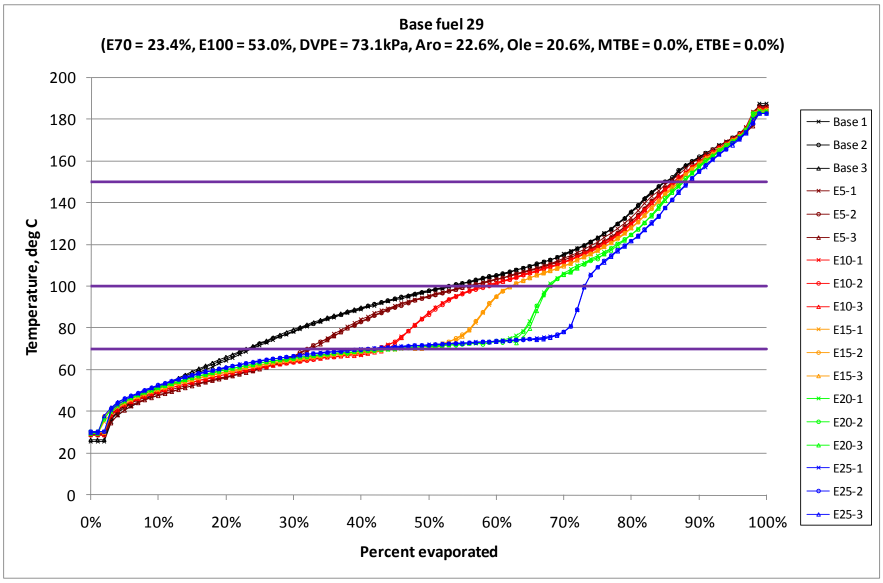


Figure A8-1 Distillation Curves 28-30





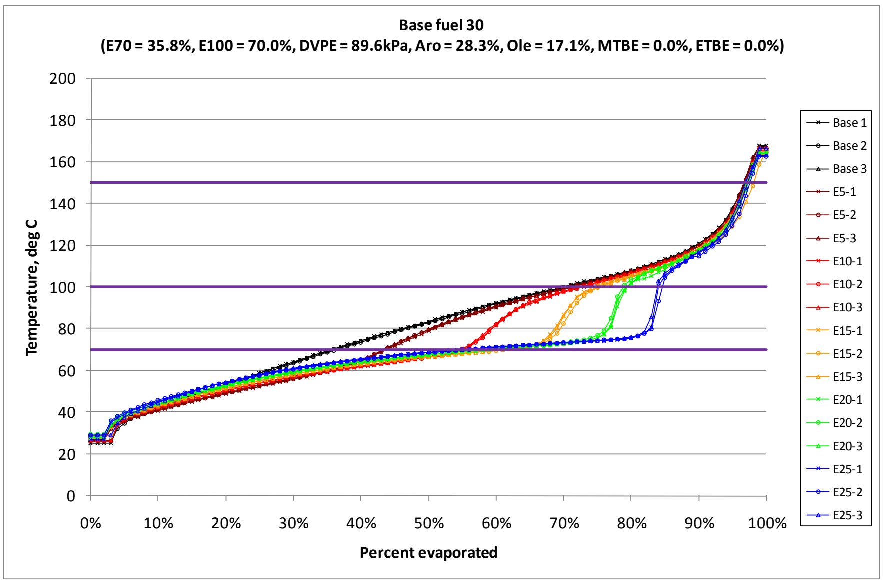
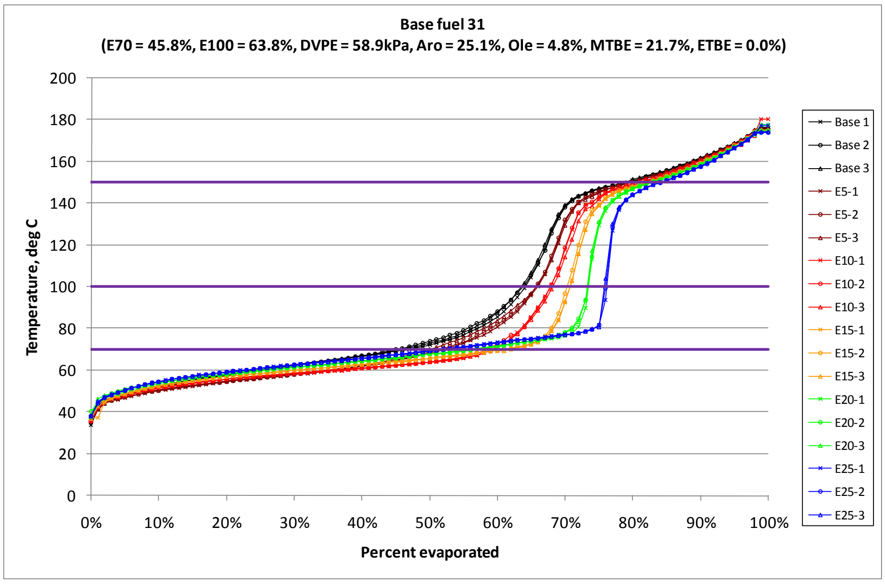
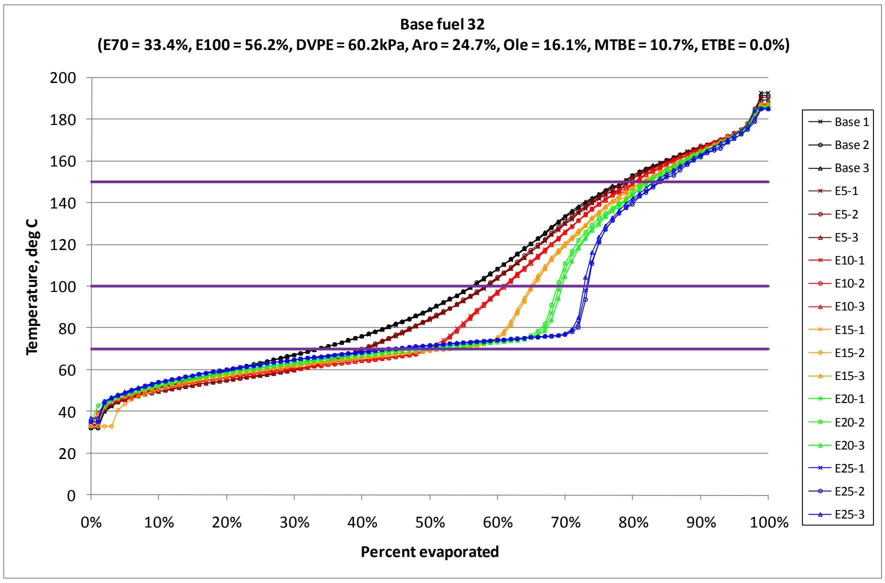


