

Review of Prior Studies of Fuel Effects on Vehicle Emissions

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ABSTRACT

A literature review was conducted to survey recent research on the effects of fuel properties on exhaust emissions from gasoline and diesel vehicles, on-road and off-road. Most of the literature has been published in SAE papers, although data have also been reported in other journals and government reports. A full report and database are available from the Coordinating Research Council (www.crao.org).

The review identified areas of agreement and disagreement in the literature and evaluated the adequacy of experimental design and analysis of results. Areas where additional research would be helpful in defining fuel effects are also identified.

In many of the research programs carried out to evaluate the effect of new blendstocks, the fuel components were splash blended in fully formulated fuels. This approach makes it extremely difficult to determine the exact cause of the emissions benefit or debit. Much of the research on Fischer-Tropsch liquids and fatty acid esters falls into this category.

A summary of effects for gasoline and diesel vehicles is shown in the accompanying tables.

The decision to carry out additional research on impacts of fuel properties should depend on the introduction of new technology, potential benefits and costs of fuel regulations, and the potential enablement of emission control systems.

INTRODUCTION

This paper summarizes the literature describing the effects of fuel properties on emissions from on-road and off-road gasoline and diesel-powered vehicles. For light duty (LD) gasoline vehicles, the time period covered in this report dates to a similar review by Koehl et al. [1] of research up to 1989.

Research on diesel engines is described separately for LD and HD diesels. For heavy duty (HD) diesel, the time period covered in this report dates from an extensive review published by Lee, Pedley and Hobbs [2] in 1998. Earlier research will be cited only when not covered by Lee. For LD diesel, not covered by Lee, research going back to 1990 was considered.

Off-road mobile sources comprise a wide variety of applications and the literature is reviewed separately for spark ignition and compression ignitions engines. Research published since 1990 was considered for inclusion in the report. Off-road emissions are subject to increasingly stringent emission standards in the U.S. and major reductions are either underway or are about to be implemented.

Within each class of vehicle, the emissions impacts of individual fuel parameters are described. Only research that tested fully built engines or vehicles using recognized emission test cycles is considered.

METHODOLOGY - The main sources of information for this report were two extensive databases maintained by the Society of Automotive Engineers (SAE), the SAE Global Mobility Database and the TechSelect Database. Searches were also conducted of EPA, DOE and ARB databases for government publications and other information.

Summary of Gasoline Emission Effects

To Reduce Emissions, Make the Directional Changes Shown Below								
	Aromatics	Benzene	Olefins	Sulfur	Oxygenates	RVP	T ₅₀	T ₉₀
HC	↓	*	↑	↓	↑	↓	↓	↓
CO	↓	*	↑	↓	↑	↓	↓	↓
NOx	↑	*	↓	↓	↓	0	↑	↑
Toxics	↓	↓	↓	↓	#	*	↓	↓
PM	*	*	*	*	*	*	*	*
0 - No effect; * - Data are lacking to estimate an effect; # - Data exist, but effect is variable								

Summary of Diesel Emission Effects

To Reduce Emissions, Make the Directional Changes Shown Below (Light Duty / Heavy Duty)							
	Density	Cetane	Aromatics/PAH	Sulfur	Back-End	FAE	FT
HC	↓/*	↑/↑	↑/↓	0/0	0/↑	↑/↑	↑/↑
CO	↓/*	↑/↑	↑/*	0/0	0/↑	↑/↑	↑/↑
NOx	*/↓	*/*	↓/↓	0/0	#/#	↓/↓	#/↑
PM	↓/*	↓/#	↓/↓	↓/↓	↓/↓	↑/↑	↑/↑
0 - No effect; * - Data are lacking to define effect; # - Data exist, but effect is variable							

In total, 215 gasoline abstracts, 457 diesel abstracts and 106 off-road abstracts were reviewed for relevance. Of these, 109 gasoline papers, 128 diesel papers and 18 off-road papers were read in full.

An Excel spreadsheet was prepared which contains summary information about all the studies reviewed in this report, as well as the complete reference. The spreadsheet is available from CRC (www.crcao.org).

PRESENTATION OF RESULTS - In general, the impacts of changing fuel properties on emissions are shown as percent change. Many publications report results only in percentage terms, and furthermore, stating changes as percentages allows a comparison of results across programs.

Changes in the concentration of one fuel component necessarily imply equal changes in one or more other components. For instance, when the concentration of aromatics is reduced by 10%, the concentration of some other component must be increased by 10%. Usually, paraffins are the swing component, so that the actual meaning of "reducing aromatics" is "reducing aromatics and replacing them by paraffins." When the change in concentration is in the parts per million range, as is the case for sulfur, the changes in concentration of the other fuel components are not measurable and can be ignored.

