the influence of
gasoline mid-range to
back-end volatility on
exhaust emissions

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a review carried out by the Special Task Force on emissions from gasoline powered
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ABSTRACT

This report is a literature review of recent published studies evaluating the effects of mid-range to back-end volatility on regulated emissions from gasoline powered vehicles. It is concluded that there are no wholly definitive data defining exactly which distillation parameters are the true causative factors in influencing tail-pipe emissions, partly due to the necessary physical constraint of a certain degree of intercorrelation between adjacent distillation parameters, e.g. T50 and T60 or E100 and E110. There is, however, a balance of evidence suggesting that the effect is best described by parameters in the mid-range region, typically between T50 and T70, or E100 and E120.

Back-end chemical compositional effects on emissions have been studied by CONCAWE and AQIRP. CONCAWE found that changing back-end composition from aromatics to paraffins and then to olefins gave relatively small but progressive reductions in HC and CO and increases in NOx emissions from catalyst cars. Fuel Volumetric Air Demand (FVAD) i.e. kg of air per litre of fuel, was thought to describe the magnitude of transient air fuel ratio excursions and hence emission effects observed, although intercorrelation between FVAD and other fuel parameters prevented firm conclusions. Distillation effects were found to be somewhat more important than back-end compositional effects for HC and CO emissions, but for NOx the opposite was true. The AQIRP Phase 2 Heavy Hydrocarbon study reported no strong effects of back-end chemical composition on emissions. The reason for the rather different findings of the two programmes is not clear.

KEYWORDS

Reformulated gasoline, back-end volatility, mid-range volatility, distillation, composition, regulated emissions, unregulated emissions, air toxics, Fuel Volumetric Air Demand

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SUMMARY

This report, prepared by CONCAWE's Automotive Emissions Management Group's Special Task Force 1 (AE/STF-1) is a literature review of recent published studies evaluating the effects of mid-range to back-end volatility on regulated emissions from gasoline powered vehicles. As part of the European Auto/Oil study, Technical Sub-Group 1 performed a brief literature survey on the effects of distillation, amongst many other fuel parameters, and summarized the findings in a Discussion Document early in 1994. However, since then significant new data have become available, not least of which are major studies by both US (AQIRP) and European Programme on Emissions, Fuels and Engine Technologies (EPEFE), plus AE/STF-1's own heavy hydrocarbon study.

There is a relatively small but distinct effect of mid-range to back-end volatility on emissions as demonstrated by all of the studies reviewed. The effect on HC and CO emissions tends to be directionally opposite to that on NOx, i.e. increasing mid-range to back-end volatility reduces HC and CO but increases NOx. Effects of distillation on HC emissions are usually greater than those on CO and NOx.

The opposite response of NOx emissions to HC and CO suggests a possible effect of distillation on engine air fuel ratio. Distillation properties may influence the magnitude of engine transient air fuel ratio excursions and hence both engine out emissions and catalyst conversion efficiency. Distillation may also have an influence on HC emissions in particular, through effects on the driveability performance of fuels.

Of the programmes reviewed which reported a stronger effect of back-end volatility, as characterised by T90 or E150, data analysis was complicated by intercorrelations between back-end and mid-range distillation parameters. Conclusions based on, for example, T90 or E150 could also be suitably based on any parameter ranging from mid-range distillation points up to the back-end, (i.e. T50-FBP or E100-FBP). Both phases of the US AQIRP programme fell into this category. In some cases marginally stronger correlations between emissions and distillation occurred with parameters around the mid-range region.

In other programmes, however, the intercorrelations between mid-range and back-end distillation parameters have been reduced. In these cases emissions data correlated better with parameters more towards the mid-range boiling region. T90, E150 or other back-end parameters, were not found to exhibit significant influences on emissions. Some programmes correlated HC emissions, in particular, with Driveability Index, DI, which is often used, particularly in the US, to describe the cold weather driveability performance of fuels. DI attempts to describe the distillation curve in terms of functions of front-end, mid-range and back-end volatility thus:

\[ DI = 1.5^*T10 + 3.0^*T50 + T90 \]

As DI is heavily influenced by T50, and therefore also E100, such programmes may also suggest mid-range distillation is best able to describe emission effects.
Overall, however, there are no wholly definitive data defining exactly which distillation parameters are the true causative factors in influencing tail-pipe emissions, partly due to the necessary physical constraint of a certain degree of intercorrelation between adjacent distillation parameters, e.g. T50 and T60 or E100 and E110. There is, however, a balance of evidence suggesting that the effect is best described by parameters in the mid-range region, typically between T50-T70, or E100-E120.