Figure A8-1 Distillation Curves 31-33





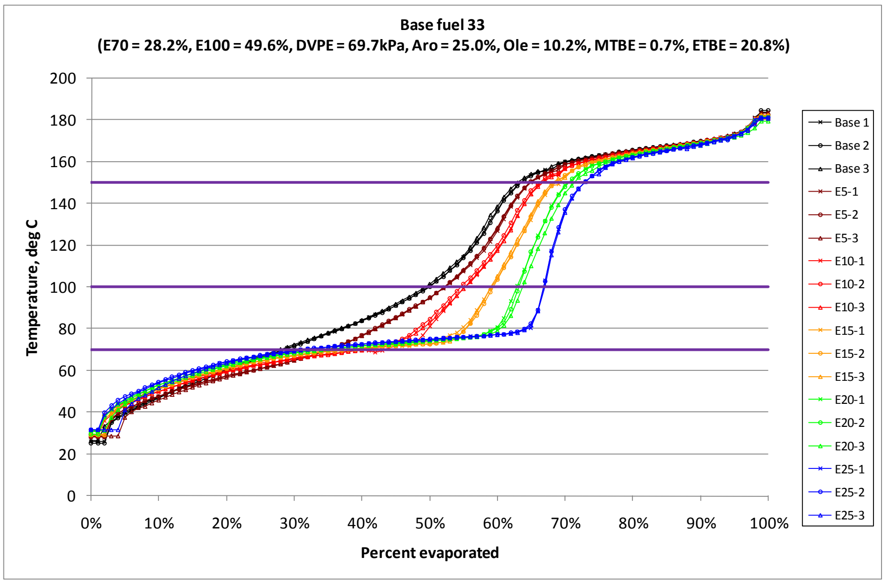
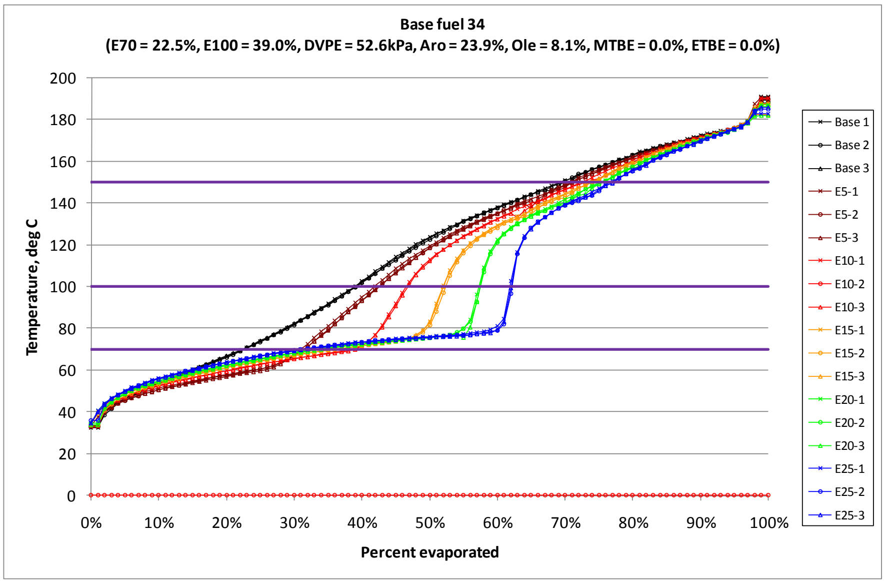
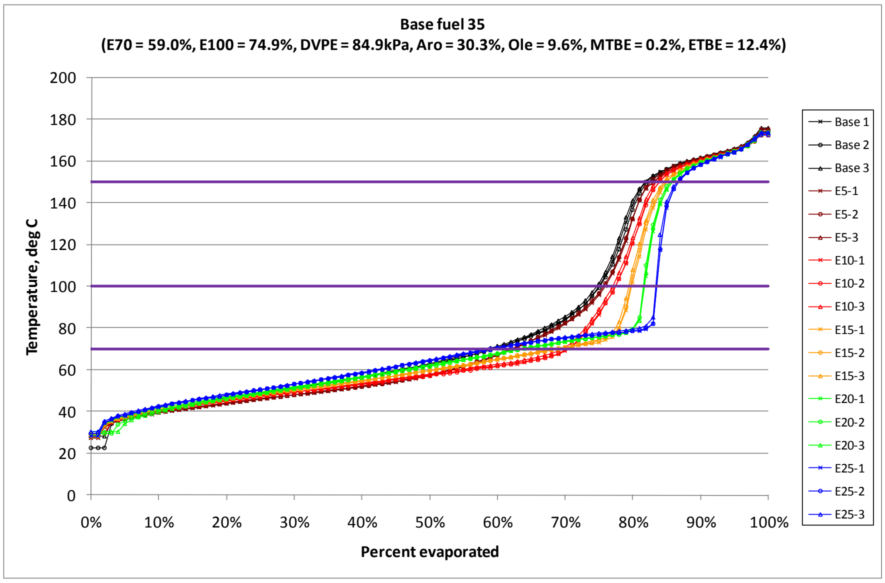