CAVEATS - When analyzing the literature, comparing results, and trying to draw generalizations, a number of problems were encountered.

- Many programs did not report the results of a statistical analysis, nor the statistical significance of the findings.
- Some programs tested a limited number of vehicles. Given the known variability in response among vehicles, it is difficult to make generalizations from a small sample.
- In some programs, the fuel properties were not independently varied, so it is not possible to assign results to fuel properties unambiguously. Many reports recognized this uncertainty.
- Some research programs were designed to demonstrate the benefits of certain fuel formulations or fuel blendstocks, and the changes in emissions could not be assigned to any one or group of fuel properties.

Programs from which there is limited ability to draw unambiguous conclusions can still be used in a broader meta analysis of emissions data. Such a meta analysis is essentially what was done in developing emissions models such as the EPA Complex Model and the ARB Predictive Model for gasoline.

GASOLINE

Various driving cycles have been used to measure exhaust emissions from LD vehicles. In the U.S., the FTP75 has been used for many years, and has been supplemented in recent years by the US06, which represents more aggressive, high speed driving, and the SC03 which measures emissions under conditions when air conditioning is used. In Europe, the UDC (Urban Driving Cycle) and EUDC (Extra-Urban Driving Cycle) measure emissions under a variety of driving conditions including cold start. In Japan the steady state 10.15 mode test was used for many years and has been supplanted by the JC08 test, which has many similarities to the U.S. and European driving cycles.

Not much research has been carried out on the differences in fuel effects when measured on the different test cycles. It appears that the results are similar, especially where the test cycle includes cold start operation.

SULFUR

From an exhaust emissions perspective, sulfur concentration is probably the most important gasoline property. Present in trace amounts, sulfur does not contribute to octane or other vehicle performance attributes, yet it impacts operation of three-way catalysts (TWC) and other components of modern emission control systems. Reducing the amount of sulfur in gasoline requires investment in new equipment and additional refinery operating expenses. Reducing sulfur concentrations consumes energy and hydrogen in the refinery, which can reduce the total amount of hydrocarbons available to blend into fuel. Reducing sulfur also increases refinery CO₂ emissions and can negatively affect fuel properties such as octane.

AQIRP (Auto/Oil Air Quality Improvement Research Program) carried out a number of studies evaluating different technologies and different sulfur ranges [3, 4, 5]. In the final AQIRP study, Rutherford et al. [6] reported on testing eight fuels, four of which represented two levels of sulfur, nominally 35 ppm and 320 ppm. Ten 1989 LD vehicles and six Federal Tier 1 vehicles (0.25 g NMHC/mi) were tested. Results are shown in Table 1 for regulated and toxics emissions. Specific reactivity was calculated and increased as sulfur was reduced, by 2.9% in the 1989 fleet and by 9.3% in the Tier 1 fleet. The results shown here are generally consistent with earlier AQIRP work, and there does not appear to be a major difference between the 1989 fleet and the Tier 1 vehicle fleet, when expressed as percentage differences.

Table 1 AQIRP Sulfur Effects

	Percent change in Emissions 320 ppm → 35 ppm Sulfur	
	1989 LDV	Fed. Tier 1 LDV
NMHC	- 13.3	- 18.5
CO	- 9.8	- 16.4
NOx	- 4.0 (NS)	- 8.9
Benzene	- 17.8	- 24.5
1,3 Butadiene	- 8.5	-12.1
Formaldehyde	+ 27.2	- 5.2 (NS)
Acetaldehyde	+ 2.9 (NS)	- 0.9 (NS)
NS: Not statistically significant		

Sztenderowicz et al. [7] reported on a program carried out by the Petroleum Environmental Research Forum on ten 1993/94 vehicles with three fuels having sulfur levels of 25, 300 and 600 ppm. Nine vehicles were certified to California TLEV standards, and one was certified to Federal Tier 1 standards. There appeared to be a non-linear response to sulfur, with a greater impact between 25 ppm and 300 ppm than between 300 ppm and 600 ppm. The results were compared to those measured in AQIRP, and it was found that the effects measured on a mass basis were somewhat smaller, in part because the overall emissions levels were significantly less. Sulfur effects expressed on a percentage basis were similar or somewhat larger, again probably reflecting the lower overall emission levels.