Back-end chemical compositional effects on emissions have been studied by CONCAWE and AQIRP. CONCAWE found that changing back-end composition from aromatics to paraffins and then to olefins gave relatively small but progressive reductions in HC and CO and increases in NOx emissions from catalyst cars. Fuel Volumetric Air Demand (FVAD), i.e. kg of air per litre of fuel, was thought to describe the magnitude of transient air fuel ratio excursions and hence emission effects observed, although intercorrelation between FVAD and other fuel parameters prevented firm conclusions. Distillation effects were found to be relatively more important than back-end compositional effects for HC and CO emissions, but for NOx the opposite was true. The AQIRP Phase 2 Heavy Hydrocarbon study reported no substantive effects of back-end chemical composition on emissions. The reason for this difference between the two programmes is not clear, although in the AQIRP programme back-end chemical composition was strongly correlated with mid-range to back-end distillation, whilst this was not true for the CONCAWE programme. Furthermore, the vehicles used in the AQIRP study were generally equipped with adaptive learning systems whilst those used in the CONCAWE programme generally were not.
1. INTRODUCTION

The European Auto/Oil Programme's Sub-Group 1 reviewed the effects of gasoline properties on exhaust emissions in late 1993/early 1994. They concluded that while effects of some properties were well understood, the effect of both mid-range and back-end volatility required further study in the EPEFE programme. However, a number of test programmes were underway and due to be reported shortly after the review, (including the US Auto/Oil Phase 2 and CONCAWE heavy hydrocarbon studies). Consequently, it was decided to defer any further work on back-end volatility until the results of these programmes were available. The EPEFE programme went on to study in detail the effect of mid-range volatility.

The results of all of these studies, including EPEFE, are now available, and this report is intended as a literature review of these and other studies on the effect of mid-range to back-end volatility on exhaust emissions from gasoline fuelled vehicles. Discussion is centred on the effects of different distillation parameters in the mid-range to back-end region. As will become apparent, intercorrelation of parameters is an inherent problem in this field and in many programmes these distillation characteristics were heavily intercorrelated, making it difficult to draw clear conclusions.

Some of the programmes discussed below, notably the US AQIRP Phase 2 and CONCAWE's AE/STF-1 Heavy Hydrocarbon studies, evaluated the impact of both distillation changes and back-end chemical composition on emissions. For clarity, the effects of distillation changes are dealt with first and back-end chemical compositional effects are discussed separately, later.
2. DISTILLATION EFFECTS ON REGULATED EMISSIONS

2.1. US AQIRP PHASE 1 STUDY

The Phase 1 US AQIRP study examined the effects of fuel composition on emissions from twenty current, (ten 1989 model year pairs), and fourteen older vehicles, (seven 1983-1985 model year pairs), tested over the FTP drive cycle. In general, the older car fleet represented vehicle technologies not widespread in Europe, with over 70% of the vehicles being equipped either with oxidation catalysts only or three-way/oxidation catalyst combinations. Only the results from the current fleet, therefore, which are more relevant to European catalyst car technologies, will be considered in the following text.

Fuel set A of the Phase 1 programme was designed to look at compositional effects on emissions. In particular, the four matrix-design variables were aromatics (20-45% v/v), MTBE (0-15% v/v), olefins (5-20% v/v) and T90 (138-182°C). These parameters were varied in a full factorial, two-level design with only the low and high target values of each parameter shown above, used. Thus it was only possible to examine linear correlations of the fuel parameters. Although the matrix was designed to differ in back-end volatility, as defined in AQIRP by T90, examination of the full distillation data demonstrates that large changes in other distillation parameters down to the mid-range boiling region existed.\(^1\) E-parameters were not used to characterise fuels in the US studies until the AQIRP Phase 2 programme, see Footnote 1.

The range of actual T90 values within the fuel matrix was from 137-181°C, whilst that of T50, for example, was 73-115°C and of T70 was 99-146°C. The ranges between the minimum and maximum values of parameters from T50-T90, and indeed FBP, were therefore similar. It is notable that while T50 and T90, for example, were not highly correlated ($R^2 = 0.62$), T70 and T90 were, ($R^2 = 0.94$).

Figure 1 illustrates the distillation curves for the sixteen matrix fuels. These have been arranged so that pairs of fuels differing only in the design variable T90 are compared. The AQIRP AMOT nomenclature has been used to identify the individual fuels, whereby "A" represents a fuel containing high aromatics (45% v/v) and "a" low aromatics (20% v/v), "M" represents a fuel containing high MTBE (15% v/v) and "m" a fuel without MTBE (0% v/v), and so on for olefins and T90.

The work reported that for the current fleet, a statistically significant reduction in HC (22%, with fleet average emissions of approximately 0.352 g/km) and an increase in NOx emissions (5%, with fleet average emissions of approximately 1.072 g/km) were observed for a reduction in T90 from 182°C to 138°C across the composite FTP cycle.\(^3\) No statistically significant effect of T90 on CO emissions was found. Results were reported in terms of the four matrix-design fuel parameters, and an extensive analysis based on other distillation parameters, in particular, was not performed. However, indications of somewhat better correlations with parameters in the mid-range region were given.\(^3\)

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1. T-parameters represent the temperature at which a fixed fraction of the fuel evaporates, e.g. T90 is the temperature at which 90% v/v of the fuel evaporates. Increasing T-parameter values represent a reduction in fuel volatility. E-parameters represent the fraction of fuel evaporated at a fixed distillation temperature, e.g. E150 is the volume of fuel evaporated at 150°C. Increasing E-parameter values represent an increase in fuel volatility, and thus there is an inverse relationship between T-numbers and E-numbers.