Figure A8-1 Distillation Curves 34-36





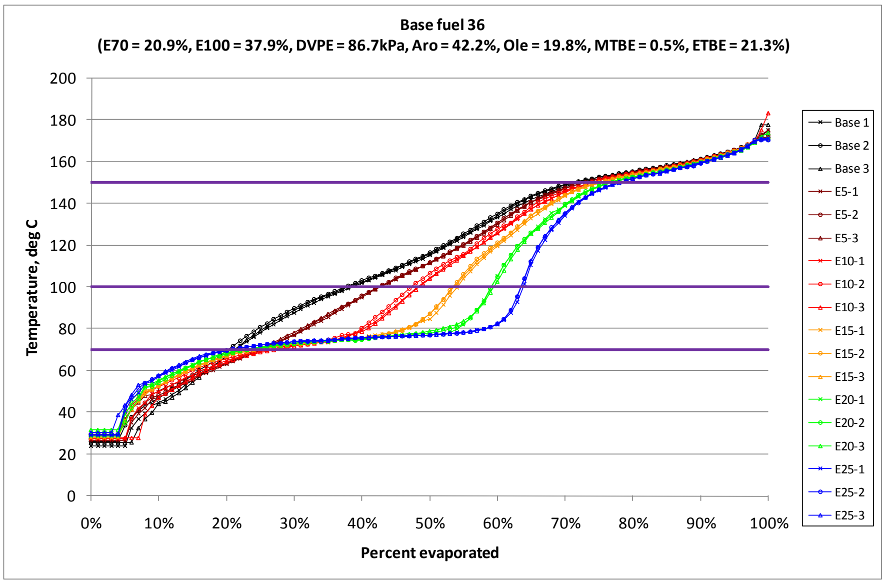
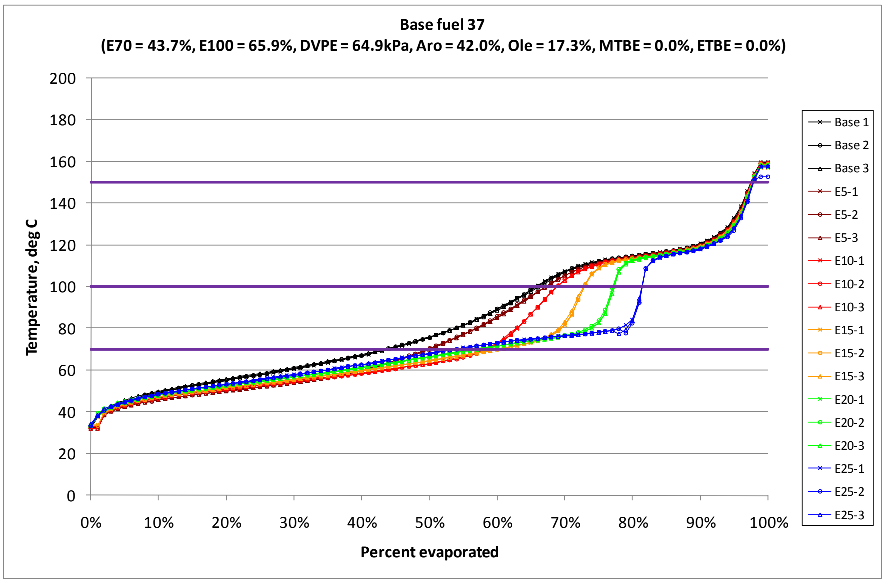
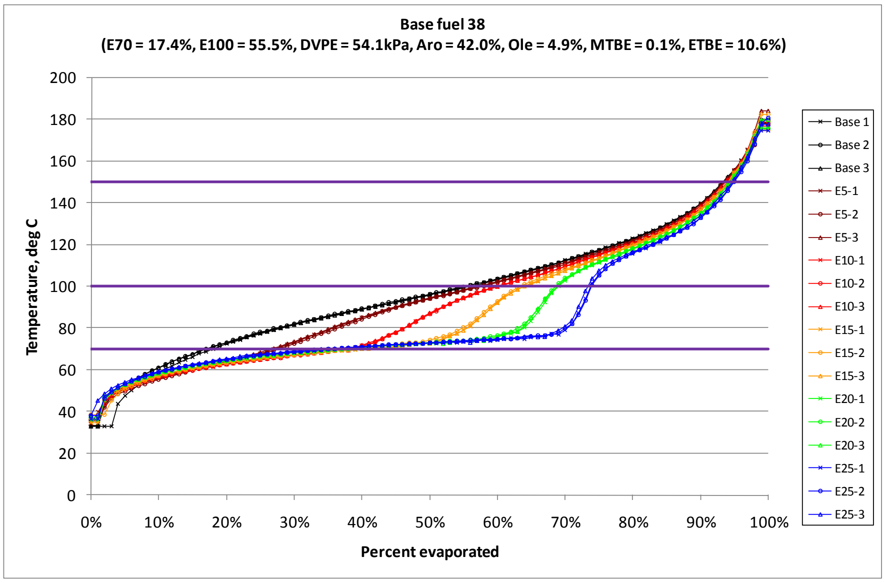