Schleyer et al. [8] reported on a program carried out by CRC which measured the impact of sulfur in twelve California LD vehicles certified to LEV standards. Four conventional fuels (30 ppm to 630 ppm) and two California fuels (27 ppm and 148 ppm) were tested. Results are shown in Table 2 for the fleet averages on the conventional fuels at 100,000 miles:

Table 2 CRC Sulfur Effects Program

	Change in Emissions 630 ppm → 30 ppm Sulfur		
	NMHC	CO	NOx
grams/mile	- 0.03	- 0.70	- 0.23
Percent	- 32 %	- 46 %	- 61 %

There was a wide range in the responses of individual vehicle models, and those with the lowest emission levels tended to have the smallest response to sulfur. The response to sulfur concentration for the 100,000 mile aged catalysts was non-linear for all three pollutants measured, with a larger response at low sulfur levels. The authors also compared results for similar sulfur ranges across four large test programs that evaluated technologies ranging from Tier 0 to LEV. When the fleet

average impacts were expressed in mass terms, the sulfur effect was similar for all fleets, with the possible exception of NO_x in the LEV fleet. However, when expressed as percentages, the effects were larger as base level emissions were reduced with newer technology.

Lyons et al. [9] tested eight 1997/98 model year California vehicles (Tier 1, LEV and ULEV) on two fuels with sulfur levels of 40 and 540 ppm. The authors concluded that there was a high degree of variability in responses to sulfur, and carried out regression analyses to determine what design factors contributed to the differences. The strong correlations among design factors did not allow them to draw specific conclusions.

In 2001, the automotive industry in the U.S. reported on a test program carried out on 13 prototype California TLEVs, LEVs and ULEVs [10]. Three levels of sulfur were tested, 1, 30 and 100 ppm. No details of the statistical analysis were provided, but the results shown in Table 3 appear to be statistically significant. Averages quoted in the presentation appear to be geometric averages of the fleet emissions.

Table 3 AAM Sulfur Effects Program

Change in Emissions 100 ppm → 1 ppm Sulfur			
	NMHC	CO	NO _x
g/mi	- 0.017	- 0.642	- 0.059
Percent	- 27%	- 42%	- 39%

Responses are generally linear, although there may be a slight curvature, such that the effect of sulfur is less at extremely low values. The authors postulated that this might be due to the effect of sulfur in the lubricant.

The most recently published major study carried out in U.S. vehicles was CRC Project E-60 [11], which tested twelve California vehicles certified to LEV and SULEV standards, and two European vehicles certified to Euro 3 standards. All vehicles were tested with three fuels (5, 30 and 150 ppm sulfur) with as-received and aged catalysts. The objective was to measure ammonia emissions, but regulated emissions were measured as well. All vehicles were tested using the US FTP and US06 cycles; the European vehicles were tested over the NEDC (New European Driving Cycle) as well. For the California vehicles, there was a small but significant effect of higher sulfur on NO_x emissions, and no effect on NMHC and CO emissions. Differences were larger on the US06 cycle, and were statistically significant for NMHC, CO and NO_x. A summary of the results is shown in Table 4.

Table 4 Sulfur Effects CRC Project E-60

Change in Emissions, 150 ppm → 5 ppm Sulfur					
	NMHC	CO	NO _x	NH ₃	N ₂ O
FTP Test Cycle					
g/mile	-0.001 (NS)	-0.045 (NS)	- 0.022	- 0.003 (NS)	- 0.011
Percent	- 2.2	- 6.4	- 31.0	- 15.8	- 64.7
US06 Test Cycle					
g/mile	- 0.025	- 0.569	- 0.102	- 0.020	- 0.010
Percent	- 64.1	- 10.2	- 70.8	- 21.3	- 90.9

The European Programme on Emissions, Fuels and Engine Technologies (EPEFE) carried out a large study on the sulfur response in European vehicles [12]. Four fuels ranging in sulfur concentration from 18 ppm to 382 ppm were tested in sixteen European vehicles, all fitted with TWC, and either single point or multi-point injection. Results are summarized in Table 5 for the combined ECE/EUDC cycle, known collectively as MVEG 2000.

Table 5 Sulfur Effects from EPEFE Program

Change in Emissions 382 ppm → 18 ppm Sulfur			
	HC	CO	NO _x
g/km	- 0.015	- 0.113	- 0.019
Percent	- 8.6	- 9.0	- 10.4

The results were generally linear over the range studied, although there was some suggestion of non-linearity for HC and CO emissions. Compared to AQIRP, the relative effects seen in this program are smaller for HC and CO and similar for NO_x.

In 2000, Hamasaki et al. [13] presented results of the Japanese Clean Air Program (JCAP), which compared two fuels (96 ppm and 22 ppm) in eleven late model year vehicles intended to approximate the current and future Japanese fleet. Two test cycles were used, the 10.15 mode test and the cold start 11 mode test. The authors found that reducing sulfur lowered emissions of THC, CO and NO_x in both test cycles, although the effect was larger in the hot start 10.15 mode test, when the catalysts were operating a higher fraction of the time. The relative effects appeared to be higher for the low emitting and lean-burn vehicles, because there were fewer pollutants emitted before catalyst light-off. No statistical analyses were presented for the results.