3. The work reported that for the current fleet, a statistically significant reduction in HC (22%, with fleet average emissions of approximately 0.352 g/km) and an increase in NOx emissions (5%, with fleet average emissions of approximately 1.072 g/km) were observed for a reduction in T90 from 182°C to 138°C across the composite FTP cycle. No statistically significant effect of T90 on CO emissions was found. Results were reported in terms of the four matrix-design fuel parameters, and an extensive analysis based on other distillation parameters, in particular, was not performed. However, indications of somewhat better correlations with parameters in the mid-range region were given.
Further analysis by CONCAWE member companies of the HC emission data in terms of other single distillation parameters has indicated that somewhat better correlations of the HC results can be achieved with distillation parameters down to T60.$^2,^4$ The best single distillation parameter correlation for this dataset was found to be T70, although it should be emphasized that any parameter between T50 and T90 gave satisfactory correlations with the data, with broadly similar goodness-of-fit statistics.

In conclusion, the Phase 1 programme demonstrated an effect of distillation on HC and NOx emissions. Whilst the results were reported by AQIRP in terms of T90, it is not possible to make definitive conclusions based solely on T90, as indeed pointed out by the AQIRP working group in their publications.$^5$ The best single distillation parameter correlation was found with T70, although in practice any distillation parameter from T50-T90 gave a satisfactory explanation of the data.

2.2. US AQIRP PHASE 2 STUDY

The Phase 2 US AQIRP heavy hydrocarbon study examined the effects of fuel composition on emissions from ten current, (1989 model year), vehicles tested over the FTP drive cycle. This fleet comprised one each of the ten pairs of current fleet vehicles used in the Phase 1 AQIRP work. The study aimed to enable further investigation into the effect of back-end volatility, previously described by AQIRP in terms of T90, on emissions, particularly with regard to the linearity of any effect, the interaction with mid-range parameters, and back-end chemical compositional effects.

The Phase 2 study used two full factorially designed fuel matrices, A and B, with the independent variables consisting of a range of catalytically cracked reformate and alkylate streams. It is important to note that the distillation characteristics T50 and T90, (and hence their E-number equivalents), and the aromatic, olefinic and paraffinic composition of the fuels were not, in fact, design variables, but rather descriptors which were dependent on the blending component design variables. AQIRP based analysis of the data largely on T90 because there was a good correlation with the design variables.$^5$ An analysis of the data based on the design variables was not presented.

The work reported a non-linear effect of T90 on HC emissions, such that for test fuels with T90 reducing across a range of 171-131°C, a reduction in fleet average tailpipe emissions of approximately 24% occurred, (from 0.448 g/km to 0.344 g/km). After allowing for the influence of olefins and aromatics, which also varied with T90 in this matrix, the residual effect of reducing T90 within this range was concluded to be 18%.$^6$ No significant effect of T90 on CO was reported, but for NOx emissions a 12% increase was observed with decreasing T90. Of this 12% increase, approximately half was attributed to a direct T90 effect, the remaining change being due to compositional effects. Note that as found in the Phase 1 study, the NOx effect was opposite in direction to that of HC.

An influence of T50 on composite cycle HC emissions was also reported for the matrix B fuels, such that at constant T90, reducing T50 gave a reduction in emissions. Figure 2 is a redrawn graph from the published report.$^6$
Prior to this work AQIRP had solely used T-parameters to describe gasoline distillation. However, at this point the use of E-numbers was introduced. E-numbers offer a distinct advantage as descriptors of fuel distillation over T-numbers since current blending models can more accurately predict E-numbers. Furthermore, correlations between emissions and distillation are usually equally applicable to E- and T-numbers. The study reported that for both matrix A and B fuels, a regression equation containing non-linear terms in $E_{149}$, (corresponding to $E_{300^\circ F}$), and $E_{93}$, (corresponding to $E_{200^\circ F}$), described the tailpipe HC emission results best:

$$\ln(\text{HC}) = -1.576 + (0.00236\cdot(E_{149}-E_{93})-41) + 0.04634\cdot\exp[0.1716\cdot(100-E_{149}-12)] + 0.0255\cdot M$$

$$M = \text{Constant} \quad R^2 = 0.979$$

This equation, derived empirically, is a double exponential relationship between HC emissions and mid-range and back-end distillation, as characterised by $E_{93}$ and $E_{149}$ respectively.

Within the programme, however, a number of fuel composition and distillation parameter intercorrelations were observed as illustrated by the distillation curves of the test fuels shown in Figure 3. For example, $T_{90}$, $T_{50}$ and aromatics, in addition to a number of other distillation parameters between $T_{90}$ and $T_{50}$, were intercorrelated to varying degrees. Analysis of data from the programme is complicated by these intercorrelations and the observed fuel effects on emissions can be explained in a number of ways. Whilst an equation of the form quoted above appears to describe the HC emissions data in a satisfactory way, other equations can give similar descriptions of the results with virtually identical $R^2$ values, (see Appendix). Such equations can contain many different combinations of distillation parameters whilst appearing to still describe the results well. Inevitably this arises due to the intercorrelations mentioned above. One particular equation, containing terms only in $T_{50}$, $T_{50}^2$, MTBE and olefins and of a much simpler overall form also gave an excellent fit to the data with $R^2 = 0.96$. Plots of composite cycle HC emissions against $T_{50}$ for both matrix B and matrix A and B combined illustrate this further, (Figures 4 and 5).