Figure A8-1 Distillation Curves 37-39





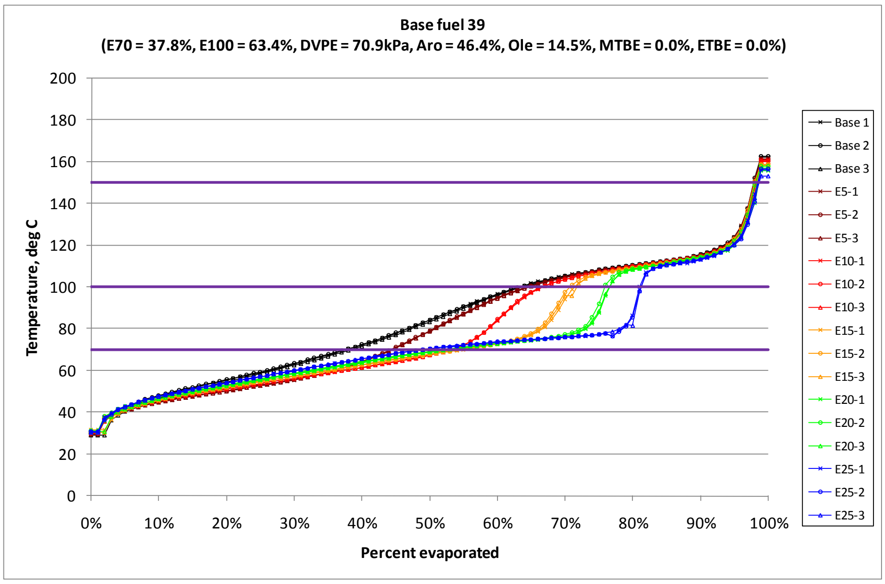
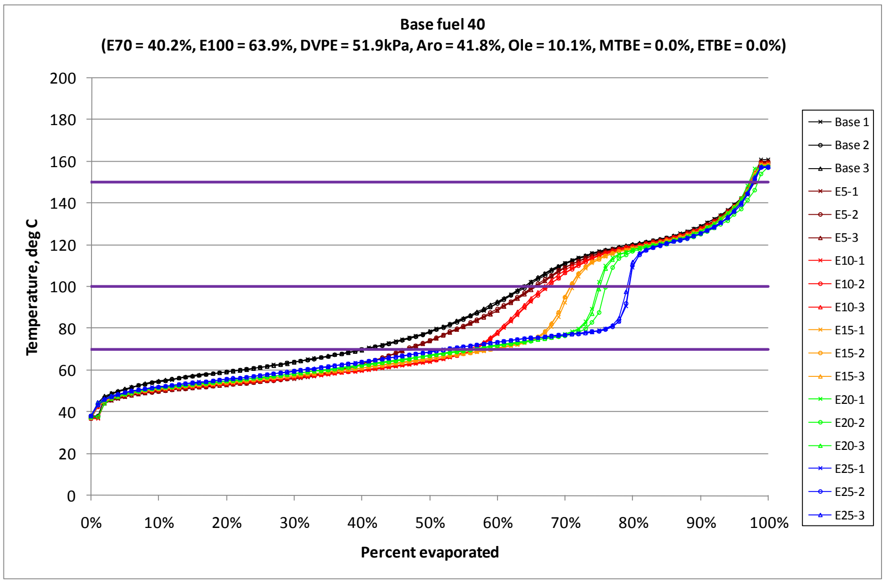
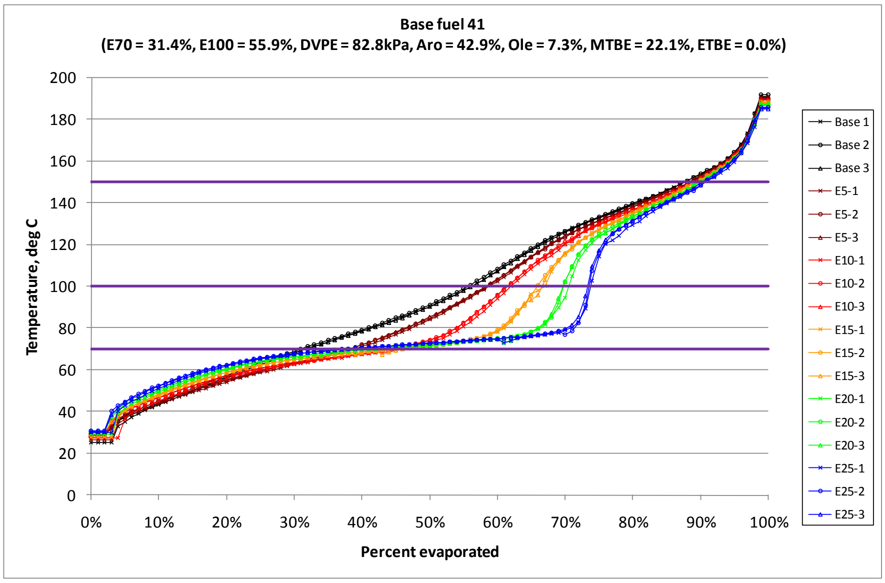