REVERSIBILITY AND AGING - Most of the earlier studies on sulfur effects found that reversibility was complete and occurred with a short mileage interval. Schleyer et al. [14] reported on a CRC program in which

two sulfur levels (30 ppm and 630 ppm) were tested over a variety of cycles and the reversibility of the sulfur effect was assessed. Six of the twelve vehicles tested in the CRC Sulfur/LEV program [8] were used. For the entire fleet, NMHC emissions were fully reversible with either the mild LA-4 driving cycle, or the more aggressive US06 driving cycle. CO emissions were fully reversible with the US06 cycle, but only 79% reversible with the LA4 cycle. NOx emissions were 84% reversible with the LA4 cycle and 95% reversible with the US06 cycle. In most cases, emissions recovery stabilized within 10 miles of driving.

Lyons et al. [9] tested eight 1997/98 model year California vehicles (Tier 1, LEV and ULEV) on two fuels with sulfur levels of 40 ppm and 540 ppm. With respect to reversibility, they concluded that “the effects of sulfur were fully reversible, although in some cases, more severe operating conditions such as those encountered in the US06 cycle were required.”

PARTICULATES - Particulate emissions as a function of fuel sulfur were studied in a number of programs carried out in Europe [15, 16]. It appears that the impact of sulfur on PM emissions from gasoline vehicles, while theoretically plausible, is too small to be seen with today’s instruments and test protocols.

REVIEW PAPERS - Hochhauser et al. [17] recently published an analysis of sulfur data in fleets with TWC covering seven published studies and one unpublished study. The newest fleets, represented by the CRC E-60 program, and the CONCAWE program on 2003 vehicles, exhibited relatively low responses to sulfur, less sensitive than data from model years 1997 and 1999. The data were analyzed on an absolute basis, and a comparison on a percentage basis would not show the same large differences. Table 6 shows the responses for NOx, for the published studies, as presented:

Table 6 Summary of NOx Responses to Sulfur

Emission Control Level	Program Sponsor	NOx Reduction, g/km 150 ppm → 50 ppm
US Tier 0	AQIRP	0.004
US Tier 1	AQIRP	0.006
Euro 2	EPEFE	0.005
California LEV	CRC	0.040
California LEV	AAM/AIAM	0.050
Euro 3/4	CONCAWE	0.001
California LEV	CRC	0.013

Uihlein carried out a similar analysis of previous work, and presented it at a public meeting organized by ARB as part of their effort to update the Predictive Model [18]. Table 7 compares the relative responses at ultra low sulfur levels from various large programs on late model

vehicles included in the ARB database. His analysis showed that at these low levels, results were very similar.

Table 7 Summary of NOx Effects at Low Sulfur Levels

Emission Control Level	Program Sponsor	NOx Reduction, % 20 ppm → 10 ppm
California LEV	CRC	- 3%
California LEV	AAM/AIAM	- 5%
California LEV	AAMA	- 5%
California LEV	CRC	- 6%

AROMATICS AND BENZENE

Hochhauser et al. [19] and Gorse et al. [20] reported on AQIRP work that measured the effect of aromatic levels between 20% and 45% in twenty 1989 vehicles. The effects of this change on fleet average tailpipe emissions are summarized in Table 8.

Table 8 AQIRP Aromatics Effects

Percent Change in Emissions 45% Aromatics → 20% Aromatics	
NMHC	- 11.6
CO	- 13.3
NOx	+ 2.0
Benzene	-41.8
1,3, Butadiene	+11.3
Formaldehyde	+23.5
Acetaldehyde	+19.5

It was interesting that for engine-out emissions, reducing aromatics reduced NOx, the opposite of the effect seen in tailpipe emissions. The effect on total HC was much smaller than the effect shown above for NMHC. It was shown by Hochhauser et al. [21] that reducing aromatics (and consequently increasing paraffins) contributed to higher methane emissions and lower NMHC emissions and that reducing aromatics did not impact the specific reactivity of the exhaust (g O₃/g HC, MIR scale).

There were a number of interactions with other properties. An interaction with MTBE (methyl *tertiary*-butyl ether) suggested that lowering aromatics increased NOx emissions to a greater extent when MTBE was present than when it was absent. Also, an interaction with T₉₀ suggested that the heavier molecular weight aromatics were more important than the lower molecular weight aromatics in affecting NMHC and CO emissions.