In conclusion, the Phase 2 heavy hydrocarbon study has, like the Phase 1 work, shown an effect of mid-range to back-end distillation on emissions, with opposing effects of distillation on HC and NOx. The HC emission results were reported qualitatively in terms of a main $T_{90}$ effect with a further secondary influence of $T_{50}$, and quantitatively in terms of a double exponential relationship with $E_{149}$ and $E_{93}$. However, further analysis has revealed that it is again not possible to make clear definitive conclusions based solely on these parameters, due to intercorrelations present in the test fuel matrices. Relatively simple regression equations containing, for example, only mid-range volatility terms also provide satisfactory explanations of the results.
2.3. CONCAWE AE/STF-1 HEAVY HYDROCARBON STUDY

The CONCAWE AE/STF-1 programme on heavy hydrocarbons was designed in the light of the US AQIRP study, to investigate whether similar effects are observed for European cars. The programme studied the effects of fuel back-end distillation and chemical composition on exhaust emissions from ten current technology European catalyst vehicles operated over the current European drive cycle, (according to Directive 91/441/EEC). The work was designed to investigate these effects independently of each other.7

The fuel matrix was based on a light gasoline base-stock, to which distillate fractions from selected heavy aromatic, paraffinic and olefinic refinery components were added to give a range of six fuels at two different T90 levels, three with nominal T90s of 160°C (I-160) and three with nominal T90s of 180°C (H-180), containing either heavy aromatics, olefins or paraffins (the actual T90 values differed, on average, by somewhat less than the desired 20°C). In addition, a low-T90 fuel was blended. This consisted of the base-stock in which the front-end distillation characteristics were adjusted with light paraffinic components to give a base fuel (B-140) which matched the heavier test fuels in distillation up to the T50 point.

The fuel matrix was not designed to unambiguously determine which distillation parameter is the most important factor in determining emissions. However, an important difference from the US AQIRP programmes was that the fuels were blended to differ only in their back-end volatilities and to be similar in mid-range volatility. With the exception of one of the six heavier fuels (O-160), the distillation curves of these fuels were similar up to the T80 point and thereafter diverged to one of the two target T90 values, (Figure 6). The base fuel, however, whilst similar in distillation to the other six fuels up to the T50 point, progressively diverged from them to give a more volatile fuel with much reduced T-values, from T50 upwards.

The effects observed on exhaust emissions due to the reduction in volatility between the light base fuel and the I-160 fuels included reduced HC emissions by 8%, (from 0.220 g/km to 0.202 g/km), and CO emissions by 12%, (from 1.217 g/km to 1.066 g/km). However, further reducing volatility from the three intermediate to the three heavy fuels (I-160 to H-180), gave no effect on HC or CO emissions. Thus, since the three I-160 and three H-180 fuels generally only differed in distillation above T80, whilst the light base fuel had progressively diverging T-parameter values from the other six fuels from the mid-range point upwards and not just at the back-end, there is some evidence from this work that back-end distillation as characterised by T90 may not be responsible for differences in emissions, and that the main effect of mid-range to back-end distillation may be in the region between T50 and T80.

For NOx emissions, as in the AQIRP programmes, an opposite response to fuel distillation characteristics was observed compared with HC and CO. As volatility increased from the heavier fuels to the base fuel, emissions increased by 13% for the aromatic based fuels, (0.218 g/km to 0.247 g/km), and 5% for the paraffinic based fuels, (0.234 g/km to 0.247 g/km), whilst no significant difference was observed for the olefinic based fuels.
Linear regression analysis performed by AE/STF-1 showed that mid-range distillation parameters appeared to correlate best with regulated emissions, despite the small spread in values across the test fuel matrix. T55 emerged as the best single T-value descriptors of HC and CO emissions and T50 the best descriptor of NOx emissions. The best E-value descriptors of HC, CO and NOx emissions were E110, E115 and E130 respectively. This analysis, however, did not prove or disprove that such mid-range factors were the true determinants of differences in emissions between the fuels, as there were intercorrelations between adjacent distillation parameters.

It is notable that the CONCAWE programme found effects of distillation on CO emissions which were not detected in the AQIRP programmes. The reasons for this are not entirely clear. However, the CONCAWE vehicle test fleet mostly consisted of vehicles without adaptive learning, (this being representative of the typical current European catalyst car fleet at the time the work was performed), whereas the opposite was true for the AQIRP current fleet. It is possible, therefore, that if distillation affects emissions through changes in transient air fuel ratio excursions, the magnitude of such changes in excursions may be influenced by the presence of an adaptive learning system. Thus, if catalyst CO oxidation efficiency is more tolerant of small air fuel ratio excursions away from stoichiometric than HC and NOx emissions, it is reasonable to expect the US vehicles, with adaptive learning and presumably smaller transient air fuel ratio excursions, to show an effect of distillation on HC and NOx before CO.