Figure A8-1 Distillation Curves 40-42





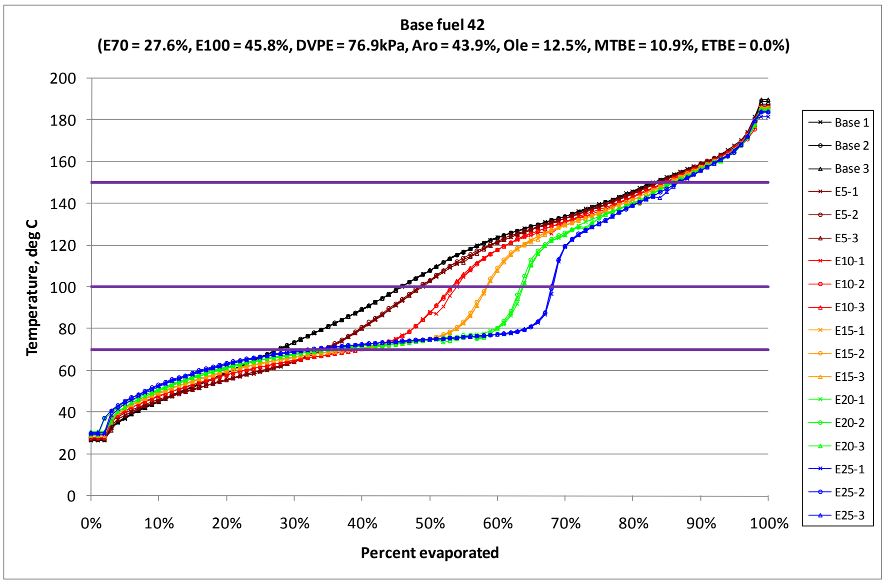
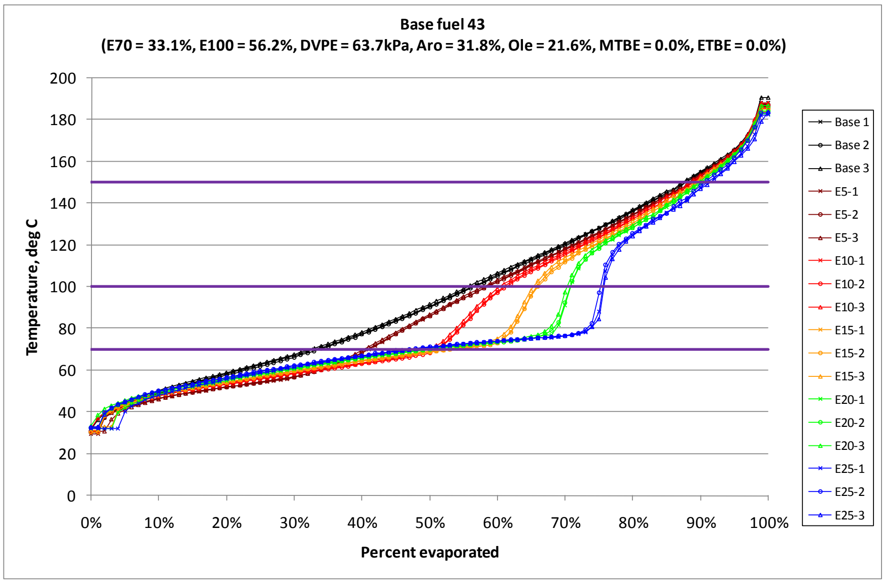
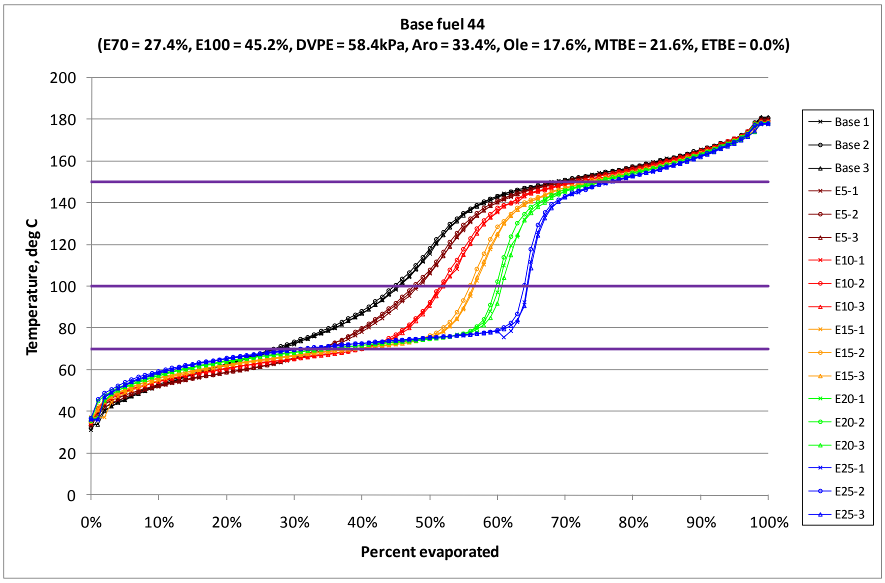


Figure A8-1 Distillation Curves 43-45





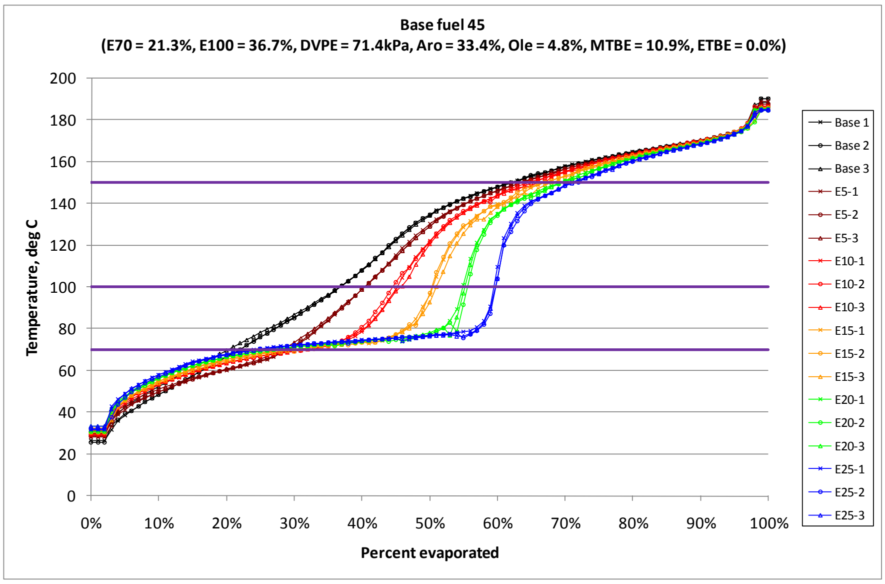
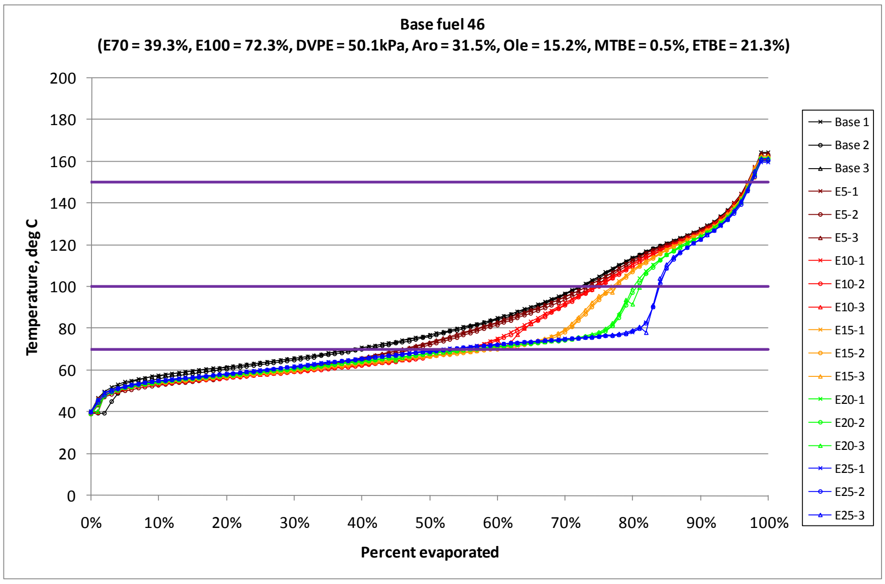
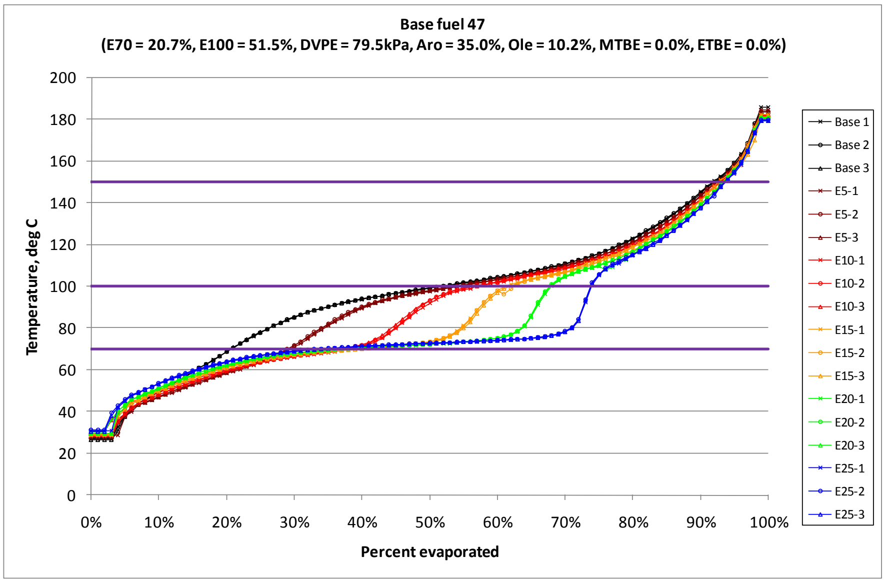