The large reduction in exhaust benzene was expected since aromatics can decompose under combustion conditions to produce benzene in the exhaust. No

attempt was made to explain the increases in the other toxic emissions in this experiment. The increase in formaldehyde might be related to the increase in exhaust methane seen when aromatics are reduced and are replaced by paraffins, as described above.

Marshall and Gurney [22] evaluated the impact of individual aromatic compounds on exhaust benzene emissions in five 1986 Model Year cars with fifteen fuels and found that fuel benzene had the highest impact on exhaust benzene. Other aromatics tested – toluene, ethyl benzene, xylenes and heavy reformat (C9+) – had an average effect of about 8% of benzene.

API conducted a study on the impact of aromatics as a function of carbon number in ten 1989-90 model year cars [23]. This effectively allowed them to separate the effects of aromatics and volatility. Two sets of fuels were blended. In the first, certain aromatics were removed and replaced by a mix of other aromatics of different carbon numbers to keep the total aromatic level constant. In the second set, certain aromatics were removed and replaced by equivalent iso-paraffins, effectively controlling distillation properties. With the first set of fuels, as the average carbon number of the aromatic compounds became heavier, exhaust emissions of NMHC, CO and NOx increased. The effect on NOx was classified as borderline significant ($0.95 > p > 0.90$). However, when the distillation properties were held constant, shifts in the distribution of aromatic carbon content had no effect on exhaust emissions. This implies that what had been measured as an aromatic effect was really an effect of distillation properties.

Jeffrey and Elliott [24] tested five European vehicles with 29 fuels, some of which were from the AQIRP study. For the catalysts vehicles tested, they found that aromatics had a significant effect on exhaust emissions. Similar to AQIRP, reducing aromatics lowered HC and CO and increased NOx. Reducing aromatics lowered benzene emissions, but increased emissions of the other toxics, 1,3 butadiene, formaldehyde and acetaldehyde.

The EPEFE program studied aromatics and mid-fill volatility in sixteen European vehicles with nine fuels [25]. A regression analysis revealed that reducing aromatics lowered HC and CO but increased NOx emissions. There were significant interactions between aromatics and E100 for HC and NOx. These results are fully consistent with other programs and also showed, as in previous studies, that reducing aromatics lowered engine-out NOx. NOx catalyst efficiency dropped for the low aromatic fuel and tailpipe NOx emissions increased. Reducing aromatics lowered benzene emissions, but increased emissions of 1,3 butadiene, and aldehydes.

CONCAWE analyzed data from European companies and an Italian industry program on the relationship between benzene and aromatics in the fuel and exhaust benzene emissions [26]. Emissions data from 21 non-

catalyst cars and 34 catalyst cars were used. Data showed that fuel benzene had the largest influence on exhaust benzene and that the impact of non-benzene aromatics was about 90% less.

The question of the aromatic effect on NOx emissions was investigated in a number of vehicle and laboratory studies in Europe [27, 28, 29]. Engine-out NOx emissions increase when aromatics increase. This effect is consistent with the higher energy content and higher flame temperatures of aromatic compounds versus paraffinic compounds. Low aromatics/high paraffin fuels also have higher levels of paraffins, methane and hydrogen in the engine-out exhaust. These factors cause a lean shift in A/F ratio, which tends to reduce NOx conversion efficiency. Depending on the relative effects in the engine and over the catalyst, the net effect could be an increase or decrease in tailpipe emissions. It is expected that as stoichiometry control improves, the engine-out effect will tend to dominate.

Most of the test work on aromatics in the past ten years has focused on direct injection gasoline (GDI) engines [30, 31, 32, 33, 34]. Since these have been more common outside the U.S., most of the published data has come from Japan and Europe. The programs generally tested small number of vehicles and the results were scattered. A combined analysis would be required to understand the impact of aromatics on GDI vehicles fully.

OLEFINS

Because of their chemical structure, olefins are reactive in the combustion process, easy to oxidize over a catalyst, but also highly efficient in forming atmospheric ozone. Olefins in the exhaust are major contributors to the total exhaust ozone reactivity.

AQIRP [19-21] studied the impact of olefin levels on exhaust emissions in twenty 1989 model year vehicles. The effect of reducing olefins from 20% to 5% on exhaust emissions is shown in Table 9.

Table 9 AQIRP Olefins Effects

	Percent Change in Emissions 20% Olefins → 5% Olefins
NMHC	+ 7.1
CO	+ 1.5 (NS)
NOx	- 6.1
Specific Reactivity	- 8.0
Benzene	- 3.0 (NS)
1,3 Butadiene	- 31.6
Formaldehyde	+ 1.3 (NS)
Acetaldehyde	-3.7 (NS)

Olefins are more reactive in the combustion process, and reducing olefins and replacing them with paraffins results in a mixture that will not burn as completely or as fast, thereby causing increases in HC emissions. Furthermore, the engine-out exhaust, since it contains lower olefins levels, will also be less reactive over the catalyst. Engine-out emissions followed the same trend as tailpipe emissions, supporting this theory. On the other hand, less complete combustion results in lower heat release and therefore lower NO_x emissions. CO emissions are generally formed when the mixture is rich, and are not affected by changes in olefin concentration, which do not affect stoichiometry.