In conclusion, the CONCAWE AE/STF-1 programme on heavy ends has shown an effect of distillation on regulated emissions in opposite directions for HC and CO compared with NOx. There is some evidence that the differences observed are due to distillation between the T50 and T80 points, (or E100 and E140). Six fuels at two different T90 levels in the range 156-176°C showed no significant differences in regulated emissions due to T90.

2.4. EUROPEAN AUTO/OIL EPEFE STUDY

In the recent European Auto/Oil EPEFE study, the effects of mid-range distillation were evaluated in sixteen European prototype vehicles meeting 1996 European Stage II emissions legislation (94/12/EC). These were operated over the new MVEG European drive cycle, due to be implemented in 2000, (11 second initial idle and key-on measurement of emissions). A nine fuel matrix was blended to determine the independent effects of aromatics content and mid-range distillation as characterised by E100, (EPEFE used only E-numbers to specify fuel distillation properties due to their relative ease of calculation within blending models). Fuel back-end volatility was fixed by defining a constant target E150 value.

The effect of E100 on composite cycle HC emissions was strongly non-linear, such that at low E100 values of around 35% v/v a large increase in HC emissions occurred. There was an apparent interaction between E100 and aromatics such that at high aromatics content (50% v/v) increasing E100 from 35 to 50% v/v gave a 43% reduction in HC emissions, (from 0.286 g/km to 0.164 g/km), whereas at intermediate aromatics content (35% v/v) a 35% reduction in emissions, (from 0.241 to 0.156 g/km), was observed and at low aromatics (20% v/v) a 25% reduction in HC emissions, (from 0.195 g/km to 0.147 g/km) was observed. Further increasing E100 from 50% v/v to 65% v/v gave only a small benefit in HC emissions.
The effect of E100 on CO emissions was non-linear and showed a minimum at intermediate levels of E100 of approximately 50% v/v. Reductions in CO emissions on increasing E100 from 35 to 50% v/v or reducing E100 from 65 to 50% v/v were approximately 6-10%.

The effect of distillation on NOx emissions was linear and opposite in direction to that of HC. An interaction between distillation and aromatics was also found. At high aromatics (50% v/v) increasing E100 from 35 to 65% v/v increased NOx by 20% (from 0.151 g/km to 0.180 g/km). At intermediate levels of aromatics (35% v/v) increasing E100 across the same range gave an increase in NOx of 13% (from 0.162 g/km to 0.183 g/km), whilst at low aromatics (20% v/v) an increase of 7% (from 0.173 g/km to 0.185 g/km) was observed.

The large increase in HC emissions observed particularly for fuels with intermediate and high aromatics content at low target E100s of 35% v/v was thought to be due to reported driveability problems on a number of the cars with these fuels. However, one fuel with low E100 and low aromatics did not generally produce noticeable driveability demerits. Analysis of the fuel distillation curves in Figure 7 reveals that the two fuels which gave driveability problems and high HC emissions both had very low E120 values, despite their E100 and E150 values being similar to the other low E100 fuel. This suggests that distillation in the E120 range may be important in controlling HC emissions, perhaps through control of driveability.

2.5. OTHER PROGRAMMES

Work performed by Chevron has studied the effect of fuel distillation and Driveability Index (DI) on regulated emissions in a four part programme which looked at a wide range of non-catalyst and catalyst vehicles driven over the FTP cycle. DI is often used, particularly in the US, to describe the cold weather driveability performance of fuels. Driveability problems are caused by misfires or partial combustion which lead to high amounts of unburnt fuel in the engine-out emissions. Clearly if fuels begin to affect driveability, even in a way which is not perceivable to a normal driver, a large effect on HC emissions is therefore quite likely. DI is defined as:

\[ \text{DI} = 1.5 \times T_{10} + 3.0 \times T_{50} + T_{90} \]

Combining the results for HC emissions from each phase of the programme, Chevron reported that percentage changes in HC emissions for test fuels relative to a baseline Indolene or industry average fuel could best be described by a quadratic regression against DI.

The effect on HC emissions was found to be most apparent during the cold phase of the cycle. This is the portion of driving where emissions are dominated by those produced before the catalyst has lit-off, and where cold driveability problems will be most likely to occur. No consistent effects of fuel distillation on CO or NOx were found in this work. It was notable that across the sixteen fuels tested, the intercorrelations between the three individual distillation parameters that comprise DI were essentially broken. The ranges of these parameters were relatively large, (T10 48-66°C, T50 78-118°C and T90 112-169°C). No analysis based on single distillation parameters was presented. It is clear from analysis of the ranges of parameters used, in conjunction with the coefficients shown, that T50 has a stronger influence on DI that T10 or T90. Thus the Chevron results are not inconsistent with the hypothesis that mid-range parameters have the dominant influence on HC exhaust emissions.
Toyota has looked at the effect of mixture preparation on HC emissions from a modern fuel injected engine under cold-start and warm-up conditions. In the first few cycles after engine firing, the degree of cylinder wall wetting and HC emission levels were measured. Three fuels were tested with T50s varying from 96-120°C. The degree of wall wetting and HC emissions correlated with fuel T50, and Toyota proposed that T50 was therefore an important factor for controlling HC emissions during cold-start and warm-up. Further analysis of the data, however, reveals that T50 and T90 parameters were highly correlated, and that the width of the range of T90s was also similar, from 144-169°C. Data on other T-parameters between T50 and T90 were not presented in the report. Explanation of the results in terms of either of these parameters is therefore not possible.