Figure A8-1 Distillation Curves 46-48


Base fuel 46
(E70 = 39.3%, E100 = 72.3%, DVPE = 50.1kPa, Aro = 31.5%, Ole = 15.2%, MTBE = 0.5%, ETBE = 21.3%)


Base fuel 47
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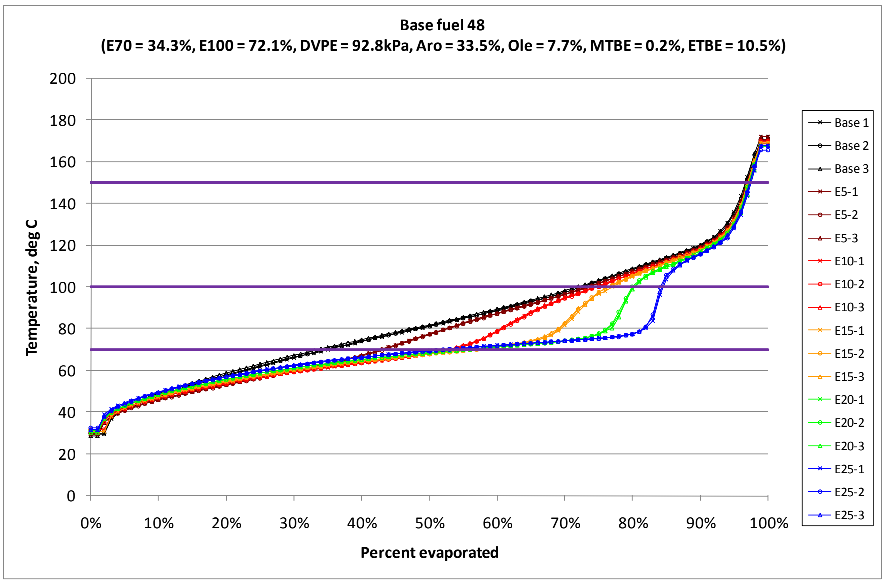

Base fuel 48
(E70 = 34.3%, E100 = 72.1%, DVPE = 92.8kPa, Aro = 33.5%, Ole = 7.7%, MTBE = 0.2%, ETBE = 10.5%)