The only significant impact of olefins on toxics emissions was to reduce emissions of 1,3 butadiene. This is not surprising, considering the high correlation between fuel olefins and exhaust olefins.

In the AQIRP study of high emitters [5], the effects of olefins were almost the same as they were on normal emitters. This suggests that the effects are due to the combustion process and not heavily dependent on catalyst efficiency or stoichiometry.

In Europe, a number of studies saw similar results to those found in AQIRP [24, 35]. Pentikainen et al. [36] tested four European vehicles, five Japanese vehicles and one U.S. vehicle from model years 1999-2003. Two levels of olefins were tested, 4% and 14%. They concluded that increasing the concentration of heavy olefins (C₈+) did not affect any of the regulated emissions (HC, CO, NO_x), ozone forming potential of the emissions, emissions of toxic compounds or PM. The only difference measured was an increase in emissions of iso-butene when heavy olefins increased. This was probably a product of iso-octene partial combustion.

Thummadetsak et al. [37] studied two olefin levels (5%, 10%) in six 1993-96 model year vehicles representative of the vehicle population in Thailand. One vehicle had no catalyst, one had an oxidation catalyst and four had TWC systems. In the catalyst vehicles, reducing olefins reduced THC emissions by 2.5% and benzene emissions by 8.6%.

VAPOR PRESSURE

AQIRP tested the effects of RVP (Reid Vapor Pressure), ethanol, MTBE and ETBE (ethyl *tertiary*-butyl ether) in twenty 1989 model year vehicles with 11 fuels. RVP varied between 55 kPa and 69 kPa (8-10 psi) [38]. A summary of the RVP effects is shown in Table 10.

Table 10 AQIRP RVP Effects

	Percent Change in Emissions Reduce RVP 6.9 kPa (1 psi) with			
	No Oxygen	Ethanol	MTBE	Average RVP Effect
NMHC	-4.0 (NS)	- 11.2	- 1.0 (NS)	- 4.3
CO	-10.4	- 14.9 (NS)	- 2.4 (NS)	- 9.1
NO _x	+ 1.5 (NS)	+ 0.4 (NS)	- 6.2 (NS)	- 0.7 (NS)

The effects of reducing RVP were statistically similar for the three base fuels, and an average was calculated. Reducing RVP was estimated to reduce emissions of NMHC and CO, but did not change NO_x emissions. The variability of the data for some of the toxics measurements was substantial and even large differences were not statistically significant. The effect of RVP on specific reactivity was small and not statistically significant.

AQIRP also studied RVP changes in seven high emitters. Knepper et al. [5] found there was no discernible effect of RVP on any exhaust emissions in the fleet of seven vehicles.

Korotney et al. [39] tested 19 LD vehicles (1986-1990 model year) and found no impact of changing RVP on any of the exhaust emissions.

Rutherford et al. [40] reported on a test carried out in Los Angeles and Las Vegas, with 30 in-use cars in each location under wintertime conditions. The Los Angeles fuel contained 11% MTBE and the Las Vegas fuel contained 10% ethanol. The authors concluded that reducing RVP from 83 kPa to 62 kPa (12 psi to 9 psi) resulted in 12% reduction in CO emissions under Las Vegas test conditions. No significant differences were seen for the Los Angeles tests. Further analysis by Hoekman et al. [41] suggested that the lack of effect in Los Angeles might have reflected a poor state of repair of some of the vehicles.

Bennett et al. [42] tested five 1992-94 model year European cars with six fuels varying in RVP and E70. In non-oxygenated fuels, reducing RVP from 104 kPa to 63 kPa (15.1 psi to 9.1 psi) lowered CO by 13% and NO_x by 15% and had no effect on HC. The effects were non-linear, with smaller changes in CO and NO_x as RVP was lowered. In the presence of MTBE, reducing RVP lowered NO_x by 10%, but did not affect HC or CO. The effect of RVP on CO was related to the canister purge strategy. Lower RVP fuels gave less enrichment during canister purge periods, probably because they generate less vapor and do not affect stoichiometry as much.

Thummadetsak et al. [37] tested three RVP levels (45 kPa, 55 kPa, and 62 kPa) in six cars representative of the vehicle population in Thailand. Changes in RVP did not have a statistically significant effect on any exhaust emissions.