Unocal performed two separate emission programmes over the FTP cycle using a fifteen fuel matrix in which ten fuel parameters were independently varied. The results showed that gasoline distillation, amongst other properties, can have an effect on emissions. A statistical model was derived for the results which was subsequently verified in a further vehicle study. Unocal pointed out the problems in previous programmes with intercorrelation between mid-range and back-end distillation points, for example T50 and T90, and the consequent problems with the inference of causal relationships due to just one of these parameters.

In the Unocal fuel matrix, T10, T50 and T90 were essentially uncorrelated, despite the fact that an extremely wide range in each of the parameters was achieved, (T10 42-66°C, T50 76-153°C and T90 133-213°C). The predictive model of HC exhaust emissions produced by Unocal showed that the only important distillation parameter was T50, not T90, and that increases in T50 could explain 75% of the increases in HC emissions observed. For CO, both T50 and T90 were included in the statistical model, but the coefficient for T50 was an order of magnitude greater than that for T90. Again increasing T50 accounted for around 75% of the increase in observed emissions, with increasing T90 only accounting for approximately 10%. NOx emissions were not influenced by either T50 or T90, although T10 was found to be important, such that increasing T10 accounted for 30% of the increase in NOx.

Work performed recently by Esso looked at exhaust emissions from three European vehicles, one catalyst and two non-catalyst, tested over the European drive cycle, (according to Directive 91/441/EEC). Eight AQIRP Phase 1 fuels plus three reference blends were used in the testing. The only statistically significant effects of back-end volatility were found for CO, where for one non-catalyst car CO reduced with increasing back-end volatility, whereas for one catalyst car an increase was observed. No effects on HC emissions from these European cars were observed. The authors pointed out in the report that within the fuel matrix tested, variation of T90 and T50 occurred simultaneously, so that true back-end distillation effects could not be separated from those of mid-range volatility.

A second part to the Esso programme looked at the effect of fuels blended from European refinery stream components on emissions from five vehicle builds, both catalyst and non-catalyst. Reducing T90 from 160 to 110°C reduced HC emissions by 13% from one of the two non-catalyst car builds, and by an average of 17% from all three catalyst cars tested. NOx emissions were increased by 36% for one catalyst car only, whilst CO was reduced by 19% in one catalyst car and increased by 8-14% in the other two. As for the Phase 1 Esso work, the authors pointed out, however, that T50 and T90 were again somewhat intercorrelated and that the emissions effects observed could be due to T50 variations between the test fuels.
Shell have carried out a scouting study on four fuels tested in four European cars over the FTP drive cycle. The fuel with the highest T90 also possessed the highest T50 and FBP, in addition to containing high levels of aromatics and olefins and being non-oxygenated. It was not possible on the basis of these data to determine the true effect of back-end volatility on emissions, in the absence of other fuel changes.

Recent work by GM studied the intercorrelation between driveability and emissions and the effect of gasoline formulation on emissions via its influence on driveability. Two fuels were tested in four catalyst vehicles over a modified version of the former CRC Cold-Start and Drive-Away schedule at 5°C. The two fuels were different in several respects. One possessed low T50, T90, aromatics, olefins and sulphur and contained 11% v/v MTBE, whilst the other non-oxygenated fuel had significantly higher T50, T90 and aromatics, and marginally higher olefins and sulphur. Although the T10 points of the two fuels were similar, the DIs varied due to the differences between the T50 and T90 points. As mentioned previously DI is most sensitive to the differences in the T50 points. Tailpipe HC emissions were reported to correlate with driveability demerits, such that increasing demerits gave increased emissions. CO and NOx emissions were not significantly correlated to driveability demerits. It is known that driveability demerits correlate well with fuel DI, and thus the conclusions from the work were that greater HC emissions associated with lower volatility fuels may be due to poorer driveability. The study did not attempt to split out the effect of mid-range distillation parameters such as T50 from T90, and furthermore, as the authors point out, the variation in fuel parameters other than distillation, for example oxygenates and aromatics, means that it was not possible to determine unambiguously the true causative effect on emissions, although it is likely that fuel volatility plays an important part.
3. BACK-END COMPOSITIONAL EFFECTS ON REGULATED EMISSIONS

3.1. US AQIRP PHASE 2 STUDY

The US AQIRP Phase 2 Heavy Hydrocarbon study aimed to determine the influence of back-end chemical composition, as well as distillation, on emissions. Two full factorially designed fuel matrices, A and B, with the independent variables consisting of a range of catalytically cracked reformate and alkylate streams were used. In matrix A, the effects of heavy aromatics at three different distillation temperature ranges derived from catalytic cracking and reforming, were evaluated. In matrix B, the effects of heavy aromatics were compared with those of heavy paraffins. The vehicles tested were from the AQIRP Current fleet, with many possessing adaptive learning of engine management systems.