Figure A8-1 Distillation Curves 49-51

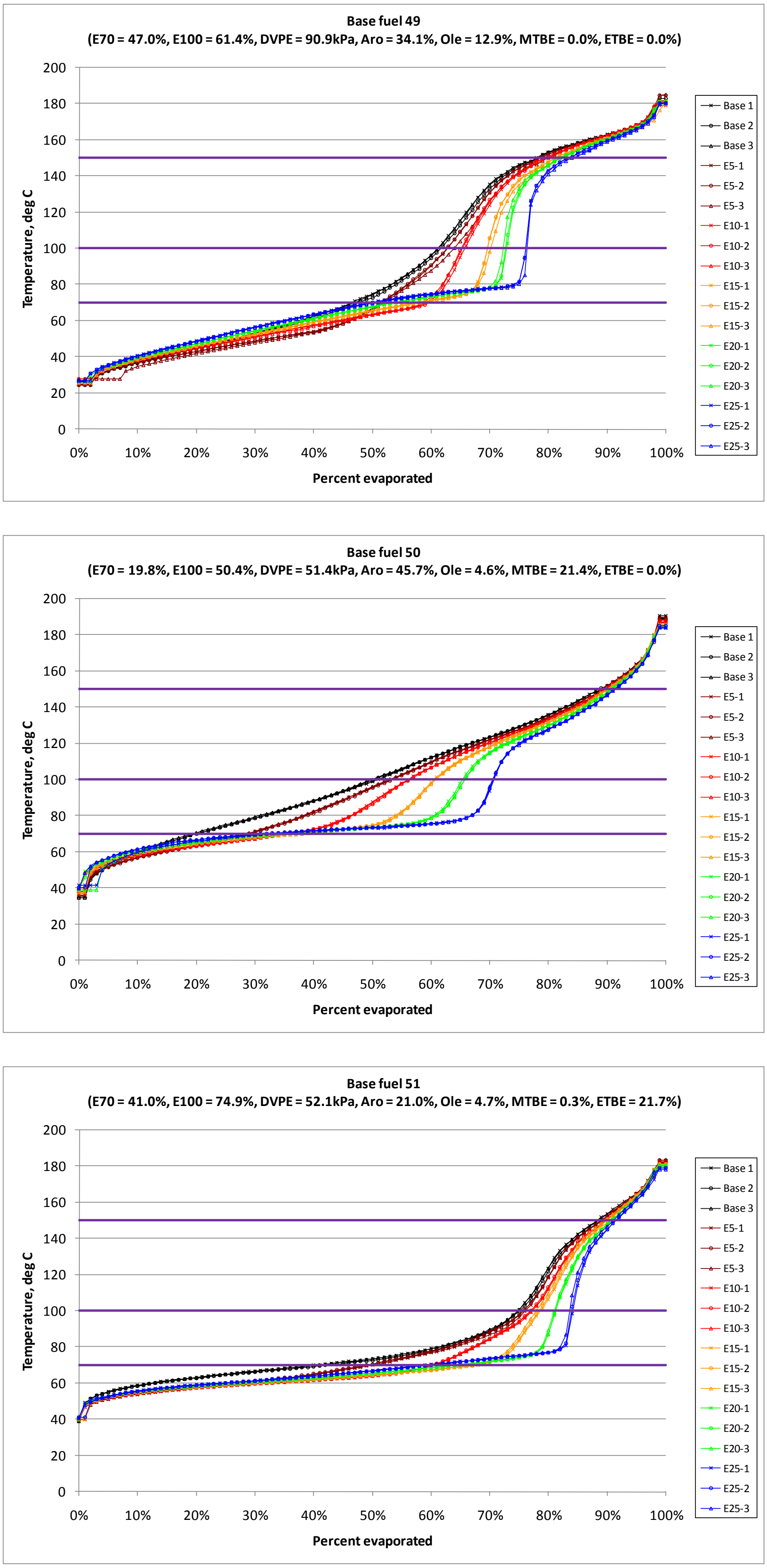
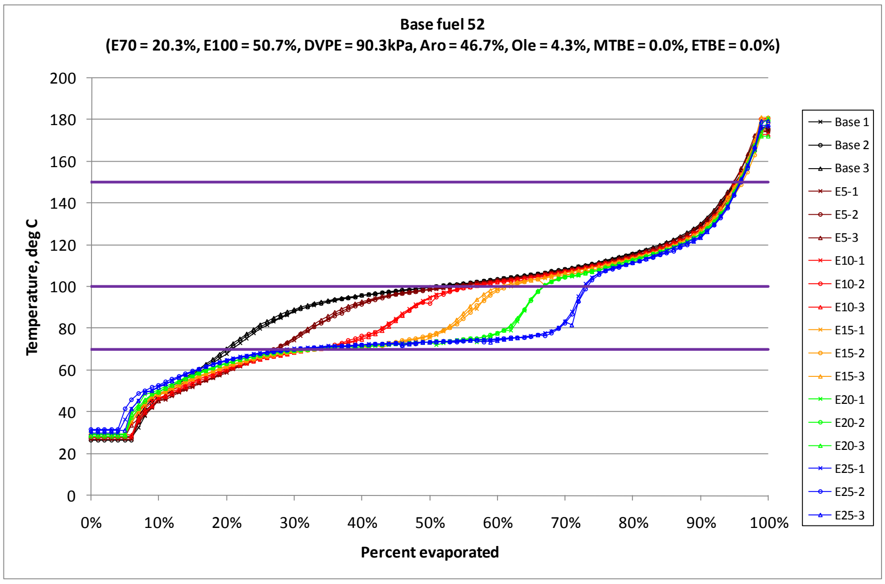
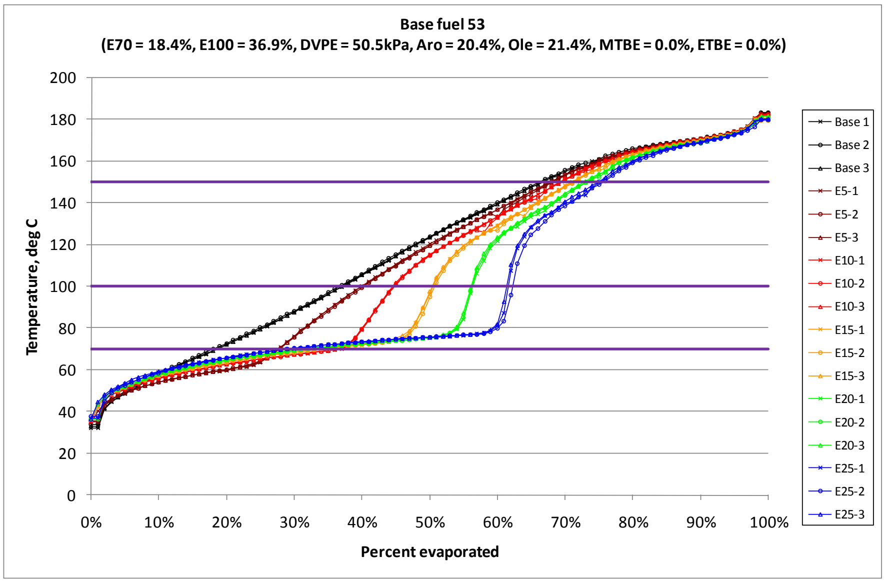