MID-FILL AND BACK-END VOLATILITY

Usually, three measures of gasoline volatility are used in order to get good separation of variables. Front-end volatility is expressed as T_{10} or RVP, mid-fill volatility is expressed as T_{50} , and back-end volatility is expressed as T_{90} . In typically refinery blends, there is a high degree of correlation between mid-fill and back-end volatility. When carrying out experimental programs, a great deal of care must be spent on choosing blendstocks to be able to determine the independent effects of mid-fill and back-end. In some papers, the authors recognized a lack of orthogonality between T_{50} and T_{90} , while in others it was ignored, calling the conclusions into question.

One of the main objectives of AQIRP was to determine the impact of volatility parameters on emissions. Hochhauser et al. [19] reported on an experiment which varied T_{90} between two relatively extreme values in 20 1989 model year LD vehicles. Results are shown in Table 11, along with toxics results reported elsewhere [20, 21]. Reducing T_{90} lowered NMHC exhaust emissions by 23%, and specific reactivity and toxic emissions by similar amounts. This was the largest effect measured in the program. There were a number of higher order interactions, some suggesting that heavy aromatics were more significant than heavy paraffins or olefins in contributing to NMHC emissions. It was speculated that T_{90} affected emissions, especially during cold start operations, because the heavy molecules represented by the back-end of the distillation curve are harder to vaporize and burn before the engine has reached full operating temperature.

Table 11 AQIRP Back-End Effects

	Percent Change in Emissions T_{90} : 138°C → 182°C (360°F → 280°F)
NMHC	- 22.9
CO	+ 1.2 (NS)
NOx	+ 4.9
Specific Reactivity	- 18.0
Benzene	- 10.8
1,3 Butadiene	- 36.8
Formaldehyde	- 25.7
Acetaldehyde	- 23.9

In AQIRP tests of high emitters [5], reducing T_{90} had little or no effect on NMHC and CO emissions, but lowered NOx emissions significantly. No attempt was made to explain the differences between the normal and high emitter results.

The AQIRP authors recognized that T_{90} and T_{50} were correlated in the fuel set, and that the results could be explained almost as well by considering T_{50} as the important variable in the regression equations, or by using both T_{50} and T_{90} . The correct interpretation of the results would be that reducing both mid-fill and back-end volatility together could help to reduce NMHC emissions. Programs carried out later in the AQIRP, which studied this effect in more detail and attempted to separate the two variables, are discussed below.

In a follow-up program [43], AQIRP reported on tests in ten 1989 model year vehicles to study mid-fill and back-end effects. The authors concluded that:

- The response of NMHC to changes in T_{90} was non-linear, with larger emissions increases occurring as heavier components were added. The effects occurred primarily in Bag 1 of the FTP test.
- The effects can be attributed to distillation characteristics, not chemical composition differences between aromatics and paraffins.
- Increasing T_{50} levels increased NMHC emissions. The effect did not appear to be non-linear, and was smaller than the T_{90} effect, especially at levels of T_{90} above 157°C (315°F).

AQIRP tested three vehicles fleets in a more targeted program to measure the independent impacts of T_{50} and T_{90} [6]. Ten 1989 model year vehicles, six 1994 model year Tier 1 vehicles, and six advanced technology vehicles were tested. The advanced technology vehicles had NMHC emission levels below 0.1 g/mi. Results for the fleets are shown in Table 12.

Both T_{50} and T_{90} reduced NMHC exhaust emissions by similar amounts for the three fleets. Since only two levels were tested, it was not possible to evaluate the non-linearity of the effects. NOx effects were generally small and not significant. Lowering T_{50} seemed to reduce CO, while lowering T_{90} seemed to raise CO. Lowering T_{50} and T_{90} generally reduced exhaust emissions of toxics, although the T_{90} impact was larger and more likely to be statistically significant.

Table 12 AQIRP Independent Effects of T_{50} and T_{90}

	Percent Change in Emissions		
	1989 MY	1994 MY	Advanced Technology
T_{50} (102°C → 85°C, 215°F → 185°F)			
NMHC	- 5.8	- 4.0	- 11.5
CO	- 5.1	- 6.9	- 5.6
NOx	+ 7.8	- 0.6	+ 6.0 (NS)
Benzene	- 3.9	- 4.1	- 10.8
1,3 Butadiene	- 3.9	- 4.2	- 11.5
Formaldehyde	+ 2.6	+ 0.8	- 5.2 (NS)
Acetaldehyde	+ 1.5	- 1.5	- 10.3 (NS)
Specific Reactivity	- 1.4	- 3.0	- 0.8 (NS)
T_{90} (163°C → 138°C, 325°F → 280°F)			
NMHC	- 7.3	- 8.0	- 10.4
CO	+ 10.7	+ 6.6	+ 17.2
NOx	+ 1.2	+ 11.0	+ 3.7 (NS)
Benzene	- 1.8	- 9.7	+ 0.7 (NS)
1,3 Butadiene	- 19.2	- 22.7	- 17.1
Formaldehyde	- 11.9	- 15.1	- 17.0
Acetaldehyde	- 11.3	- 15.1	- 4.6 (NS)
Specific Reactivity	- 11.5	- 8.8	- 4.9