The results suggested that hydrocarbon type had no important effect on HC emissions. The design of the matrix A fuels caused aromatics to be correlated with fuel blending component composition, and data plots suggested overall that aromatics did not have an important effect on HC emissions other than by an indirect effect of fuel distillation. One fuel, containing medium, heavy and tail-cuts of reformate did directionally indicate that increasing aromatics could increase hydrocarbons, but the effect was not statistically significant. Furthermore, in matrix B similar results for HC emissions were observed with both heavy alkylate and reformate fractions. Similarly, no statistically significant effects were found for back-end chemical composition on CO or NOx emissions.

3.2. CONCAWE AE/STF-1 STUDY

The CONCAWE AE/STF-1 programme discussed above was designed to look, in part, at the effect of back-end compositional changes on emissions, independently of distillation. Three intermediate fuels (I-160) and three heavy fuels (H-180) were blended whereby the back-end portion of the distillation curve consisted predominantly of heavy aromatics or olefins or paraffins. Analysis of emission results over the European drive cycle, (according to Directive 91/441/EEC), from ten catalyst cars, (only one of which was equipped with an adaptive learning engine management system for fuelling), revealed compositional effects for HC and CO emissions which, while smaller than the distillation effects observed between these six fuels and the base fuel, were nevertheless still statistically significant. NOx emissions, however, were more dependent on back-end chemical composition than distillation.

The aromatic fuels tested gave a fleet average HC emission (0.227g/km) increase of 5% over the paraffinic (0.218 g/km) and olefinic (0.214 g/km) fuels. Such an increase was observed for a reduction in aromatics from approximately 55 to 40% v/v, with, in the case of the olefinic fuels, a concomitant increase in heavy olefins from approximately 0 to 15% vol. The aromatic fuels also gave 6% higher CO emissions (1.268 g/km), than the paraffinic fuels (1.213 g/km) which, in turn gave 5% higher emissions than the olefinic fuels (1.156 g/km). Back-end chemical composition effects on NOx emission were in the opposite direction to those for HC and CO. The aromatic fuels gave a fleet average reduction in NOx emissions (0.218 g/km) of 7% compared to the paraffinic fuels (0.234 g/km), which in turn gave 8% lower emissions than the olefinic fuels (0.254 g/km).
It was suggested that the opposite direction of response of NOx and HC or CO emissions may be due to the effect of fuel composition on fuel stoichiometric air fuel ratio, and hence engine air fuel ratio, especially during transients. Fuel Volumetric Air Demand, \( FVAD = \text{stoichiometric air fuel ratio (m/m)} \times \text{fuel density} \), was shown to correlate with emissions equally as well as distillation parameters, and may be wholly or partly the cause of the effect of composition on emissions, although it was impossible to prove or disprove this from the programme.

Differences between this programme and the US AQIRP Phase 2 study could be due to differences between the car fleets, the CONCAWE programme using vehicles generally not possessing adaptive learning systems, which was not the case with the US study.
4. OVERALL CONCLUSIONS

There is undoubtedly an effect of gasoline mid-range to back-end distillation on emissions, and all of the programmes reviewed above have, to some degree, demonstrated this. Distillation effects on HC emissions are generally larger and more significant than those on CO and NOx. Effects of distillation on NOx emissions tend to be in the opposite direction to those on HC and CO, i.e. increasing volatility increases NOx emissions. This suggests that the effect on emissions may be at least partially due to changes in the magnitude of transient air fuel ratio excursions caused by wall wetting effects.

Of the programmes reviewed which reported a stronger effect of T90 or E150 on emissions, an intercorrelation between T90 or E150 values within the fuels tested and mid-range parameters such as T50, T60, T70 or E100, E110, E120 etc. was always found. This is true for both AQIRP programmes. In view of such intercorrelations, it becomes impossible to causatively assign distillation effects on emissions to a single distillation parameter or combination of parameters, since many could be selected which would adequately describe the data to a similar degree.

For some of the programmes which reported strong T90 or E150 effects, statistical analysis revealed equivalent, or even stronger correlations with T- or E-parameters down to, for example, T50 or E100.

However, some of the programmes reviewed used test fuel matrices, where the intercorrelations between, for example, T50, T70 and T90 or their equivalent E-parameters had essentially been broken; (CONCAWE, EPEFE, Unocal and Chevron). The Unocal programme demonstrated a weak effect of T90 on emissions, and attributed most of the distillation effects observed to T50. The Chevron programme also showed results which supported this hypothesis. This is apparent in the statistical models that these programmes generated. The CONCAWE work showed no effect of T90 on emissions in the nominal range 160-180°C. Nevertheless, there was an effect of distillation between a base fuel and six heavier test fuels, which could not be unequivocally attributed to any single distillation parameter within the range T50-T90. The EPEFE programme demonstrated an effect of mid-range distillation, E100, on all three regulated emissions. In this programme, high HC emissions caused by driveability malfunctions were observed for two fuels with very low E120 values. This suggested that E120 may be influential in controlling driveability and hydrocarbon exhaust emissions.