Figure A8-1 Distillation Curves 52-54





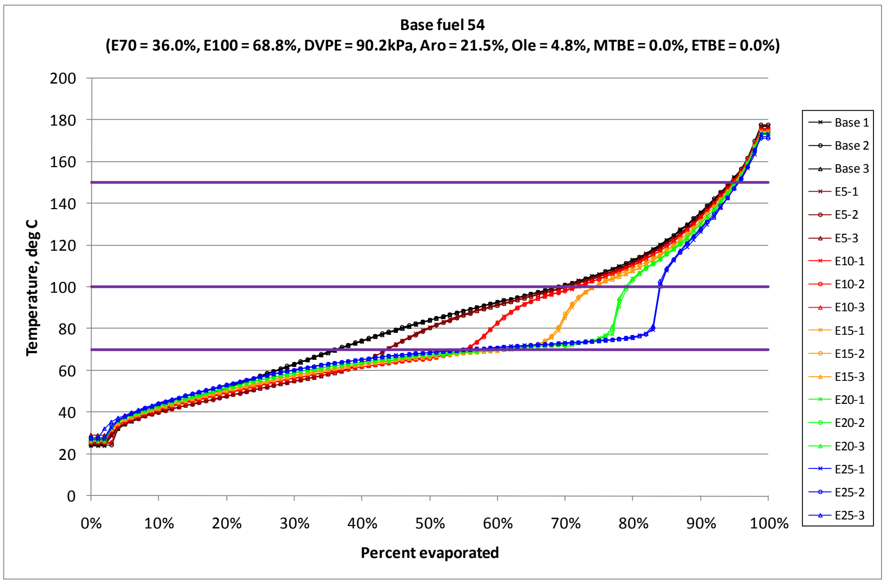
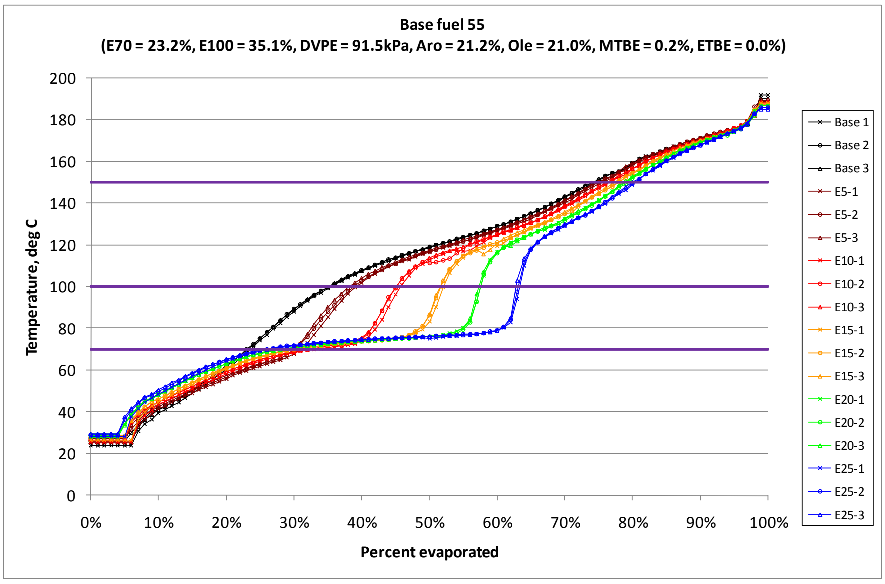
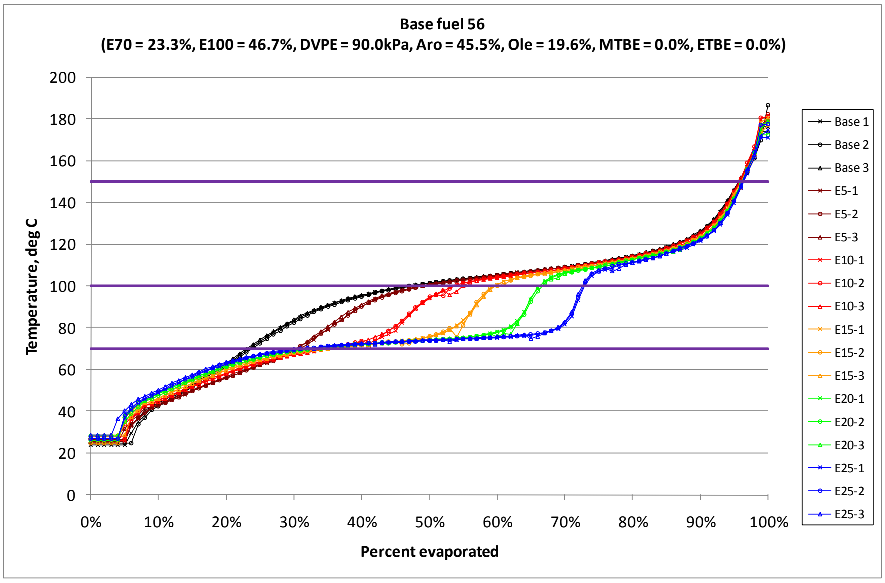


Figure A8-1 Distillation Curves 55-57





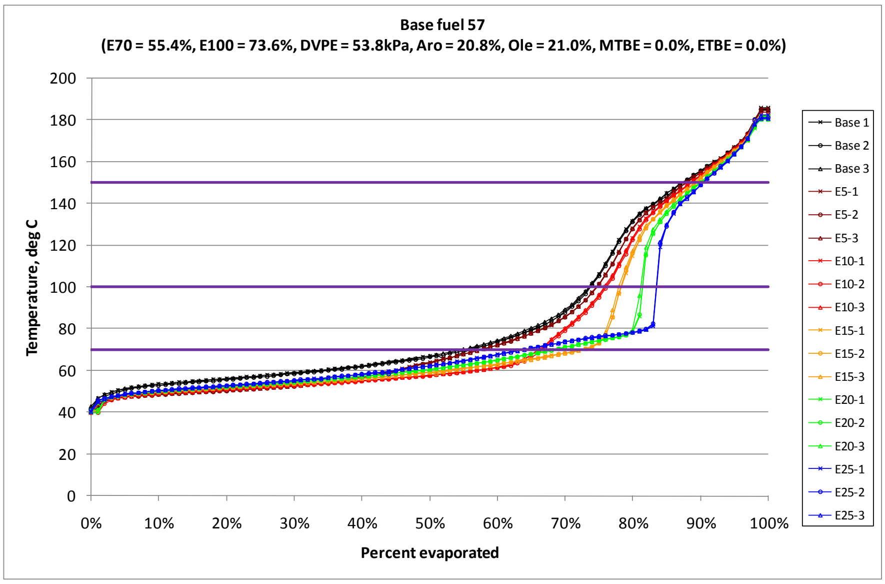


Figure A8-1 Distillation Curves 58-60