The most recent program to study mid-fill and back-end volatility was CRC Project E-67 [44] in which 12 California certified vehicles were tested with 12 fuels varying in T_{50} , T_{90} and ethanol. Three levels of each variable were tested in a fractional factorial design that allowed second order interactions to be evaluated. The vehicles were 2001-2003 model years and had certification levels of LEV, ULEV and SULEV. Fuels properties spanned the 10th and 90th percentiles for T_{50} and T_{90} based on U.S. summertime surveys. In addition, two levels of T_{50} were evaluated for speciation and toxics emissions.

The effects of T_{50} and T_{90} on NMHC emissions were non-linear, similar to the response seen in earlier studies. At low levels, the response was lower than at high levels. Fleet average increase in emissions of NMHC were 36% and 25% in going from the low T_{50} (91°C, 195°F) and midpoint T_{50} (102°C, 215°F) to the high T_{50} (113°C, 235°F). The T_{90} response depended on the ethanol concentration in the blend. When no ethanol was present, changing T_{90} did not affect NMHC emissions. At 5.7% and 10% ethanol, the effect was non-linear, with a smaller effect going from low T_{90} (146°C, 295°F) to mid T_{90} (166°C, 330°F) than going from mid T_{90} to high T_{90} (179°C, 355°F). Effects of T_{50} and T_{90} on CO emissions were somewhat mixed. The T_{50} response appeared to be non-linear for fuels that contained ethanol, but was essentially flat for the non-ethanol fuels. CO emissions decreased as T_{90} increased.

Neither T_{50} nor T_{90} affected NOx emissions. There was a small statistically significant interaction between ethanol and T_{50} . NOx emissions tended to decrease as T_{50} increased when the fuel contained 10% ethanol, but not at 5.7% or in the absence of ethanol.

Reducing T_{50} reduced formaldehyde, benzene and 1,3 butadiene emissions, but did not affect acetaldehyde emissions.

A number of programs have been carried out in Europe to measure the emissions impact of mid-fill and back-end volatility. CONCAWE conducted a program to determine whether the results seen in AQIRP for U.S. vehicles would be similar for European LD vehicles [45, 46]. Seven fuels had T_{90} levels between 145°C and 176°C. RVP and T_{50} values were held constant. The chemical composition of the back-end was also varied in the test fuel design. Aromatics varied in the range 38-50%, olefins in the range 0-9% and paraffins in the range 43-54%. Ten European LD vehicles were tested, all having TWC and fuel injection. HC and CO emissions increased by 9% and 14%, respectively when T_{90} increased from 140°C to 160°C, but did not change between 160°C and 180°C. NOx emissions behaved in an opposite manner and were 5% lower when T_{90} increased versus the base level of 140°C. This behavior is similar in direction to the AQIRP results, but smaller in magnitude for HC. Also, the non-linearity seen in AQIRP results is different. Here, the lowest level of T_{90} provides the biggest effect. In AQIRP, changing T_{90} from the highest level provided the biggest benefits. The report recognized that assigning a specific volatility cut-point to an emissions effect was not a possibility because the parameters were not independent of each other. Within the range of T_{50} to T_{90} , it was not possible to ascribe the fuel effects to any one distillation point.

The EPEFE program [25] tested sixteen prototype vehicles designed to meet 1996 European emission limits. E100 targets were 35%, 50% and 65% corresponding to T_{50} values of approximately 85°C, 100°C and 120°C. The response of HC was non-linear, as seen in AQIRP. Mid-fill volatility had little, if any, impact on CO and NOx emissions.

In 1995, CONCAWE [47] published a thorough literature review and analysis of studies that measured the influence of mid-fill and back-end volatility on emissions. They compared studies to date from AQIRP, EPEFE, CONCAWE and others, and concluded that the preponderance of evidence suggested that mid-fill volatility was more important than back-end volatility. They found differences between U.S.-based AQIRP and European-based CONCAWE programs on the influence of back-end composition on emissions (as opposed to back-end volatility). AQIRP [48] found no major impact while CONCAWE found some effects. The report was not able to account for these differences,