Overall, there are no wholly definitive data defining exactly which distillation parameter or combination of parameters is the true causative factor in influencing tail-pipe emissions. There is, however, a balance of evidence suggesting that the effect is best described by mid-range parameters T50-T70 or E100-E120.
Whilst the US AQIRP Phase 2 programme reported no statistically significant influence of back-end composition on emissions, the CONCAWE programme did find some effects. In general, changing back-end composition from aromatics to paraffins and then to olefins resulted in progressive reductions in HC and CO and increases in NOx emissions. It is possible that these effects could be wholly or partially due to changes in fuel stoichiometry, as described by FVAD, although intercorrelations between FVAD and distillation parameters prevented firm conclusions on this. Back-end compositional effects were secondary in importance to mid-range to back-end distillation effects for HC and CO, but were more important for NOx. The reason for the difference in conclusions between the AQIRP Phase 2 and CONCAWE programmes regarding back-end chemical composition is not totally clear, although it should be noted that in the US programme back-end chemical composition was highly correlated with mid-range to back-end distillation, whilst this was not true for the CONCAWE programme.
5. REFERENCES


4. CONCAWE (1994) Internal member company analysis


APPENDIX  HC MODELS BASED ON DATA FROM THE US AQIRP PHASE 2 HEAVY HYDROCARBON STUDY - MATRICES A AND B.

In the US AQIRP Phase 2 Heavy Hydrocarbon Study, an empirical non-linear exponential model has been fitted to \( \ln(\text{HC}) \) emissions including the distillation parameters E149, (E300°F), and E93, (E200°F). This is described as the best description of HC emissions, and there is therefore a tendency to conclude that E149 and E93 are the two important distillation parameters for control of HC emissions.

However, it is possible to fit many other models of the same or different structure, but with different distillation parameters which have similar goodness-of-fit statistics, (for example \( R^2 \) values above 0.95). This is due to the fact that the distillation parameters for this dataset are strongly intercorrelated from the mid-range point onwards, as a result of their not being design variables. Some further models illustrate this point, although there are many other models which adequately describe the data in addition to those shown below.

The "Non-Linear Estimation" module in STATISTICA has been employed to estimate the coefficients in the models below. A "Quasi Newton" iteration method has been used. There are, of course, other ways to estimate the coefficients, and different methods will, in general, lead to slightly different estimates. The differences between the coefficients in the AQIRP model and the "Reproduced AQIRP" model, (based on the above mentioned method), illustrate this.

The following models are merely meant to show that there are alternative ways of modelling the HC emissions and that one cannot, based on this dataset, claim one model to be more appropriate than any other in describing HC emissions and identifying the causative parameters.

**PUBLISHED AQIRP MODEL**

\[
\ln(\text{HC}) = -1.576 + [0.00236*(E149 - E93 - 41) + 0.04634]\exp[0.1716*(100 - E149 - 12)] + 0.0255M
\]

\[ R^2 = 0.979 \]

**REPRODUCED AQIRP MODEL**

\[
\ln(\text{HC}) = -1.573 + [0.00214*(E149 - E93 - 41) + 0.04138]\exp[0.1808*(100 - E149 - 12)] + 0.0251M
\]

\[ R^2 = 0.977 \]

**CONCAWE MODEL 1**

\[
\ln(\text{HC}) = -1.569 + [0.00470*(E149 - E93 - 41) + 0.03432]\exp[0.1869*(52 - E100)] + 0.0263M
\]

\[ R^2 = 0.976 \]
CONCAWE MODEL 2

\[ \ln(HC) = -1.572 + [-0.00536 \cdot (E150 - E100 - 36) + 0.04334] \cdot \exp[0.1855 \cdot (52 - E100)] + 0.0255M \]

\[ R^2 = 0.977 \]

CONCAWE MODEL 3

\[ \ln(HC) = -1.569 + [-0.00879 \cdot (E149 - E93 - 41) + 0.04686] \cdot \exp[0.1806 \cdot (46 - E93)] + 0.0260M \]

\[ R^2 = 0.976 \]

CONCAWE MODEL 4

\[ \ln(HC) = -1.559 + [-0.00339 \cdot (E127 - E75 - 38) + 0.02743] \cdot \exp[0.2081 \cdot (52 - E100)] + 0.0248M \]

\[ R^2 = 0.966 \]

CONCAWE MODEL 5

\[ HC = 0.9053 - 0.02173 \cdot T50 + 0.00001 \cdot T50^2 + 0.02744 \cdot MTBE - 0.00223 \cdot Olefins \]

\[ R^2 = 0.9600 \]
Figure 1   US AQIRP Phase 1 Study AMOT Matrix Fuel Distillation Curves
Figure 2  US AQIRP Phase 2 Study. T90 Versus Composite HC Emissions Matrix B

Figure 3  US AQIRP Phase 2 Study. Matrix A and B Fuel Distillation Curves
Figure 4  US AQIRP Phase 2 Study. T50 Versus Composite HC Emissions Matrix B

Figure 5  US AQIRP Phase 2 Study. T50 Versus Composite HC Emissions Matrix A and B Combined
Figure 6  CONCAWE AE/STF-1 Heavy Hydrocarbon Study Fuel Distillation Curves

Figure 7  EPEFE Aromatics/E100 Study Fuel Distillation Curves